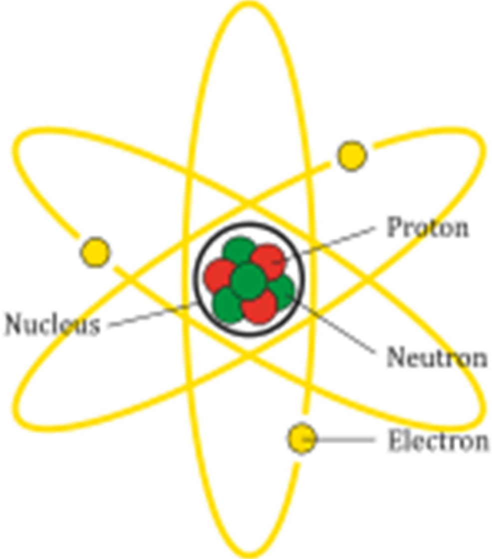
MODULE FOR GENERAL CHEMISTRY

(CHEM.1012)



Ministry of Science and Higher Education

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Bishoftu

Module Overview

The module is designed to meet the scope and sequence requirements of a one semester general chemistry course. The module provides an important opportunity for students to recall and summarize the previous High and preparatory School chemistry concepts and ensure readiness and develop interest towards basics of chemistry. Moreover the module helps the students to learn the core concepts of chemistry and understand how those concepts apply to their lives and the world around them. The module also includes a number of innovative features, including interactive exercises and real-world applications, designed to enhance student learning. The module covers essential ideas in chemistry, measurements and units, classification of matter, composition of substances and solution, chemical reactions, reactions stoichiometry, electronic structure and periodic properties of elements, the chemical bond and molecular geometry, concepts of equilibrium and acid-base equilibrium, basic concepts of organic chemistry and some selected laboratory activities.

For this course the following experiments are recommended to be carried out by the students.

1. Introduction to laboratory safety rules

   General Objectives: To become acquainted with the safety rules for working with chemicals and participating in a safe manner when carrying out lab procedures
2. Basic laboratory techniques

   General Objective: To learn the use of common, simple laboratory equipment.
3. Mass and volume measurements

   General Objective: To become familiar with measuring, Reading and recording measurements correctly (significant digits and unit).
4. Identification of substances by physical properties

   General Objective: To become acquainted with procedures used in evaluating physical properties and the use of these properties in identifying substances
5. Separation of the components of a mixture

   General Objective: To become familiar with the methods of separating substances from one another using filtration, decantation and distillation techniques.
6. Solution preparation

General Objective: To practice the preparation of solutions of known concentration from a solid and by dilution from a stock solution.

7. Chemical Reactions

   General Objective: To observe some typical chemical reactions, identify some of the products, and summarize the chemical changes in terms of balanced chemical equations

8. Solubility of Salts in Water

   General Objectives: To predict the solubility of common inorganic compounds by using solubility rules

9. Vinegar Analysis

   General Objective: To determine the percentage by mass of acetic acid in vinegar.

Coverage and Scope

The module of General Chemistry course adheres to the scope and sequence of most general chemistry courses nationwide. We strive to make chemistry, as a discipline, interesting and accessible to students. With this objective in mind, the content of this module has been developed and arranged to provide a logical progression about the fundamental concepts of chemical science with application. Topics are introduced within the context of familiar experiences whenever possible, treated with an appropriate rigor to satisfy the intellect of the learner, and reinforced in subsequent discussions of related content.

Acknowledgment

We would like to acknowledge the Ministry of Science and Higher Education for giving us the opportunity to prepare this course syllabus and module. Moreover, we are very grateful to the whole staff members of Gold Mark International Hotel for their exceptional hospitality during our stay in Bishoftu.

The Module Team

November 13, 2019

Bishoftu

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CHAPTER ONE

Essential Ideas in Chemistry

Introduction

✍**Brain storming**

- Why should you study Chemistry? Do you have an answer?

Chemical substances and processes are essential for our existence, providing sustenance, keeping us clean and healthy, fabricating electronic devices, enabling transportation, and much more.

You may be studying chemistry because it fulfills an academic requirement, but if you consider your daily activities, you might find chemistry interesting for other reasons. Most everything you do and encounter during your day involves chemistry. Making coffee, cooking eggs, and toasting bread involve chemistry. The products you use like soap and shampoo, the fabrics you wear, the electronics that keep you connected to your world, the gasoline that propels your car all of these and more involve chemical substances and processes. Whether you are aware or not, chemistry is part of your everyday world. In this chapter, you will learn many of the essential principles underlying the chemistry of modern-day life.

Learning Objectives of the Chapter: At the end of this chapter you will be able to

- Describe the scientific method
- Differentiate among hypotheses, theories, and laws
- Provide examples illustrating macroscopic, microscopic, and symbolic domains
- Describe the basic properties of each physical state of matter: solid, liquid, and gas
- Classify matter as an element, compound, homogeneous mixture, or heterogeneous mixture with regard to its physical state and composition
- Identify properties of matter as extensive or intensive
- Define accuracy and precision
- Correctly represent uncertainty in quantities using significant figures
- Apply proper rounding rules to computed quantities

1.1. Chemistry in Context

Throughout human history, people have tried to convert matter into more useful forms. Our Stone Age ancestors chipped pieces of flint into useful tools and carved wood into statues and toys. These endeavors involved changing the shape of a substance without changing the substance itself. But as our knowledge increased, humans began to change the composition of the substances as well clay was converted into pottery, hides were cured to make garments, copper ores were transformed into copper tools and weapons, and grain was made into bread.

Humans began to practice chemistry when they learned to control fire and use it to cook, make pottery, and smelt metals. Subsequently, they began to separate and use specific components of matter. A variety of drugs such as aloe, myrrh, and opium were isolated from plants. Dyes, such as indigo and Tyrian purple, were extracted from plant and animal matter. Metals were combined to form alloys for example, copper and tin were mixed together to make bronze and more elaborate smelting techniques produced iron. Alkalis were extracted from ashes, and soaps were prepared by combining these alkalis with fats. Alcohol was produced by fermentation and purified by distillation.

Attempts to understand the behavior of matter extend back for more than 2500 years. As early as the sixth century BC, Greek philosophers discussed a system in which water was the basis of all things. You may have heard of the Greek postulate that matter consists of four elements: earth, air, fire, and water. Subsequently, an amalgamation of chemical technologies and philosophical speculations was spread from Egypt, China, and the eastern Mediterranean by alchemists, who endeavored to transform “base metals” such as lead into “noble metals” like gold, and to create elixirs to cure disease and extend life.

From alchemy came the historical progressions that led to modern chemistry: the isolation of drugs from natural sources, metallurgy, and the dye industry. Today, chemistry continues to deepen our understanding and improve our ability to harness and control the behavior of matter.

1.1.1. Chemistry as 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 (Figure 1.1). 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 organismsalive. 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.

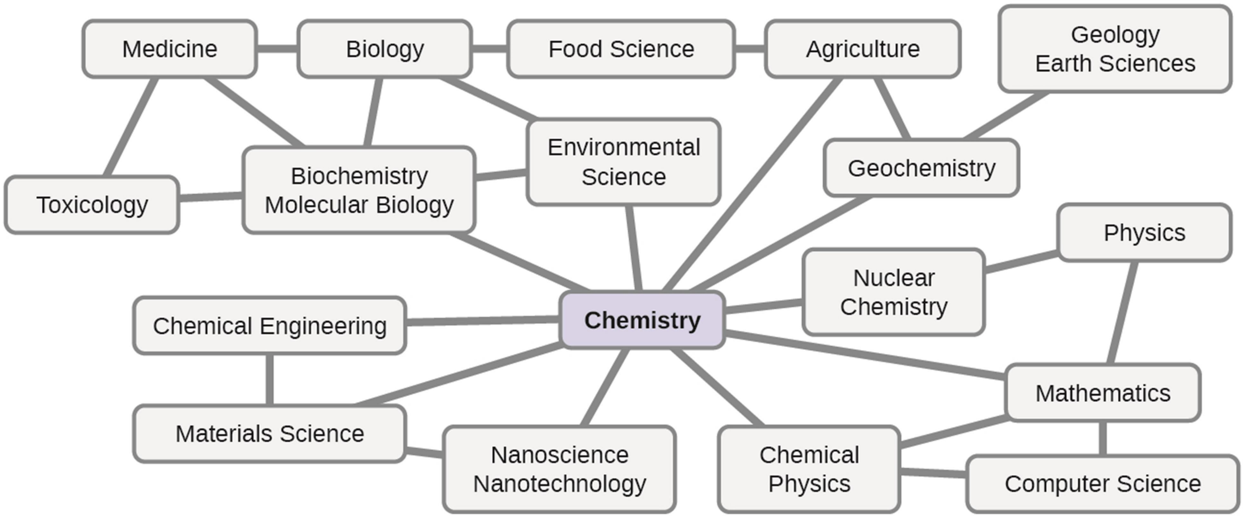


Figure 1.1: Knowledge of chemistry is central to understanding a wide range of scientific disciplines. This diagram shows just some of the interrelationships between chemistry and other fields.

A flowchart shows a box containing chemistry at its center. Chemistry is connected to geochemistry, nuclear chemistry, chemical physics, nanoscience and nanotechnology, materials science, chemical engineering, biochemistry and molecular biology, environmental science, agriculture, and mathematics. Each of these disciplines is further connected to other related fields including medicine, biology, food science, geology earth sciences, toxicology, physics, and computer science.

- Here instructors are expected to give specific examples of application of chemistry in a wide range of scientific disciplines.

✍**Brain storming**

➢ What are some changes in matter that are essential to daily life?

Digesting and assimilating food, synthesizing polymers that are used to make clothing, containers, cookware, and credit cards, and refining crude oil into gasoline and other products are just a few examples. As you proceed through this course, you will discover many different examples of changes in the composition and structure of matter, how to classify these changes, how they occurred and the principles and laws involved. As you learn about these things, you will be learning **chemistry**, the study of the composition, properties, and interactions of matter. The practice of chemistry is not limited to chemistry books or laboratories: It happens whenever someone is involved in changes in matter or in conditions that may lead to such changes.

1.1.2. The Scientific Method

Chemistry is a science based on observation and experimentation. Doing chemistry involves attempting to answer questions and explain observations in terms of the laws and theories of chemistry, using procedures that are accepted by the scientific community. There is no single route to answering a question or explaining an observation, but there is an aspect common to every approach: Each uses knowledge based on experiments that can be reproduced to verify the results. Some routes involve **a hypothesis**, a tentative explanation of observations that acts as a guide for gathering and checking information. A hypothesis is tested by experimentation, calculation, and/or comparison with the experiments of others and then refined as needed.

Some hypotheses are attempts to explain the behavior that is summarized in laws. The **laws** of science summarize a vast number of experimental observations, and describe or predict some facet of the natural world. If such a hypothesis turns out to be capable of explaining a large body of experimental data, it can reach the status of a theory. Scientific **theories** are well-substantiated, comprehensive, testable explanations of particular aspects of nature. Theories are accepted because they provide satisfactory explanations, but they can be modified if new data become available. The path of discovery that leads from question and observation to law or hypothesis to theory, combined with experimental verification of the hypothesis and any necessary modification of the theory, is called the scientific method (Figure 1.2).

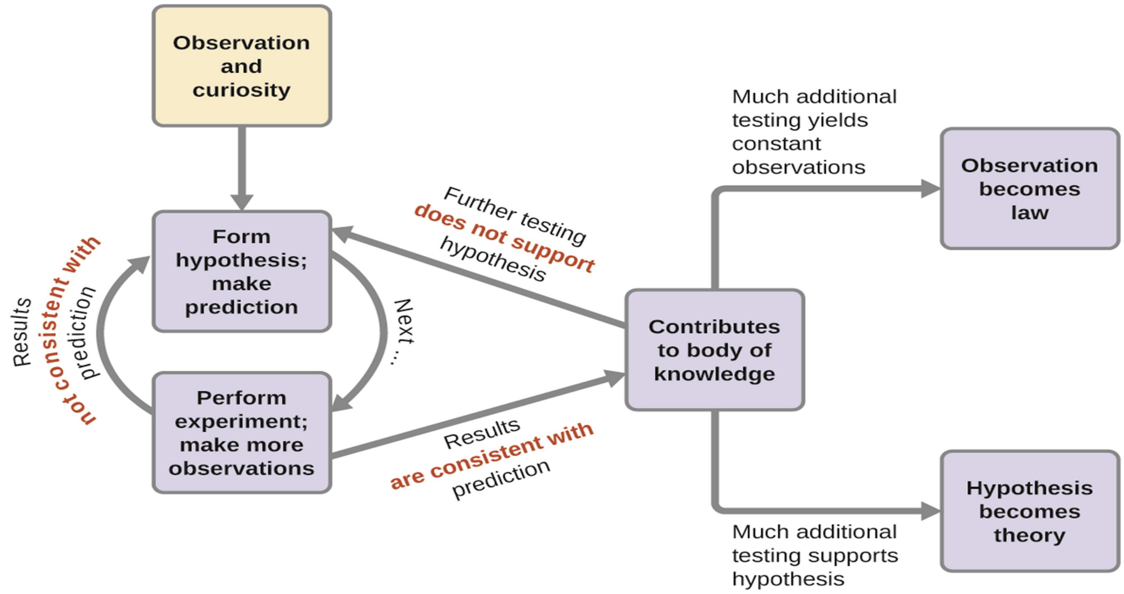


Figure 1.2: The scientific method follows a process similar to the one shown in this diagram. All the key components are shown, in roughly the right order. Scientific progress is seldom neat and clean: It requires open inquiry and the reworking of questions and ideas in response to findings.

In this flowchart, the observation and curiosity box has an arrow pointing to a box labeled form hypothesis; make prediction. A curved arrow labeled next connects this box to a box labeled perform experiment; make more observations. Another arrow points back to the box that says form hypothesis; make prediction. This arrow is labeled results not consistent with prediction. Another arrow, labeled results are consistent with prediction points from the perform experiment box to a box labeled contributes to body of knowledge. However, an arrow also points from contributes to body of knowledge back to the form hypothesis; make prediction box. This arrow is labeled further testing does not support hypothesis. There are also two other arrows leading out from contributes to body of knowledge. One arrow is labeled much additional testing yields constant observations. This leads to the observation becomes law box. The other arrow is labeled much additional testing supports hypothesis. This arrow leads to the hypothesis becomes theory box.

1.1.3. The Domains of Chemistry

Chemists study and describe the behavior of matter and energy in three different domains: macroscopic, microscopic, and symbolic. These domains provide different ways of considering and describing chemical behavior.

Macro is a Greek word that means "large." The **macroscopic domain** is familiar to us: It is the realm of everyday things that are large enough to be sensed directly by human sight or touch. In daily life, this includes the food you eat and the breeze you feel on your face. The macroscopic domain includes everyday and laboratory chemistry, where we observe and measure physical and chemical properties such as density, solubility, and flammability.

Micro comes from Greek and means "small." The **microscopic domain** of chemistry is often visited in the imagination. Some aspects of the microscopic domain are visible through standard optical microscopes, for example, many biological cells. More sophisticated instruments are capable of imaging even smaller entities such as molecules and atoms (see Figure 1.3 (b)).

However, most of the subjects in the microscopic domain of chemistry are too small to be seen even with the most advanced microscopes and may only be pictured in the mind. Other components of the microscopic domain include ions and electrons, protons and neutrons, and chemical bonds, each of which is far too small to see.

The **symbolic domain** contains the specialized language used to represent components of the macroscopic and microscopic domains. Chemical symbols (such as those used in the periodic table), chemical formulas, and chemical equations are part of the symbolic domain, as are graphs, drawings, and calculations. These symbols play an important role in chemistry because they help interpret the behavior of the macroscopic domain in terms of the components of the microscopic domain. One of the challenges for students learning chemistry is recognizing that the same symbols can represent different things in the macroscopic and microscopic domains, and one of the features that make chemistry fascinating is the use of a domain that must be imagined to explain behavior in a domain that can be observed.

A helpful way to understand the three domains is via the essential and ubiquitous substance of water. That water is a liquid at moderate temperatures will freeze to form a solid at lower temperatures, and boil to form a gas at higher temperatures (Figure 1.3) are macroscopic observations. But some properties of water fall into the microscopic domain, what cannot be observed with the naked eye. The description of water as comprising two hydrogen atoms and one oxygen atom, and the explanation of freezing and boiling in terms of attractions between these molecules, is within the microscopic arena. The formula H_2O, which can describe water at either the macroscopic or microscopic levels, is an example of the symbolic domain. The abbreviations (g) for gas, (s) for solid, and (l) for liquid are also symbolic.

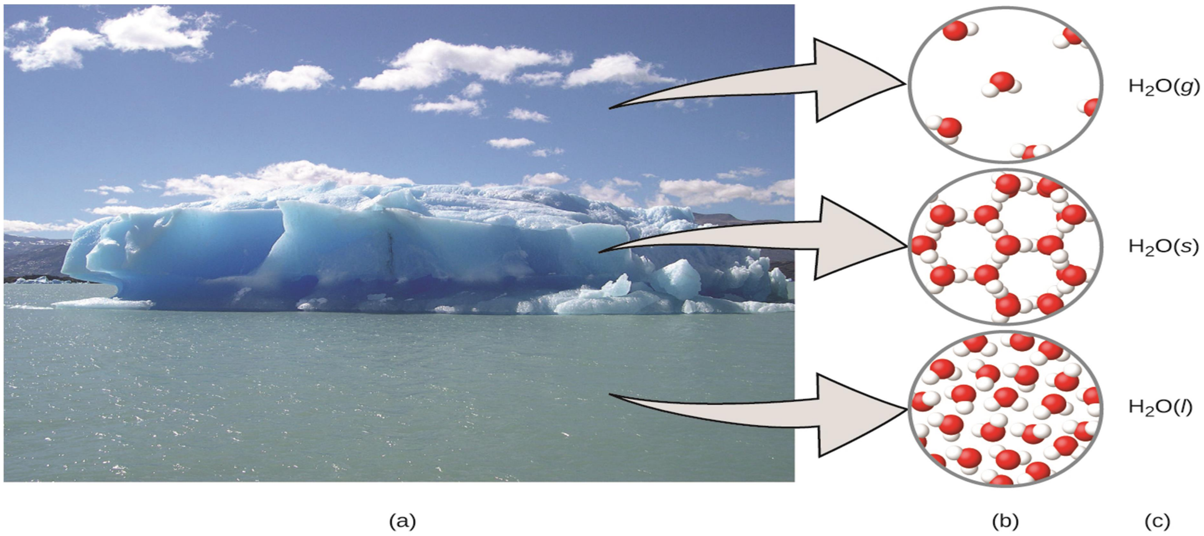


Figure 1.3: (a) Moisture in the air, icebergs, and the ocean represent water in the macroscopic domain. (b) At the molecular level (microscopic domain), gas molecules are far apart and disorganized, solid water molecules are close together and organized, and liquid molecules are close together and disorganized. (c) The formula H_2O symbolizes water, and (g), (s), and (l) symbolize its phases. Note that clouds actually comprise either very small liquid water droplets or solid water crystals; gaseous water in our atmosphere is not visible to the naked eye, although it may be sensed as humidity.

Figure ashows a photo of an iceberg floating in a sea has three arrows. Each arrow points to figure b, which contains three diagrams showing how the water molecules are organized in the air, ice, and sea. In the air, which contains the gaseous form of water, $H_2O(g)$, the water molecules are disconnected and widely spaced. In the ice, which is the solid form of water, $H_2O(s)$, the water molecules are bonded together into rings, with each ring containing six water molecules. Three of these rings are connected to each other. In the sea, which is the liquid form of water, $H_2O(l)$, the water molecules are very densely packed. The molecules are not bonded together.

1.2. State and Classification of Matter

1.2.1. State of Matter

Matter is defined as anything that occupies space and has mass, and it is all around us. Solids and liquids are more obviously matter: We can see that they take up space, and their weight tells us that they have mass. Gases are also matter; if gases did not take up space, a balloon would not inflate (increase its volume) when filled with gas.

Solids, liquids, and gases are the three states of matter commonly found on earth (Figure 1.4). A **solid** is rigid and possesses a definite shape. A **liquid** flows and takes the shape of its container, except that it forms a flat or slightly curved upper surface when acted upon by gravity. (In zero gravity, liquids assume a spherical shape.) Both liquid and solid samples have volumes that are very nearly independent of pressure. A **gas** takes both the shape and volume of its container.

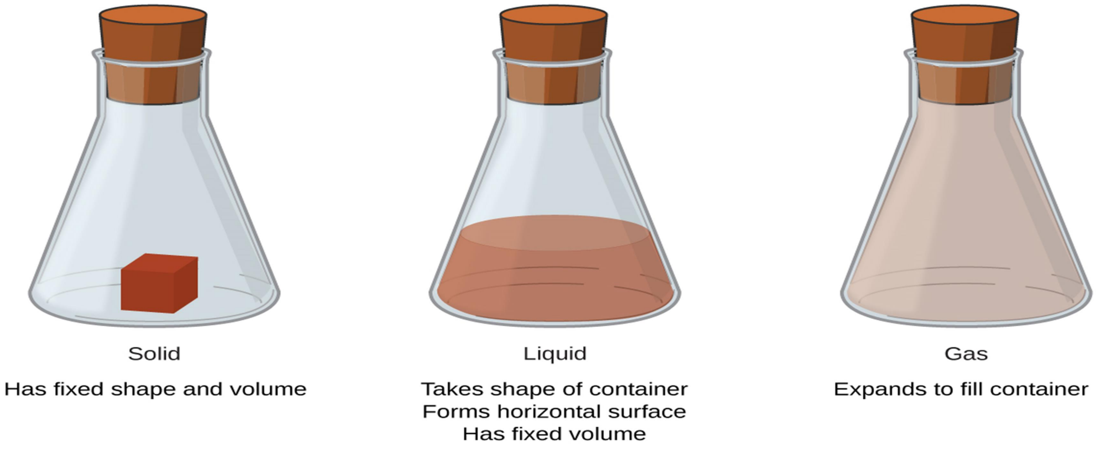


Figure 1.4: The three most common states or phases of matter are solid, liquid, and gas.

A fourth state of matter, plasma occurs naturally in the interiors of stars. **Plasma** is a gaseous state of matter that contains appreciable numbers of electrically charged particles (Figure 1.5). The presence of these charged particles imparts unique properties to plasmas that justify their classification as a state of matter distinct from gases. In addition to stars, plasmas are found in some other high-temperature environments (both natural and man-made), such as lightning strikes, certain television screens, and specialized analytical instruments used to detect trace amounts of metals.

Figure 1.5: A plasma torch can be used to cut metal.

- In a tiny cell in a plasma television, the plasma emits ultraviolet light, which in turn causes the display at that location to appear a specific color. The composite of these tiny dots of color makes up the image that you see.

Some samples of matter appear to have properties of solids, liquids, and/or gases at the same time. This can occur when the sample is composed of many small pieces. For example, we can pour sand as if it were a liquid because it is composed of many small grains of solid sand. Matter can also have properties of more than one state when it is a mixture, such as with clouds. Clouds appear to behave somewhat like gases, but they are actually mixtures of air (gas) and tiny particles of water (liquid or solid).

The **mass** of an object is a measure of the amount of matter in it. One way to measure an object's mass is to measure the force it takes to accelerate the object. It takes much more force to accelerate a car than a bicycle because the car has much more mass. A more common way to determine the mass of an object is to use a balance to compare its mass with a standard mass.

Although weight is related to mass, it is not the same thing. **Weight** refers to the force that gravity exerts on an object. This force is directly proportional to the mass of the object. The weight of an object changes as the force of gravity changes, but its mass does not. An astronaut's mass does not change just because she/he goes to the moon. But her/his weight on the moon is only one-sixth her/his earth-bound weight because the moon's gravity is only one-sixth that of the earth's. She/he may feel "weightless" during her/his trip when she/he experiences negligible external forces (gravitational or any other), although she/he is, of course, never "massless."

The **law of conservation of matter** summarizes many scientific observations about matter: It states that *there is no detectable change in the total quantity of matter present when matter converts from one type to another (a chemical change) or changes among solid, liquid, or gaseous states (a physical change)*. Brewing beer and the operation of batteries provide examples of the conservation of matter (Figure 1.6). During the brewing of beer, the ingredients (water, yeast, grains, malt, hops, and sugar) are converted into beer (water, alcohol, carbonation, and flavoring substances) with no actual loss of substance. This is most clearly seen during the bottling process, when glucose turns into ethanol and carbon dioxide, and the total mass of the substances does not change. This can also be seen in a lead-acid car battery: The original substances (lead, lead oxide, and sulfuric acid), which are capable of producing electricity, are changed into other substances (lead sulfate and water) that do not produce electricity, with no change in the actual amount of matter.

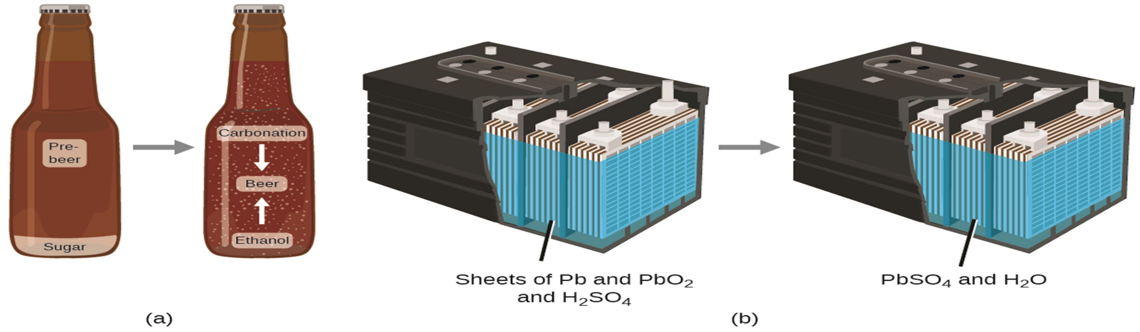


Figure 1.6: (a) The mass of beer precursor materials is the same as the mass of beer produced: Sugar has become alcohol and carbon dioxide. (b) The mass of the lead, lead oxide, and sulfuric acid consumed by the production of electricity is exactly equal to the mass of lead sulfate and water that is formed.

Although this conservation law holds true for all conversions of matter, convincing examples are few and far between because, outside of the controlled conditions in a laboratory, we seldom collect all of the material that is produced during a particular conversion. For example, when you eat, digest, and assimilate food, all of the matter in the original food is preserved. But because some of the matter is incorporated into your body, and much is excreted as various types of waste, it is challenging to verify by measurement.

1.2.2. Classification of Matter

Matter can be classified into several categories. Two broad categories are mixtures and pure substances. A **pure substance** has a constant composition. All specimens of a pure substance have exactly the same makeup and properties. Any sample of sucrose (table sugar) consists of 42.1% carbon, 6.5% hydrogen, and 51.4% oxygen by mass. Any sample of sucrose also has the same physical properties, such as melting point, color, and sweetness, regardless of the source from which it is isolated.

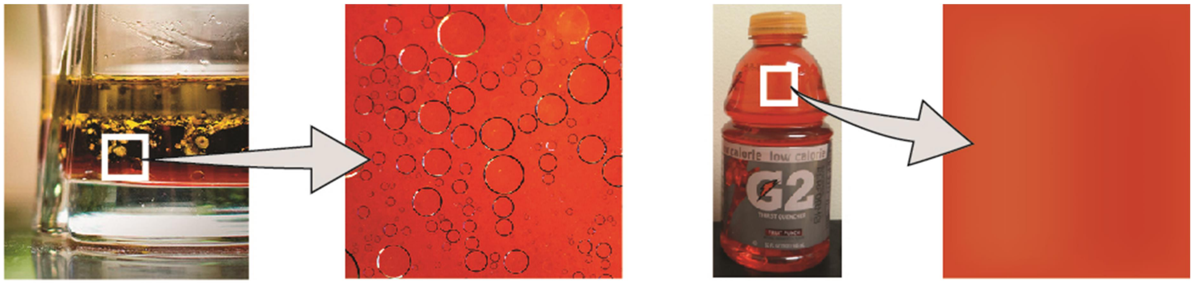
Pure substances may be divided into two classes: elements and compounds. Pure substances that cannot be broken down into simpler substances by chemical changes are called **elements**. Iron, silver, gold, aluminum, sulfur, oxygen, and copper are familiar examples of the more than 100 known elements, of which about 90 occur naturally on the earth, and two dozen or so have been created in laboratories.

Pure substances that can be broken down by chemical changes are called **compounds**. This breakdown may produce either elements or other compounds, or both. Mercury (II) oxide, an orange, crystalline solid, can be broken down by heat into the elements mercury and oxygen. When heated in the absence of air, the compound sucrose is broken down into the element carbon and the compound water. (The initial stage of this process, when the sugar is turning brown, is known as caramelization-this is what imparts the characteristic sweet and nutty flavor to caramel apples, caramelized onions, and caramel). Silver (I) chloride is a white solid that can be broken down into its elements, silver and chlorine, by absorption of light. This property is the basis for the use of this compound in photographic films and photochromic eyeglasses (those with lenses that darken when exposed to light).

The properties of combined elements are different from those in the free, or uncombined, state. For example, white crystalline sugar (sucrose) is a compound resulting from the chemical combination of the element carbon, which is a black solid in one of its uncombined forms, and the two elements hydrogen and oxygen, which are colorless gases when uncombined. Free sodium, an element that is a soft, shiny, metallic solid and free chlorine, an element that is a yellow-green gas, combine to form sodium chloride (table salt), a compound that is a white, crystalline solid.

A **mixture** is composed of two or more types of matter that can be present in varying amounts and can be separated by physical changes, such as evaporation (you will learn more about this later). A mixture with a composition that varies from point to point is called a **heterogeneous mixture**. Italian dressing is an example of a heterogeneous mixture (Figure 1.7). Its composition can vary because it may be prepared from varying amounts of oil, vinegar, and herbs. It is not the same from point to point throughout the mixture-one drop may be mostly vinegar, whereas a different drop may be mostly oil or herbs because the oil and vinegar separate and the herbs settle. Other examples of heterogeneous mixtures are chocolate chip cookies (we can see the separate bits of chocolate, nuts, and cookie dough) and granite (we can see the quartz, mica, feldspar, and more).

A **homogeneous mixture**, also called a **solution**, exhibits a uniform composition and appears visually the same throughout. An example of a solution is a sports drink, consisting of water, sugar, coloring, flavoring, and electrolytes mixed together uniformly (Figure 1.7). Each drop of a sports drink tastes the same because each drop contains the same amounts of water, sugar, and other components. Note that the composition of a sports drink can vary-it could be made with somewhat more or less sugar, flavoring, or other components, and still be a sports drink. Other examples of homogeneous mixtures include air, maple syrup, gasoline, and a solution of salt in water.



(a) (b)

Figure 1.7: (a) Oil and vinegar salad dressing is a heterogeneous mixture because its composition is not uniform throughout. (b) A commercial sports drink is a homogeneous mixture because its composition is uniform throughout.

Although there are just over 100 elements, tens of millions of chemical compounds result from different combinations of these elements. Each compound has a specific composition and possesses definite chemical and physical properties that distinguish it from all other compounds. And, of course, there are innumerable ways to combine elements and compounds to form different mixtures. A summary of how to distinguish between the various major classifications of matter is shown in (Figure 1.8).

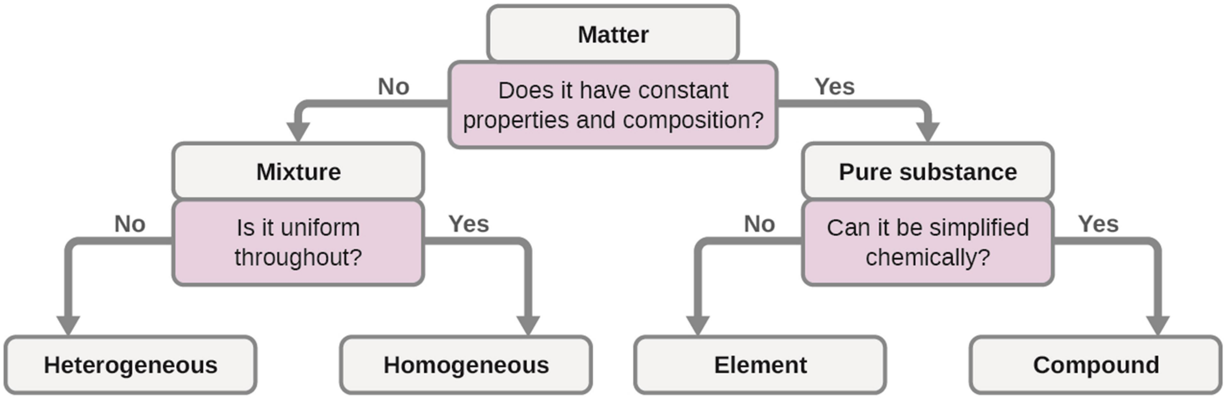


Figure 1.8: Depending on its properties, a given substance can be classified as a homogeneous mixture, a heterogeneous mixture, a compound, or an element.

Eleven elements make up about 99% of the earth’s crust and atmosphere (Table 1.1). Oxygen constitutes nearly one-half and silicon about one-quarter of the total quantity of these elements. A majority of elements on earth are found in chemical combinations with other elements; about one-quarter of the elements are also found in the Free State.

Table1.1: Elemental Composition of Earth

Element	Symbol	% Mass		Element	Symbol	Percent Mass
Oxygen	O	49.20		Chlorine	Cl	0.19
Silicon	Si	25.67		Phosphorus	P	0.11
Aluminum	Al	7.50		Manganese	Mn	0.09
Iron	Fe	4.71		Carbon	C	0.08
Calcium	Ca	3.39		Sulfur	S	0.06
Sodium	Na	2.63		Barium	Ba	0.04
Potassium	K	2.40		Nitrogen	N	0.03
Magnesium	Mg	1.93		Fluorine	F	0.03
Hydrogen	H	0.87		Strontium	Sr	0.02
Titanium	Ti	0.58		All Others	-	0.47

1.3. Physical and Chemical Properties

The characteristics that 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. Some physical properties, such as density and color, may be observed without changing the physical state of the matter. 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 the chemical identities of the substances contained in the matter. Physical changes are observed when wax melts, when sugar dissolves in coffee, and when steam condenses into liquid water (Figure 1.9). 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.


(a) (b)

Figure 1.9: (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.

Figure a, is a photograph of butter melting in a pot on a stove. Figure b is a photograph of something being heated on a stove in a pot. Water droplets are forming on the underside of a glass cover that has been placed over the pot.

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, and many other types of reactivity. Iron, for example, combines with oxygen in the presence of water to form rust; chromium does not oxidize (Figure 1.10). Nitroglycerin is very dangerous because it explodes easily; neon poses almost no hazard because it is very unreactive.

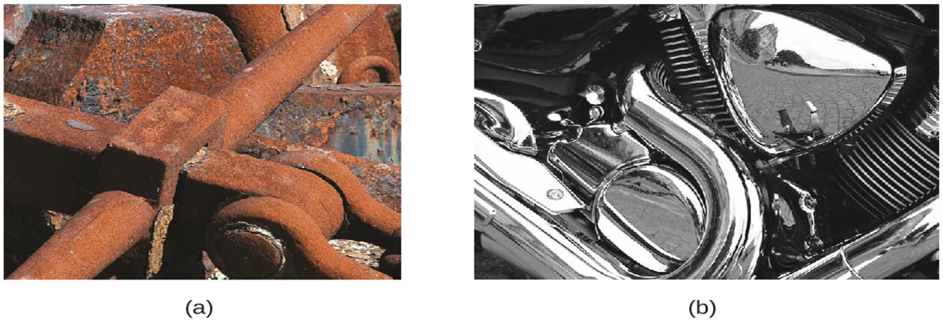

(a) (b)

Figure 1.10: (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.

Figure a, is a photo of metal machinery that is now mostly covered with reddish orange rust. Figure b shows the silver colored chrome parts of a motorcycle. One of the parts is so shiny that you can see a reflection of the surrounding street and buildings.

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 1.11).

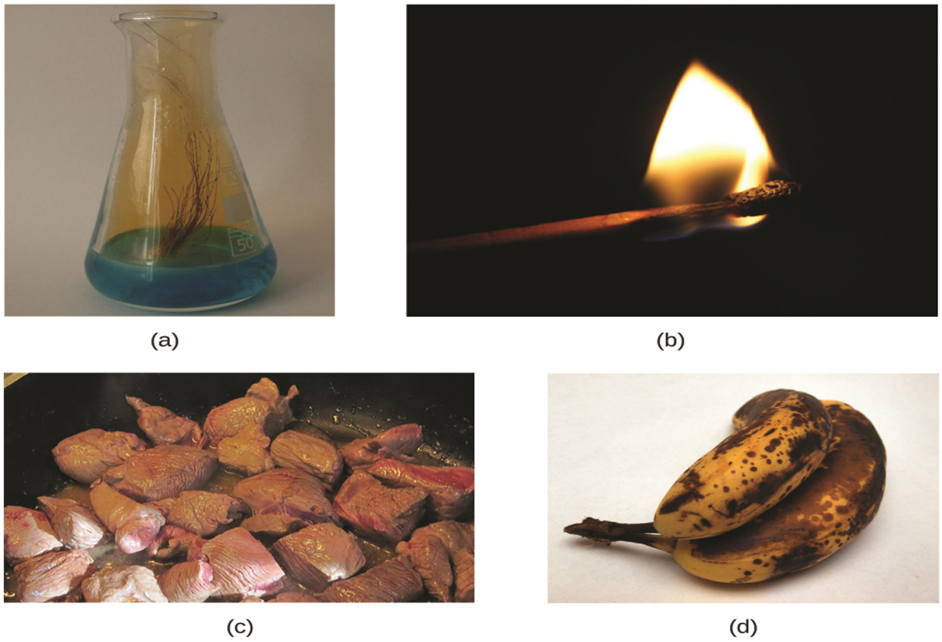

(a) (b) (c) (d)

Figure 1.11: (a) Copper and nitric acids 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.

1.4. Extensive and Intensive Property

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 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).

1.5. Measurements and Units

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

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

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

The measurement units for seven fundamental properties ("base units") are listed in Table 1.2. The standards for these units are fixed by international agreement, and they are called the

International System of Units or SI Units (from the French, Le Système International d'Unités). Units for other properties may be derived from these seven base units.

Table1.2: Base Units of the SI System

Property Measured	Name of Unit	Symbol of Unit
Length	Meter	m
Mass	Kilogram	kg
Time	Second	s
Temperature	Kelvin	K
electric current	Ampere	A
amount of substance	Mole	mol
luminous intensity	Candela	cd

Everyday measurement units are often defined as fractions or multiples of other units. Liquid glycerin is commonly packaged in containers of 20ml of bottle (0.0053gallon). This same approach is used with SI units, but these fractions or multiples are always powers of 10. Fractional or multiple SI units are named using a prefix and the name of the base unit. For example, a length of 1000 meters is also called a kilometer because the prefix kilo means "one thousand," which in scientific notation is 10^3 (1 kilometer = 1000 m = 10^3 m). The prefixes used and the powers to which 10 are raised are listed in Table 1.3.

Table1.3: Common Unit Prefixes

Prefix	**Symbol**	**Factor**	**Example**
Femto	F	10^{-15}	1 femtosecond (fs) = 1 × 10^{-15} s (0.000000000000001 s)
Pico	P	10^{-12}	1 picometer (pm) = 1 ×10^{-12} m (0.000000000001 m)
Nano	N	10^{-9}	4 nanograms (ng) = 4 × 10^{-9} g (0.000000004 g)
Micro	µ	10^{-6}	1 microliter (µL) = 1 × 10^{-6} L (0.000001 L)
Milli	M	10^{-3}	2 millimoles (mmol) = 2 × 10^{-3} mol (0.002 mol)
Centi	C	10^{-2}	7 centimeters (cm) = 7 × 10^{-2} m (0.07 m)
Deci	D	10^{-1}	1 deciliter (dL) = 1 × 10^{-1} L (0.1 L)
Kilo	K	10^{3}	1 kilometer (km) = 1 × 10^{3} m (1000 m)
Mega	M	10^{6}	3 megahertz (MHz) = 3 × 10^{6} Hz (3,000,000 Hz)
Giga	G	10^{9}	8 gigayears (Gyr) = 8 × 10^{9} yr (8,000,000,000 yr)
Tera	T	10^{12}	5 terawatts (TW) = 5 ×10^{12} W (5,000,000,000,000 W)

1.5.1. SI Base Units

This section introduces four of the SI base units commonly used in chemistry.

Length

The standard unit of length in both the SI and original metric systems is the meter (m). A meter was originally specified as 1/10,000,000 of the distance from the North Pole to the equator. It is now defined as the distance light in a vacuum travels in 1/299,792,458 of a second. A meter is about 3 inches longer than a yard (Figure 1.12); one meter is about 39.37 inches or 1.094 yards. Longer distances are often reported in kilometers (1 km = 1000 m = 10^{3} m), whereas shorter distances can be reported in centimeters (1 cm = 0.01 m = 10^{-2} m) or millimeters (1 mm = 0.001 m = 10^{-3} m).

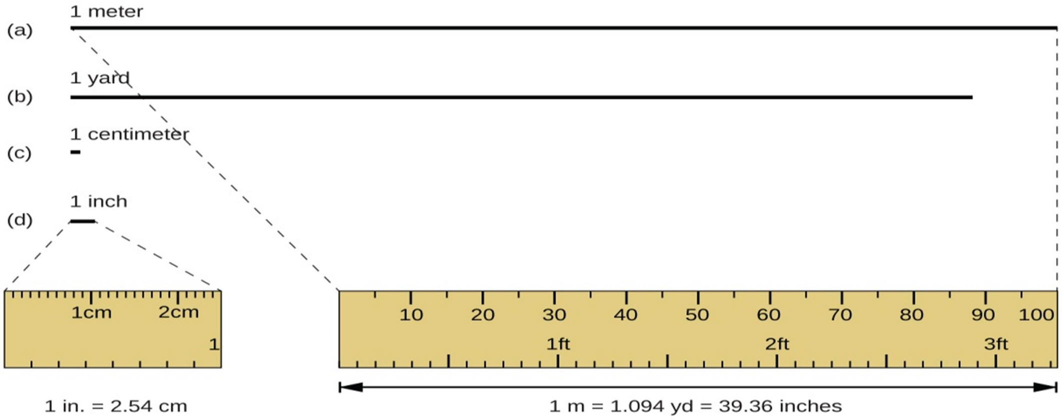


Figure 1.12:The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd.

One meter is slightly larger than a yard and one centimeter is less than half the size of one inch. 1 inch is equal to 2.54 cm. 1 m is equal to 1.094 yards which is equal to 39.36 inches.

Mass

The standard unit of mass in the SI system is the kilogram (kg). The kilogram was previously defined by the International Union of Pure and Applied Chemistry (IUPAC) as the mass of a specific reference object. This object was originally one liter of pure water, and more recently it was a metal cylinder made from a platinum-iridium alloy with a height and diameter of 39 mm (Figure 1.13). In May 2019, this definition was changed to one that is based instead on precisely measured values of several fundamental physical constants. One kilogram is about 2.2 pounds. The gram (g) is exactly equal to 1/1000 of the mass of the kilogram (10^{-3} kg).

Figure 1.13: This replica prototype kilogram as previously defined is housed at the National Institute of Standards and Technology (NIST) in Maryland.

The photo shows a small metal cylinder on a stand. The cylinder is covered with 2 glass lids, with the smaller glass lid encased within the larger glass lid.

Temperature

Temperature is an intensive property. The SI unit of temperature is the kelvin (K). The IUPAC convention is to use kelvin (all lowercase) for the word, K (uppercase) for the unit symbol, and neither the word "degree" nor the degree symbol (°). The degree Celsius (°C) is also allowed in the SI system, with both the word "degree" and the degree symbol used for Celsius measurements. Celsius degrees are the same magnitude as those of kelvin, but the two scales place their zeros in different places. Water freezes at 273.15 K (0°C) and boils at 373.15 K (100 °C) by definition, and normal human body temperature is approximately 310 K (37°C). The conversion between these two units and the Fahrenheit scale will be discussed later in this chapter.

Time

The SI base unit of time is the second (s). Small and large time intervals can be expressed with the appropriate prefixes; for example, 3 microseconds = 0.000003 s = 3×10^{-6} and 5 megaseconds = 5,000,000 s = 5×10^{6} s. alternatively, hours, days, and years can be used.

1.5.2. Derived SI Units

We can derive many units from the seven SI base units. For example, we can use the base unit of length to define a unit of volume, and the base units of mass and length to define a unit of density.

Volume

Volume is the measure of the amount of space occupied by an object. The standard SI unit of volume is defined by the base unit of length (Figure 1.14). The standard volume is a cubic meter (m^3), a cube with an edge length of exactly one meter. To dispense a cubic meter of water, we could build a cubic box with edge lengths of exactly one meter. This box would hold a cubic meter of water or any other substance.

A more commonly used unit of volume is derived from the decimeter (0.1 m, or 10 cm). A cube with edge lengths of exactly one decimeter contains a volume of one cubic decimeter (dm^3). A liter (L) is the more common name for the cubic decimeter. One liter is about 1000ml.

A cubic centimeter (cm^3) is the volume of a cube with an edge length of exactly one centimeter. The abbreviation cc (for cubic centimeter) is often used by health professionals. A cubic centimeter is equivalent to a milliliter (mL) and is 1/1000 of a liter.

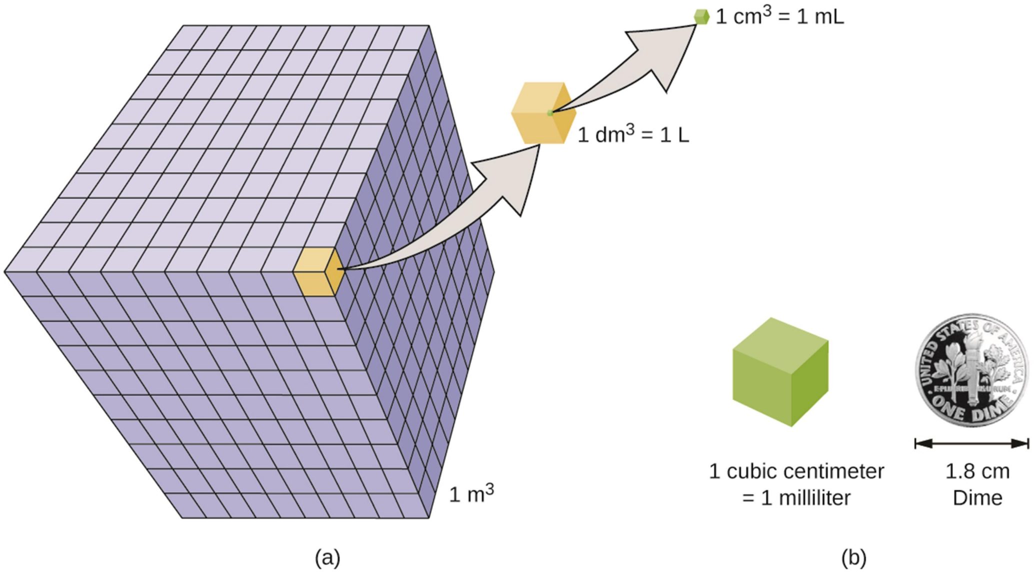


Figure 1.14: (a) The relative volumes are shown for cubes of 1 m^3, 1 dm^3 (1 L), and 1 cm^3 (1 mL) (not to scale). (b) The diameter of a dime is compared relative to the edge length of a 1cm^3 (1mL) cube.

Figure a shows a large cube, which has a volume of 1 meter cubed. This larger cube is made up of many smaller cubes in a 10 by 10 pattern. Each of these smaller cubes has a volume of 1 decimeter cubed, or one liter. Each of these smaller cubes is, in turn, made up of many tiny cubes. Each of these tiny cubes has a volume of 1 centimeter cubed, or one milliliter. A one cubic centimeter cube is about the same width as a dime, which has a width of 1.8 centimeter.

Density

We use the mass and volume of a substance to determine its density. Thus, the units of density are defined by the base units of mass and length.

The density of a substance is the ratio of the mass of a sample of the substance to its volume. The SI unit for density is the kilogram per cubic meter (kg/m^3). For many situations, however, this as an inconvenient unit and we often use grams per cubic centimeter (g/cm^3) for the densities of solids and liquids, and grams per liter (g/L) for gases. Although there are exceptions, most liquids and solids have densities that range from about 0.7 g/cm^3 (the density of gasoline) to 19 g/cm^3 (the density of gold). The density of air is about 1.2 g/L. Table 1.4 shows the densities of some common substances.

Table1.4: Densities of Common Substances

Solids	**Liquids**	**Gases (at 25 °C and 1 atm.)**
ice (at 0 °C) 0.92 g/cm^3	water 1.0 g/cm^3	dry air 1.20 g/L
iron 7.9 g/cm^3	ethanol 0.79 g/cm^3	oxygen 1.31 g/L
copper 9.0 g/cm^3	acetone 0.79 g/cm^3	nitrogen 1.14 g/L
lead 11.3 g/cm^3	glycerin 1.26 g/cm^3	carbon dioxide 1.80 g/L
silver 10.5 g/cm^3	olive oil 0.92 g/cm^3	helium 0.16 g/L
gold 19.3 g/cm^3	gasoline 0.70–0.77 g/cm^3	neon 0.83 g/L
Zinc 7.140g/ cm^3	mercury 13.6 g/cm^3	radon 9.1 g/L

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

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

Example 1.1

Calculation of Density

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

Solution

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

Volume of lead cube=2.00 cm×2.00 cm×2.00 cm=8.00 cm^3

$$\boldsymbol{density = \frac{mass}{volume} = \frac{90.7g}{8cm^3} = 11.3g/cm^3}$$

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

✍**Check Your Learning**

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

1.6. Measurement Uncertainty

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**. By counting the eggs in a carton, one can determine *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.

1.6.1. 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.

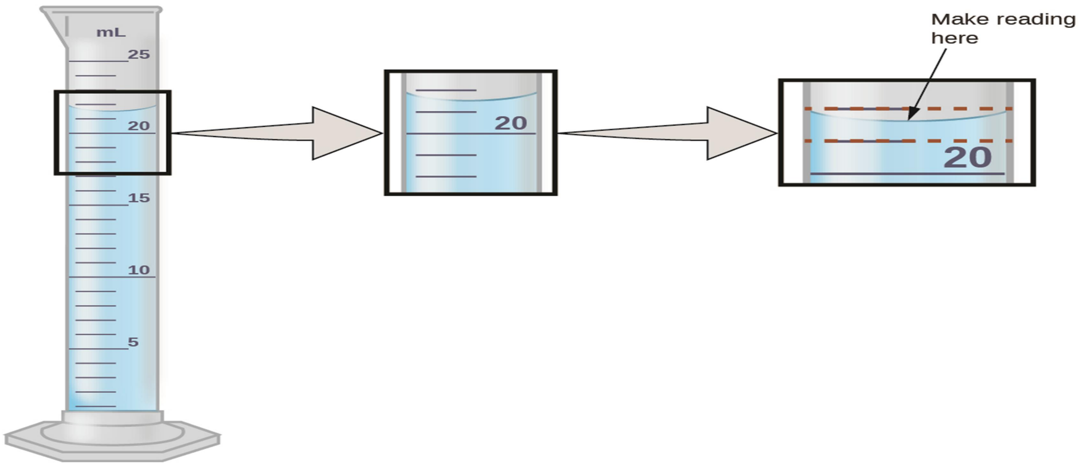
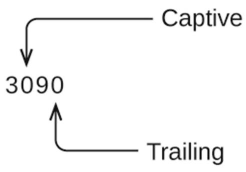


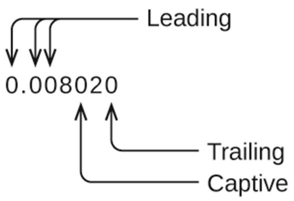
Figure 1.15: To measure the volume of liquid in this graduated cylinder, you must mentally subdivide the distance between the 21 and 22 mL marks into tenths of a milliliter, and then make a reading (estimate) at the bottom of the meniscus.

Refer to the illustration in Figure 1.15. 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.

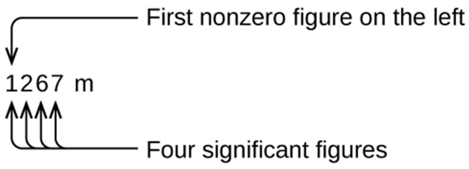
This concept holds true for all measurements, even if you do not actively make an estimate. If you place a quarter on a standard electronic balance, you may obtain a reading of 6.72 g. The digits 6 and 7 are certain, and the 2 indicates that the mass of the quarter is likely between 6.71 and 6.73 grams.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

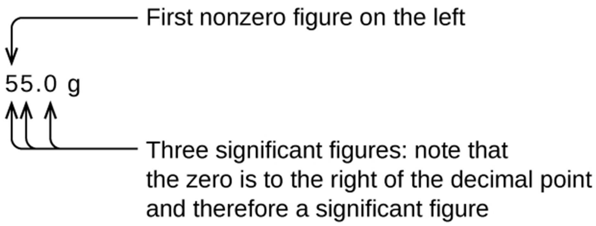
A measurement result is properly reported when its significant digits accurately represent the certainty of the measurement process. But what if you were analyzing a reported value and trying to determine what is significant and what is not? Well, for starters, all nonzero digits are significant, and 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.



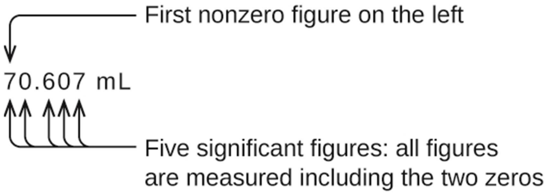


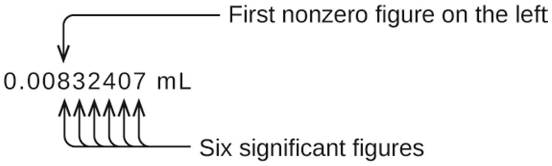
Starting with the first nonzero digit on the left, count this digit and all remaining digits to the right. This is the number of significant figures in the measurement unless the last digit is a trailing zero lying to the left of the decimal point.





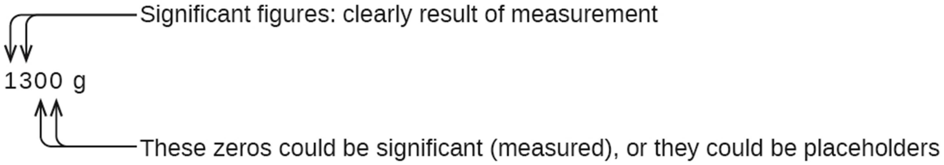
Captive zeros result from measurement and are therefore always significant. Leading zeros, however, are never significant—they merely tell us where the decimal point is located.





The leading zeros in this example are not significant. We could use exponential notation 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.



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 when evaluating 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 3.17×10^8 people.

1.6.2. 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. Take the uncertainty in 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 adding or subtracting numbers, round the result to the same number of decimal places as the number with the least number of decimal places (the least certain value in terms of addition and subtraction).
2. When multiplying or dividing numbers, round the result to the same number of digits as the number with the least number of significant figures (the least certain value in terms of multiplication and division).
3. If the digit to be dropped (the one immediately to the right of the digit to be retained) is less than 5, "round down" and leave the retained digit unchanged; if it is more than 5, "round up" and increase the retained digit by 1; if the dropped digit *is* 5, 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 1.2

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)

✍ Check Your Learning

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)

Example 1.3

Addition and Subtraction with Significant Figures

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

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

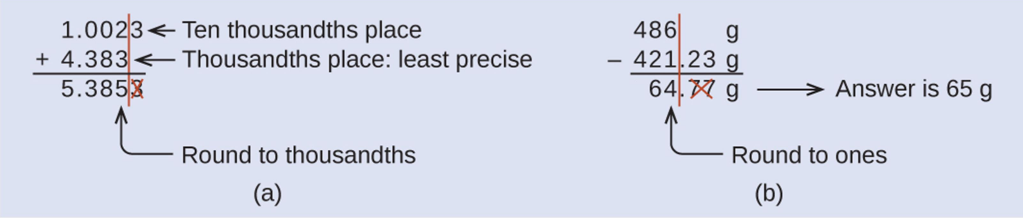
Solution

a) 1.0023 g+ 4.383 g =5.3853 g

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

b) 486 g–421.23 g = 64.77 g

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



✍Check Your Learning

Round the following to the indicated number of significant figures:

(a) Add 2.334 mL and 0.31 mL

(b) Subtract 55.8752 m from 56.533 m.

Example 1.4

Multiplication and Division with Significant Figures

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

(a) Multiply 0.6238 cm by 6.6 cm.

(b) Divide 421.23 g by 486 mL.

Solution

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

four significant figures × two significant figures ⟶ two significant figures

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

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

✍Check Your Learning

(a) Multiply 2.334 cm and 0.320 cm.

(b) Divide 55.8752 m by 56.53 s

Example 1.5

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

V = lxwxd

= 13.44 dmx5.920 dmx2.54 dm

= 202.09459 dm3 (value from calculator)

= 202 dm3 or 202 (answer round to three significant figures)

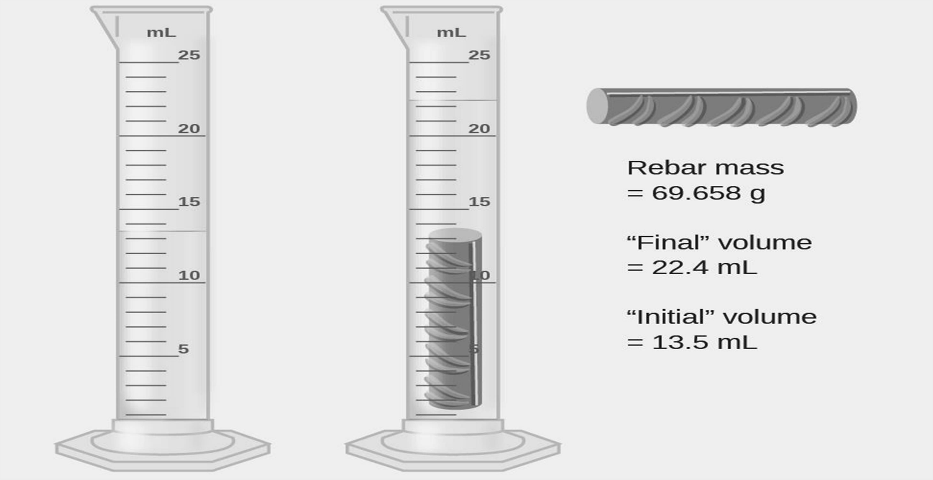
✍Check Your Learning

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

Example 1.6

Experimental Determination of Density Using Water Displacement

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



(a) Use these values to determine the density of this piece of rebar.

(b) Rebar is mostly iron. Does your result in (a) support this statement? How?

Solution

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

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

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

The density is the mass-to-volume ratio:

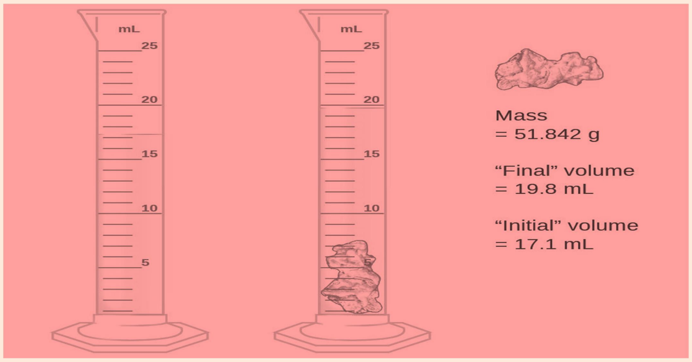
$$density = \frac{mass}{volume} = \frac{69.658g}{8.9\ cm^3} = 7.8g/cm^3$$

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

From Table 1.4, 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.

✍Check Your Learning

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



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.

1.6.3. Accuracy and Precision

Scientists typically make repeated measurements of a quantity to ensure the quality of their findings and to evaluate both the **precision** and the **accuracy** of their results. Measurements are said to be precise if they yield very similar results when repeated in the same manner. A measurement is considered accurate if it yields a result that is very close to the true or accepted value. Precise values agree with each other; accurate values agree with a true value. These characterizations can be extended to other contexts, such as the results of an archery competition (Figure 1.17).

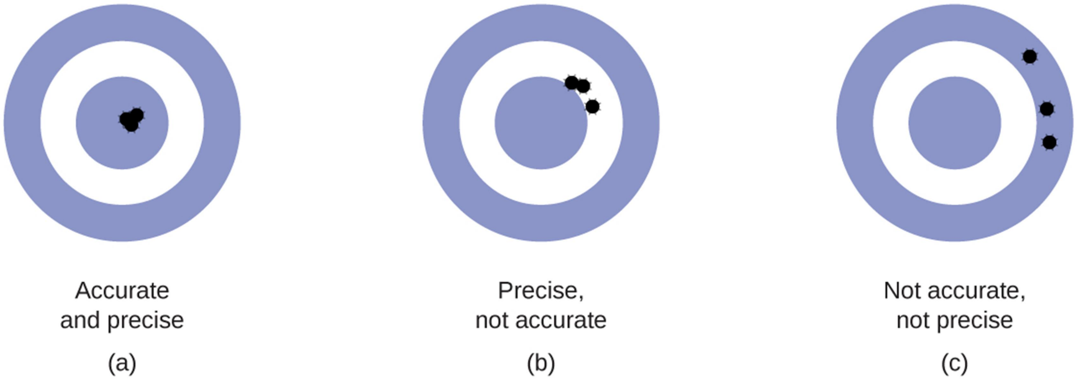


Figure 1.17: (a) These arrows are close to both the bull's eye and one another, so they are both accurate and precise. (b) These arrows are close to one another but not on target, so they are precise but not accurate. (c) These arrows are neither on target nor close to one another, so they are neither 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 283.5g (296 mL) of cough syrup into storage bottles. She/he proceeds to use each machine to fill five bottles and then carefully determines the actual volume dispensed, obtaining the results tabulated in Table 1.5.

Table1.5: Volume (mL) of Cough Medicine Delivered by 283.5g (296 mL) Dispensers

Dispenser #1	Dispenser #2	Dispenser #3
283.3	298.3	296.1
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/he 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/he 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).

1.7. 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,

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

Several other commonly used conversion factors are given in Table 1.6.

Table1.6: Common Conversion Factors

Length	**Volume**	**Mass**
1 in. = 2.54 cm (exact)	1 liter (l) = 1000cm^3 = 3.78544gl=1.057 quart (qt) = 61.02 in^3 = 0.03532 ft^3	1 kg = 2.2046 lb
1cm=0.01m	1 cubic meter (m^3) = 1000 l = 35.32 ft^3	1 lb = 453.59 g
1mm=0.001m	1 ft^3 = 28.317 L	1 (avoirdupois) oz = 28.349 g

When a quantity (such as distance in inches) is multiplied by an appropriate unit conversion factor, the quantity is converted to an equivalent value with different units (such as distance in centimeters). For example, a basketball player's vertical jump of 34 inches can be converted to centimeters by:$\mathbf{34\ \cancel{in}} \times \frac{\mathbf{2.54\ cm}}{\mathbf{1\ \cancel{in}}} = \mathbf{86\ cm}$

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 unitsare multiplied to yield $in.\times\frac{cm}{in}$. Just as for numbers, a ratio of identical units is also numerically equal to one, $\frac{in.}{in} = 1$, and the unit product thus simplifies to cm. (When identical units divide to yield a factor of 1, they are said to "cancel.") Dimensional analysis may be used to confirm the proper application of unit conversion factors as demonstrated in the following example.

✍Check Your Learning

- Convert a volume of 9.345 ml to liters and m^3

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 ensure that their labels (units) will appropriately cancel and/or combine to yield the desired unit in the result. As your study of chemistry continues, you will encounter many opportunities to apply this approach.

Example 1.7

Computing Quantities from Measurement Results and Known Mathematical Relations

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

Solution

Since $density = \frac{mass}{volume} d$, we need to divide the mass in grams by the volume in milliliters. In general: the number of units of B = the number of units of A × unit conversion factor. The necessary conversion factors are given in Table 1.6: 1 lb = 453.59 g; 1 L = 1.0567 qt; 1 L = 1,000 mL. Mass may be converted from pounds to grams as follows:

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

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

1. Step 1. *Convert quarts to liters.*

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

Step 2.*Convert liters to milliliters.*

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

Then,

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

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

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

✍Check Your Learning

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

Example 1.8

Computing Quantities from Measurement Results and Known Mathematical Relations

While being driven from Addis Ababa to Asmara, a distance of about 1250 km, a Land Cruiser uses 213 L gasoline.

(a) What (average) fuel economy, in miles per gallon, did the vehicle get during this trip?

(b) If gasoline costs ETB 48.80 per gallon, what was the fuel cost for this trip?

Solution

(a) First convert distance from kilometers to miles:

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

and then convert volume from liters to gallons:

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

Finally,

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

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

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

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

$$56.3\ \cancel{gal} \times \frac{ETB\ 48.80}{1\cancel{gal}} = ETB2747.44$$

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, and the position of the trapped liquid along a printed scale may be used as a measure of temperature.

Temperature scales are defined relative to selected reference temperatures: 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:

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

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:

$$m = \frac{\Delta y}{\Delta x} = \frac{212\ °F - 32\ °F}{100\ °C - 0\ °C} = \frac{180\ °F}{100\ °C} = \frac{9\ °F}{5\ °C}$$

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:

$$\boldsymbol{b = y - mx = 32\ °F - \frac{9\ °F}{5\ °C} \times 0\ °C = 32\ °F}$$

The equation relating the temperature (*T*) scales is then:

$$\boldsymbol{T°F = (\frac{9\ °F}{5\ °C} \times T°C) + 32\ °C}$$

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

$$\boldsymbol{T\ °F = \left(\frac{9}{5} \times T°C\right) + 32}$$

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

$$\boldsymbol{T\ °C = \frac{5}{9}(T°F - 32)}$$

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. Since the kelvin temperature scale is absolute, a degree symbol is not included in the unit abbreviation, K. The early 19thcentury 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.

The freezing temperature of water on this scale is 273.15 K and its boiling temperature is 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$1\frac{\mathrm{K}}{°\mathrm{C}}$. Following the same approach, the equations for converting between the Kelvin and Celsius temperature scales are derived to be:

$$\boldsymbol{T_K = T_{°C} + 273.15}$$

$$T_{°C} = T_K - 273.15$$

The 273.15 in these equations has been determined experimentally, so it is not exact. Figure 1.18 shows the relationship among the three temperature scales.

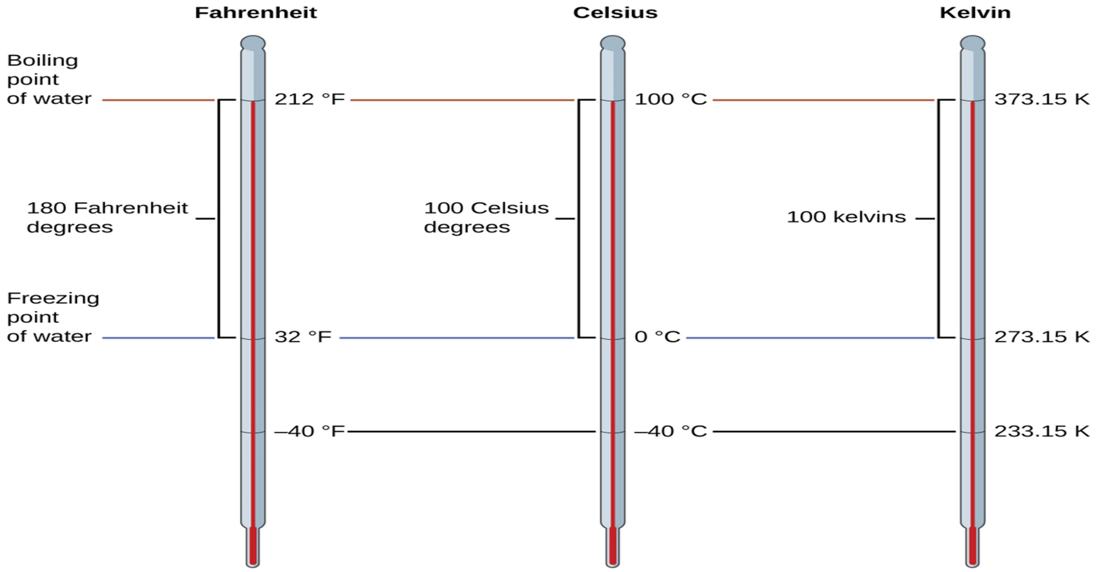


Figure 1.18: The Fahrenheit, Celsius, and kelvin temperature scales are compared.

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 non-science contexts in almost all areas of the world. Very few countries (the U.S. and its territories) still use Fahrenheit for weather, medicine, and cooking.

Example 1.9

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

$$K = °C + 273.15 = 37.0 + 273.2 = 310.2\ K$$

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

Example 1.10

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

$$^\circ C = \frac{5}{9}(^\circ F - 32) = \frac{5}{9}(450 - 32) = \frac{5}{9} \times 418 = 232\ ^\circ C$$

$$\longrightarrow set\ oven\ to\ 230\ ^\circ C(two\ significant\ figures)^\circ C = 59(^\circ F - 32)$$

$$= 59(450 - 32) = 59 \times 418 = 232\ ^\circ C$$

$$\longrightarrow set\ oven\ to\ 230\ ^\circ C(two\ significant\ figures)$$

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

$$= {}^\circ C + 273.15 = 230 + 273 = 503\ K$$

$$\longrightarrow 5.0 \times 102K(two\ significant\ figures)$$

Check Your Learning

- Convert 80.92 °C to K and °F.
- Convert 50 °F to °C and K.
- Show that at what temperature does °C and °F are equal?

Review Exercise

1. Explain how you could experimentally determine whether the outside temperature is higher or lower than 0 °C (32 °F) without using a thermometer.
2. Identify each of the following statements as being most similar to a hypothesis, a law, or a theory. Explain your reasoning.
    (a) Falling barometric pressure precedes the onset of bad weather.
    (b) All life on earth has evolved from a common, primitive organism through the process of natural selection.
3. Identify each of the following statements as being most similar to a hypothesis, a law, or a theory. Explain your reasoning.

   (a) The pressure of a sample of gas is directly proportional to the temperature of the gas.
   (b) Matter consists of tiny particles that can combine in specific ratios to form substances with specific properties.
   (c) At a higher temperature, solids (such as salt or sugar) will dissolve better in water.

4. Identify each of the underlined items as a part of either the macroscopic domain, the microscopic domain, or the symbolic domain of chemistry. For any in the symbolic domain, indicate whether they are symbols for a macroscopic or a microscopic feature.
   (a) The mass of a lead pipe is 14 kg.
   (b) The mass of a certain chlorine atom is 35 amu.
   (c) A bottle with a label that reads Al contains aluminum metal.
   (d) Al is the symbol for an aluminum atom.
   (e) A certain molecule contains one H atom and one Cl atom.
   (f) Copper wire has a density of about 8 g/cm^3.
   (g) The bottle contains 15 grams of Ni powder.
   (h) A sulfur molecule is composed of eight sulfur atoms.
5. Why is an object’s mass, rather than its weight, used to indicate the amount of matter it contains?
6. What properties distinguish solids from liquids? Liquids from gases? Solids from gases?
7. How does a heterogeneous mixture differ from a homogeneous mixture? How are they similar?
8. How does a homogeneous mixture differ from a pure substance? How are they similar?
9. How does an element differ from a compound? How are they similar?
10. How do molecules of elements and molecules of compounds differ? In what ways are they similar?
11. How does an atom differ from a molecule? In what ways are they similar?
12. Many of the items you purchase are mixtures of pure compounds. Select three of these commercial products and prepare a list of the ingredients that are pure compounds.
13. A sulfur atom and a sulfur molecule are not identical. What is the difference?
14. How are the molecules in oxygen gas, the molecules in hydrogen gas, and water molecules similar? How do they differ?
15. Why are astronauts in space said to be “weightless,” but not “massless”?

16. Prepare a list of the principal chemicals consumed and produced during the operation of an automobile.
17. Matter is everywhere around us. Make a list by name of fifteen different kinds of matter that you encounter every day. Your list should include (and label at least one example of each) the following: a solid, a liquid, a gas, an element, a compound, a homogenous mixture, a heterogeneous mixture, and a pure substance.
18. When elemental iron corrodes it combines with oxygen in the air to ultimately form red brown iron(III) oxide called rust. (a) If a shiny iron nail with an initial mass of 23.2 g is weighed after being coated in a layer of rust, would you expect the mass to have increased, decreased, or remained the same? Explain. (b) If the mass of the iron nail increases to 24.1 g, what mass of oxygen combined with the iron?
19. As stated in the text, convincing examples that demonstrate the law of conservation of matter outside of the laboratory are few and far between. Indicate whether the mass would increase, decrease, or stay the same for the following scenarios where chemical reactions take place:
    (a) When magnesium burns in air a white flaky ash of magnesium oxide is produced. Is the mass of magnesium oxide less than, greater than, or the same as the original piece of magnesium? Explain.
    (b) Antoine Lavoisier, the French scientist credited with first stating the law of conservation of matter, heated a mixture of tin and air in a sealed flask to produce tin oxide. Did the mass of the sealed flask and contents decrease, increase, or remain the same after the heating?
20. Yeast converts glucose to ethanol and carbon dioxide during anaerobic fermentation as depicted in the simple chemical equation here:

    $$\text{glucose} \longrightarrow \text{ethanol} + \text{carbon dioxide}$$

    (a) If 200.0 g of glucose is fully converted, what will be the total mass of ethanol and carbon dioxide produced?
    (b) If the fermentation is carried out in an open container, would you expect the mass of the container and contents after fermentation to be less than, greater than, or the same as the mass of the container and contents before fermentation? Explain.
    (c) If 97.7 g of carbon dioxide is produced, what mass of ethanol is produced?
21. Classify each of the following changes as physical or chemical:

(a)condensation of steam

(b) burning of gasoline

(c) souring of milk

(d) dissolving of sugar in water

(e) melting of gold

(f) coal burning

(g) ice melting

(h) mixing chocolate syrup with milk

(h)explosion of a firecracker

(j)magnetizing of a screwdriver

22. The volume of a sample of oxygen gas changed from 10 mL to 11 mL as the temperature changed. Is this a chemical or physical change?
23. A 2.0-liter volume of hydrogen gas combined with 1.0 liter of oxygen gas to produce 2.0 liters of water vapor. Does oxygen undergo a chemical or physical change?
24. Identify the following properties as either extensive or intensive.

(a) volume

(b) temperature

(c) humidity

(d) heat

(e) boiling point

25. A large piece of jewelry has a mass of 132.6 g. A graduated cylinder initially contains 48.6 mL water. When the jewelry is submerged in the graduated cylinder, the total volume increases to 61.2 mL.

(a) Determine the density of this piece of jewelry.

(b) Assuming that the jewelry is made from only one substance, what substance is it likely to be? Explain.

26. Express each of the following numbers in scientific notation with correct significant figures:

(a) 711.0

(b) 0.239

(c) 90743

(d) 134.2

(e) 0.05499

(f) 10000.0

(g) 0.000000738592

27. Indicate whether each of the following can be determined exactly or must be measured with some degree of uncertainty:

a. the number of eggs in a basket

b. the mass of a dozen eggs

c. the number of gallons of gasoline necessary to fill an automobile gas tank

d. the number of cm in 2 m

e. the mass of a textbook

f. the time required to drive from Addis Ababa to Adama at an average speed of 53 mi/h

g. the number of seconds in an hour

h. the number of pages in this book

i. the number of grams in your weight

j. the number of grams in 3 kilograms

k. the volume of water you drink in one day

28. How many significant figures are contained in each of the following measurements?

a. 38.7 g

b. 2×10^{18} m

c. 3,486,002 kg

d. 9.74150×10^{-4} J

e. 0.0613 cm^3

f. 17.0 kg

g. 0.01400 g/mL

29. Round off each of the following numbers to two significant figures:

a. 0.436

b. 9.000

c. 27.2

d. 135

e. 1.497×10^{-3}

f. 0.445

30. Perform the following calculations and report each answer with the correct number of significant figures.

a. 628×342

b. $(5.63 \times 10^2) \times (7.4 \times 10^3)$

c. 28.0/13.483

d. 8119×0.000023

e. $14.98 + 27{,}340 + 84.7593$

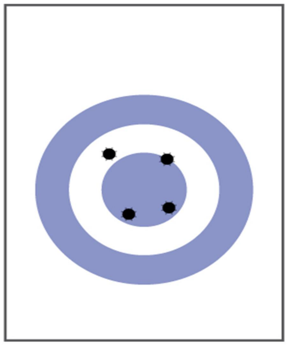
f. $42.7 + 0.259$

31. Consider the results of the archery contest shown in this figure.

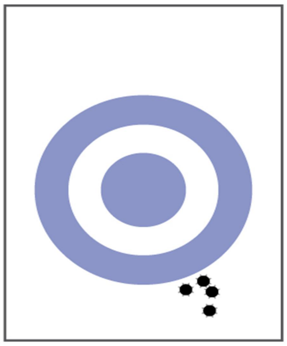
a. Which archer is most precise?

b. Which archer is most accurate?

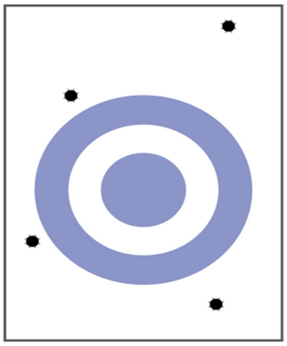
c. Who is both least precise and least accurate?



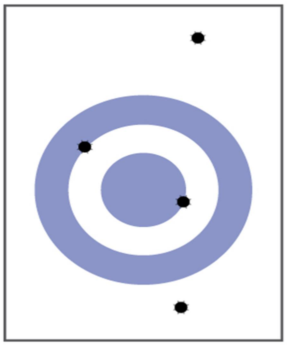
Archer W



Archer X



Archer Y



Archer Z

32. Classify the following sets of measurements as accurate, precise, both, or neither.
    a. Checking for consistency in the weight of chocolate chip cookies: 17.27 g, 13.05 g, 19.46 g, 16.92 g
    b. Testing the volume of a batch of 25-mL pipettes: 27.02 mL, 26.99 mL, 26.97 mL, 27.01 mL
    c. Determining the purity of gold: 99.9999%, 99.9998%, 99.9998%, 99.9999%
33. A barrel of oil is exactly 42 gal. How many liters of oil are in a barrel?
34. The diameter of a red blood cell is about 3×10^{-4} in. What is its diameter in centimeters?
35. The distance between the centers of the two oxygen atoms in an oxygen molecule is 1.21×10^{-8} cm. What is this distance in inches?
36. . Many medical laboratory tests are run using 5.0 µL blood serum. What is this volume in milliliters?
37. If an aspirin tablet contains 325 mg aspirin, how many grams of aspirin does it contain?
38. The gas tank of a certain luxury automobile holds 22.3 gallons according to the owner's manual. If the density of gasoline is 0.8206 g/mL, determine the mass in kilograms of the fuel in a full tank.
39. As an instructor is preparing for an experiment, he requires 225 g phosphoric acid. The only container readily available is a 150-mL Erlenmeyer flask. Is it large enough to contain the acid, whose density is 1.83 g/mL?
40. To prepare for a laboratory period, a student lab assistant needs 125 g of a compound. A bottle containing 1/4 lb is available. Did the student have enough of the compound?
41. Calculate the density of aluminum if 27.6 cm^3 has a mass of 74.6 g.
42. Osmium is one of the densest elements known. What is its density if 2.72 g has a volume of 0.121 cm^3?

43. Convert the boiling temperature of gold, 2966 °C, into degrees Fahrenheit and kelvin.
44. Convert the temperature of scalding water, 54 °C, into degrees Fahrenheit and kelvin.
45. Convert the temperature of the coldest area in a freezer, −10 °F, to degrees Celsius and kelvin.
46. Convert the temperature of dry ice, −77 °C, into degrees Fahrenheit and kelvin.
47. Convert the boiling temperature of liquid ammonia, −28.1 °F, into degrees Celsius and kelvin.
48. The label on a pressurized can of spray disinfectant warns against heating the can above 130 °F. What are the corresponding temperatures on the Celsius and kelvin temperature scales?

CHAPTER TWO

Atoms, Molecules and Ions

Introduction

Your overall health and susceptibility to disease depends upon the complex interaction between your genetic makeup and environmental exposure, with the outcome difficult to predict. Early detection of biomarkers, substances that indicate an organism's disease or physiological state, could allow diagnosis and treatment before a condition becomes serious or irreversible. Recent studies have shown that your exhaled breath can contain molecules that may be biomarkers for recent exposure to environmental contaminants or for pathological conditions ranging from asthma to lung cancer. Scientists are working to develop biomarker "fingerprints" that could be used to diagnose a specific disease based on the amounts and identities of certain molecules in a patient's exhaled breath. An essential concept underlying this goal is that of a molecule's identity, which is determined by the numbers and types of atoms it contains, and how they are bonded together. This chapter will describe some of the fundamental chemical principles related to the composition of matter, including those central to the concept of molecular identity.

Learning Objective of the Chapter: At the end of this chapter you will be able to

- Define the atomic mass unit and average atomic mass
- Calculate average atomic mass and isotopic abundance
- Represent the bonding arrangement of atoms within molecules using structural formulas
- Predict the general properties of elements based on their location within the periodic table
- Predict the type of compound formed from elements based on their location within the periodic table
- Derive names for common types of inorganic compounds using a systematic approach

2.1. Atomic structure and symbolism

The development of modern atomic theory revealed much about the inner structure of atoms. It was learned that an atom contains a very small nucleus composed of positively charged protons and uncharged neutrons, surrounded by a much larger volume of space containing negatively charged electrons. The nucleus contains the majority of an atom's mass because protons and neutrons are much heavier than electrons, whereas electrons occupy almost all of an atom's volume. The diameter of an atom is on the order of 10^{-10} m, whereas the diameter of the nucleus is roughly 10^{-15} m, about 100,000 times smaller. For a perspective about their relative sizes, consider this: If the nucleus were the size of a blueberry, the atom would be about the size of a football stadium (Figure 2.1).

Figure 2.1: If an atom could be expanded to the size of a football stadium, the nucleus would be the size of a single blueberry.

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.) The 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.

A proton has a mass of 1.0073 amu and a charge of 1+. A neutron is a slightly heavier particle with a mass 1.0087 amu and a charge of zero; as its name suggests, it is neutral. The electron has a charge of 1- and is a much lighter particle with a mass of about 0.00055 amu (it would take about 1800 electrons to equal the mass of one proton). The properties of these fundamental particles are summarized in Table 2.1. (An observant student might notice that the sum of an atom’s subatomic particles does not equal the atom’s actual mass: The total mass of six protons, six neutrons, and six electrons is 12.0993 amu, slightly larger than 12.00 amu. This "missing" mass is known as the mass defect.

Table2.1: Properties of Subatomic Particles

Name	**Location**	**Charge (C)**	**Unit Charge**	**Mass (amu)**	**Mass (g)**
Electron	outside nucleus	-1.602×10^{-19}	1−	0.00055	0.00091×10^{-24}
Proton	Nucleus	1.602×10^{-19}	1+	1.00727	1.67262×10^{-24}
Neutron	Nucleus	0	0	1.00866	1.67493×10^{-24}

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.

$$\boldsymbol{atomic\ number(Z) = number\ of\ protons}$$

$$\boldsymbol{mass\ number(A) = number\ of\ protons + number\ of\ neutrons}$$

$$\boldsymbol{A - Z = number\ of\ neutrons}$$

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:

Atomic charge = number of protons − 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 2.1

Composition of an Atom

Iodine is an essential trace element in our diet; it is needed to produce thyroid hormone. Insufficient iodine in the diet can lead to the development of a goiter, an enlargement of the thyroid gland (Figure 2.2).

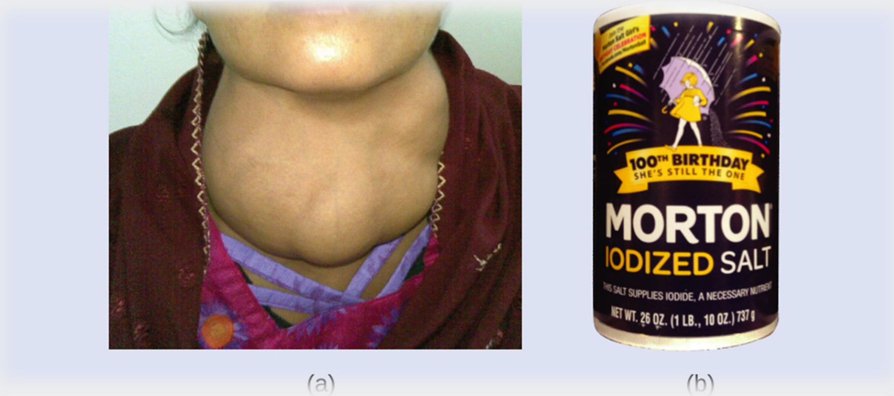


Figure 2.2: (a) Insufficient iodine in the diet can cause an enlargement of the thyroid gland called a goiter. (b) The addition of small amounts of iodine to salt (iodized salt) prevents the formation of goiters.

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].

✍**Check Your Learning**

- 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?

2.1.1. Chemical Symbols and Isotopes

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. 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).

The symbols for several common elements and their atoms are listed in Table 2.2. Some symbols are derived from the common name of the element; others are abbreviations of the name in another language. Most symbols have one or two letters, but three-letter symbols have been used to describe some elements that have atomic numbers greater than 112. 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).

Table2.2: 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 occasionally 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 2.3). The atomic number is sometimes written as a subscript preceding the symbol, but since this number defines the element's identity, as does its symbol, it is often omitted. For example, magnesium exists as a mixture of three isotopes, each with an atomic number of 12 and with mass numbers of 24, 25, and 26, respectively. These isotopes can be identified as ^{24}Mg, ^{25}Mg, and ^{26}Mg. These isotope symbols are read as "element, mass number" and can be symbolized consistent with this reading. For instance, ^{24}Mg is read as "magnesium 24," and can be written as "magnesium-24" or "Mg-24." ^{25}Mg is read as "magnesium 25," and can be written as "magnesium-25" or "Mg-25." All magnesium atoms have 12 protons in their nucleus. They differ only because a ^{24}Mg atom has 12 neutrons in its nucleus, a ^{25}Mg atom has 13 neutrons, and a ^{26}Mg has 14 neutrons.

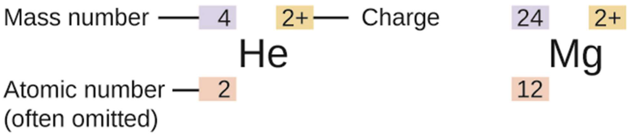


Figure 2.3: The symbol for an atom indicates the element via its usual two-letter symbol, the mass number as a left superscript, the atomic number as a left subscript (sometimes omitted), and the charge as a right superscript.

Information about the naturally occurring isotopes of elements with atomic numbers 1 through 10 is given in Table 2.3. 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}H, is also called deuterium and sometimes symbolized D. Hydrogen-3, symbolized ^{3}H, is also called tritium and sometimes symbolized T.

Table2.3: Nuclear Compositions of Atoms of the Very Light Elements

Element	**Symbol**	**Atomic No.**	**No of Protons**	**No of Neutrons**	**Mass (amu)**	**% Natural Abundance**
hydrogen	${}^{1}_{1}$H(protium)	1	1	0	1.0078	99.989
	${}^{2}_{1}$H(deuterium)	1	1	1	2.0141	0.0115
	${}^{3}_{1}$H(**t**ritium)	1	1	2	3.01605	— (trace)
Helium	${}^{3}_{2}$He	2	2	1	3.01603	0.00013
	${}^{4}_{2}$He	2	2	2	4.0026	100

Element	**Symbol**	**Atomic No.**	**No̲ of Protons**	**No̲ of Neutrons**	**Mass (amu)**	**% Natural Abundance**
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	${}^{10}_{5}B$	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
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

2.1.2. Atomic mass unit and average 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}B with a mass of 10.0129 amu, and the remaining 80.1% are ^{11}B with a mass of 11.0093 amu. The average atomic mass for boron is calculated to be:

$$boron\ average\ mass = (0.199 \times 10.0129\ amu) + (0.801 \times 11.0093\ amu)$$
$$= 1.99\ amu + 8.82\ amu = 10.81\ amu$$

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

Example 2.2

Calculation of Average Atomic Mass

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

Solution

$$average\ mas = (0.9184 \times 19.9924\ amu) + (0.0047 \times 20.9940\ amu) + (0.0769 \times 21.9914\ amu) = (18.36 + 0.099 + 1.69) amu = 20.15\ amu$$

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.)

✍Check Your Learning

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

Example 2.3

Calculation of Percent Abundance

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

Solution

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

Average mass=(fraction of^{35}Cl×mass of^{35}Cl)+(fraction of^{37}Cl×mass of^{37}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:

$$35.453 \text{ amu} = (x\times 34.96885 \text{ amu})+[(1.00-x)\times 36.96590 \text{ amu}]$$

$$35.453 = 34.96885x + 36.96590 - 36.96590x$$

$$1.99705x = 1.513$$

$$x = \frac{1.513}{1.99705} = 0.7576$$

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.

✍**Check Your Learning**

➢ 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?

2.2. Chemical Formulas

A molecular formula is a+ representation of a molecule that uses chemical symbols to indicate the types of atoms followed by subscripts to show the number of atoms of each type in the molecule. (A subscript is used only when more than one atom of a given type is present.) Molecular formulas are also used as abbreviations for the names of compounds.

The structural formula for a compound gives the same information as its molecular formula (the types and numbers of atoms in the molecule) but also shows how the atoms are connected in the molecule. The structural formula for methane contains symbols for one C atom and four H atoms, indicating the number of atoms in the molecule (Figure 2.4). The lines represent bonds that hold the atoms together. (A chemical bond is an attraction between atoms or ions that holds them together in a molecule or a crystal.) We will discuss chemical bonds and see how to predict the arrangement of atoms in a molecule later. For now, simply know that the lines are an indication of how the atoms are connected in a molecule. 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.

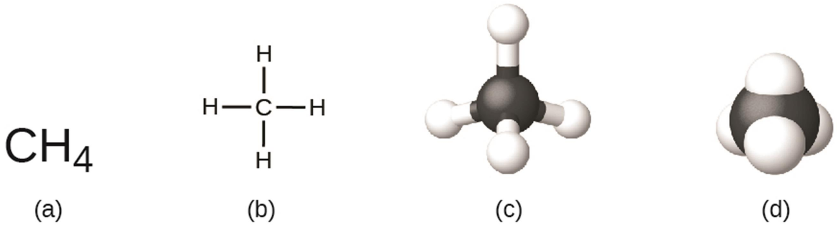


Figure 2.4: A methane molecule can be represented as (a) a molecular formula, (b) a structural formula, (c) a ball-and-stick model, and (d) a space-filling model. Carbon and hydrogen atoms are represented by black and white spheres, respectively.

Although many elements consist of discrete, individual atoms, some exist as molecules made up of two or more atoms of the element chemically bonded together. For example, most samples of the elements hydrogen, oxygen, and nitrogen are composed of molecules that contain two atoms each (called diatomic molecules) and thus have the molecular formulas H_2, O_2, and N_2, respectively. Other elements commonly found as diatomic molecules are fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2). The most common form of the element sulfur is composed of molecules that consist of eight atoms of sulfur; its molecular formula is S_8 (Figure 2.5).

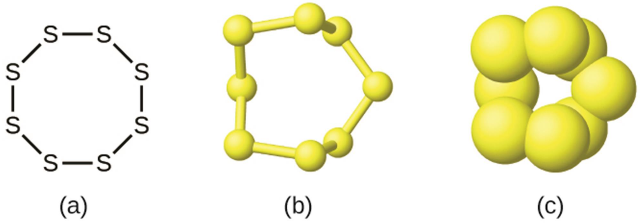


Figure 2.5: A molecule of sulfur is composed of eight sulfur atoms and is therefore written as S_8. It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres.

It is important to note that a subscript following a symbol and a number in front of a symbol do 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 2.6).

This figure shows four diagrams. The diagram for H shows a single, white sphere and is labeled one H atom. The diagram for 2 H shows two white spheres that are not bonded together. It is labeled 2 H atoms. The diagram for H subscript 2 shows two white spheres bonded together. It is labeled one H subscript 2 molecule. The diagram for 2H subscript 2 shows two sets of bonded, white spheres. It is labeled 2H subscript 2 molecules.

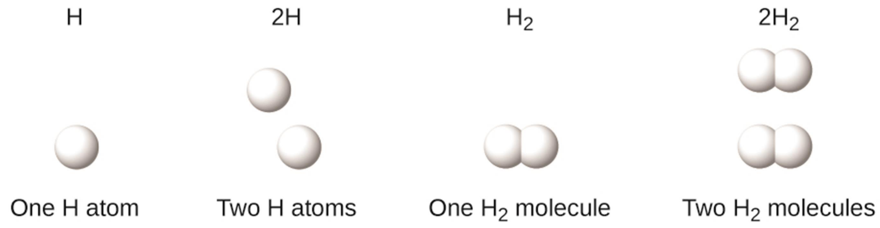


Figure 2.6: The symbols H, 2H, H_2, and $2H_2$ represent very different entities.

Compounds are formed when two or more elements chemically combine, resulting in the formation of bonds. For example, hydrogen and oxygen can react to form water, and sodium and chlorine can react to form table salt. We sometimes describe the composition of these compounds with an empirical formula, which indicates the types of atoms present and the simplest whole-number ratio of the number of atoms (or ions) in the compound. For example, titanium dioxide (used as pigment in white paint and in the thick, white, blocking type of sunscreen) has an empirical formula of TiO_2. This identifies the elements titanium (Ti) and oxygen (O) as the constituents of titanium dioxide, and indicates the presence of twice as many atoms of the element oxygen as atoms of the element titanium (Figure 2.7).

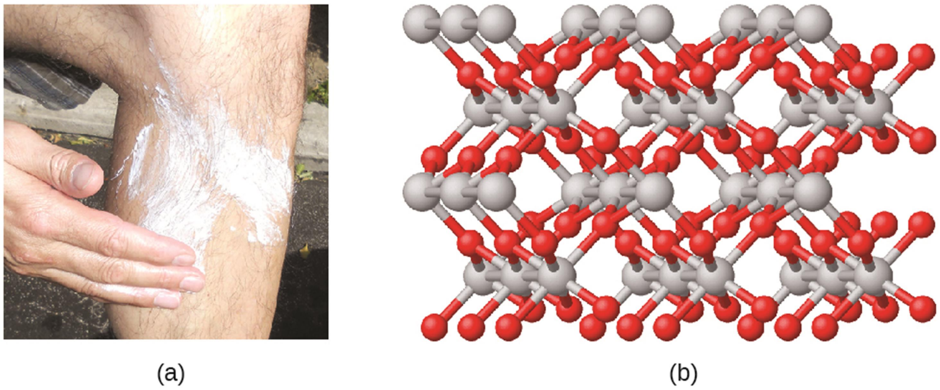


Figure 2.7: (a) The white compound titanium dioxide provides effective protection from the sun. (b) A crystal of titanium dioxide, TiO_2, contains titanium and oxygen in a ratio of 1 to 2. The titanium atoms are gray and the oxygen atoms are red.

Figure a, shows a photo of a person applying suntan lotion to his or her lower leg. Figure b shows a 3-D ball-and-stick model of the molecule titanium dioxide, which involves a complicated interlocking of many titanium and oxygen atoms. The titanium atoms in the molecule are shown as silver spheres and the oxygen atoms are shown as red spheres. There are twice as many oxygen atoms as titanium atoms in the molecule.

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 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 2.8).

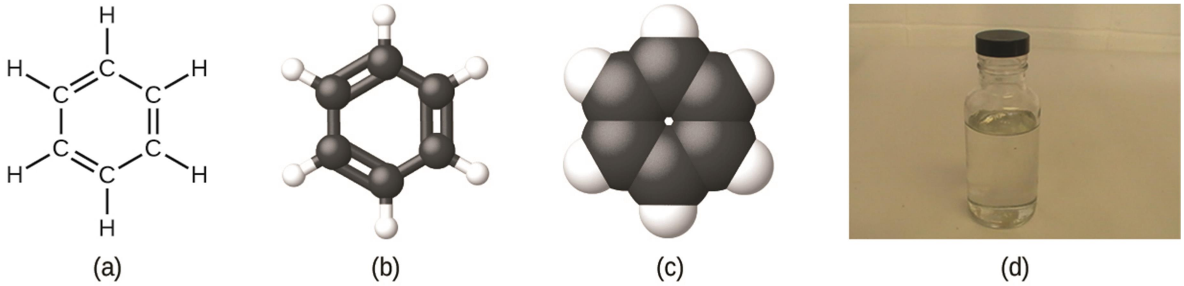


Figure 2.8: Benzene, C_6H_6, is produced during oil refining and has many industrial uses. A benzene molecule can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. (d) Benzene is a clear liquid.

If we know a compound's 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 2.9) 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.

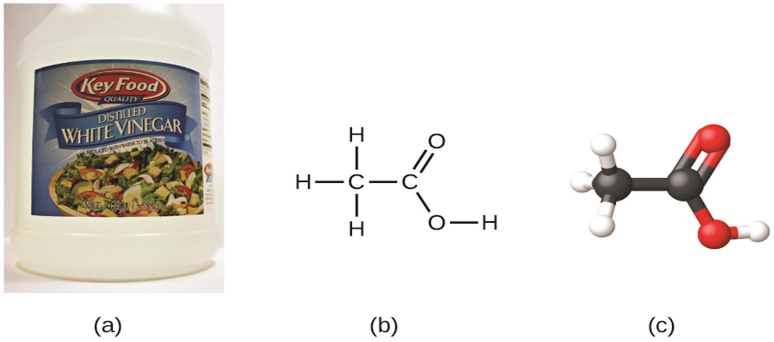


Figure 2.9: (a) Vinegar contains acetic acid, $C_2H_4O_2$, which has an empirical formula of CH_2O. It can be represented as (b) a structural formula and (c) as a ball-and-stick model.

Example 2.4

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 actually contains 6C, 12H, and 6O 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.

✍**Check Your Learning**

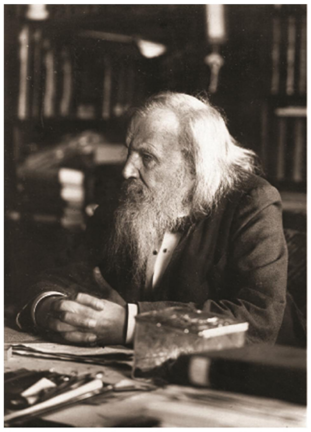
- A molecule of metaldehyde (a pesticide used for snails and slugs) contains 8 carbon atoms, 16 hydrogen atoms, and 4 oxygen atoms. What are the molecular and empirical formulas of metaldehyde?

2.3. The Periodic Table

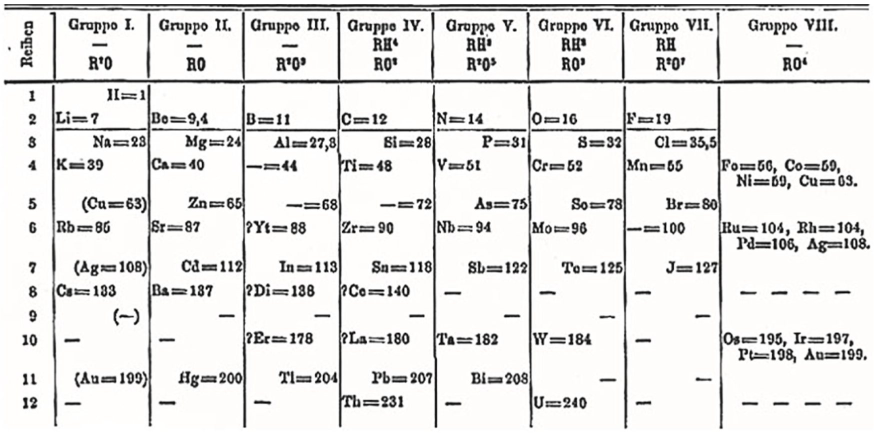
2.3.1. Historical development of the periodic table

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

Dimitri Mendeleev in Russia (1869) and Lothar Meyer in Germany (1870) independently recognized that there was a periodic relationship among the properties of the elements known at that time. Both published tables with the elements arranged according to increasing atomic mass. But Mendeleev went one step further than Meyer: He used his table to predict the existence of elements that would have the properties similar to aluminum and silicon, but were yet unknown. The discoveries of gallium (1875) and germanium (1886) provided great support for Mendeleev's work. Although Mendeleev and Meyer had a long dispute over priority, Mendeleev's contributions to the development of the periodic table are now more widely recognized (Figure 2.10).



(a)



Reihen	Gruppo I. — R^2O	Gruppo II. — RO	Gruppo III. — R^2O^3	Gruppo IV. RH^4 RO^2	Gruppo V. RH^3 R^2O^5	Gruppo VI. RH^2 RO^3	Gruppo VII. RH R^2O^7	Gruppo VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=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	—	— — — —

(b)

Figure 2.10: (a) Dimitri Mendeleev is widely credited with creating (b) the first periodic table of the elements.

Figure "a" shows a photograph of Dimitri Mendeleev. Figure "b" shows the first periodic table developed by Mendeleev, which had eight groups and twelve periods.

By the twentieth century, it became apparent that the periodic relationship involved atomic numbers rather than atomic masses. The modern statement of this relationship, the periodic law, is as follows: the properties of the elements are periodic functions of their atomic numbers. A modern periodic table arranges the elements in increasing order of their atomic numbers and groups atoms with similar properties in the same vertical column (Figure 2.11). Each box represents an element and contains its atomic number, symbol, average atomic mass, and (sometimes) name. The elements are arranged in seven horizontal rows, called periods or series, and 18 vertical columns, called groups. Groups are labeled at the top of each column. In the United States, the labels traditionally were numerals with capital letters. However, IUPAC recommends that the numbers 1 through 18 be used, and these labels are more common. For the table to fit on a single page, parts of two of the rows, a total of 14 columns, are usually written below the main body of the table.

The Periodic Table of Elements is shown. The 18 columns are labeled “Group” and the 7 rows are labeled “Period.” Below the table to the right is a box labeled “Color Code” with different colors for metals, metalloids, and nonmetals, as well as solids, liquids, and gases. To the left of this box is an enlarged picture of the upper-left most box on the table. The number 1 is in its upper-left hand corner and is labeled “Atomic number.” The letter “H” is in the middle in red indicating that it is a gas. It is labeled “Symbol.” Below that is the number 1.008 which is labeled “Atomic Mass.” Below that is the word hydrogen which is labeled “name.” The color of the box indicates that it is a nonmetal. Each element will be described in this order: atomic number; name; symbol; whether it is a metal, metalloid, or nonmetal; whether it is a solid, liquid, or gas; and atomic mass.

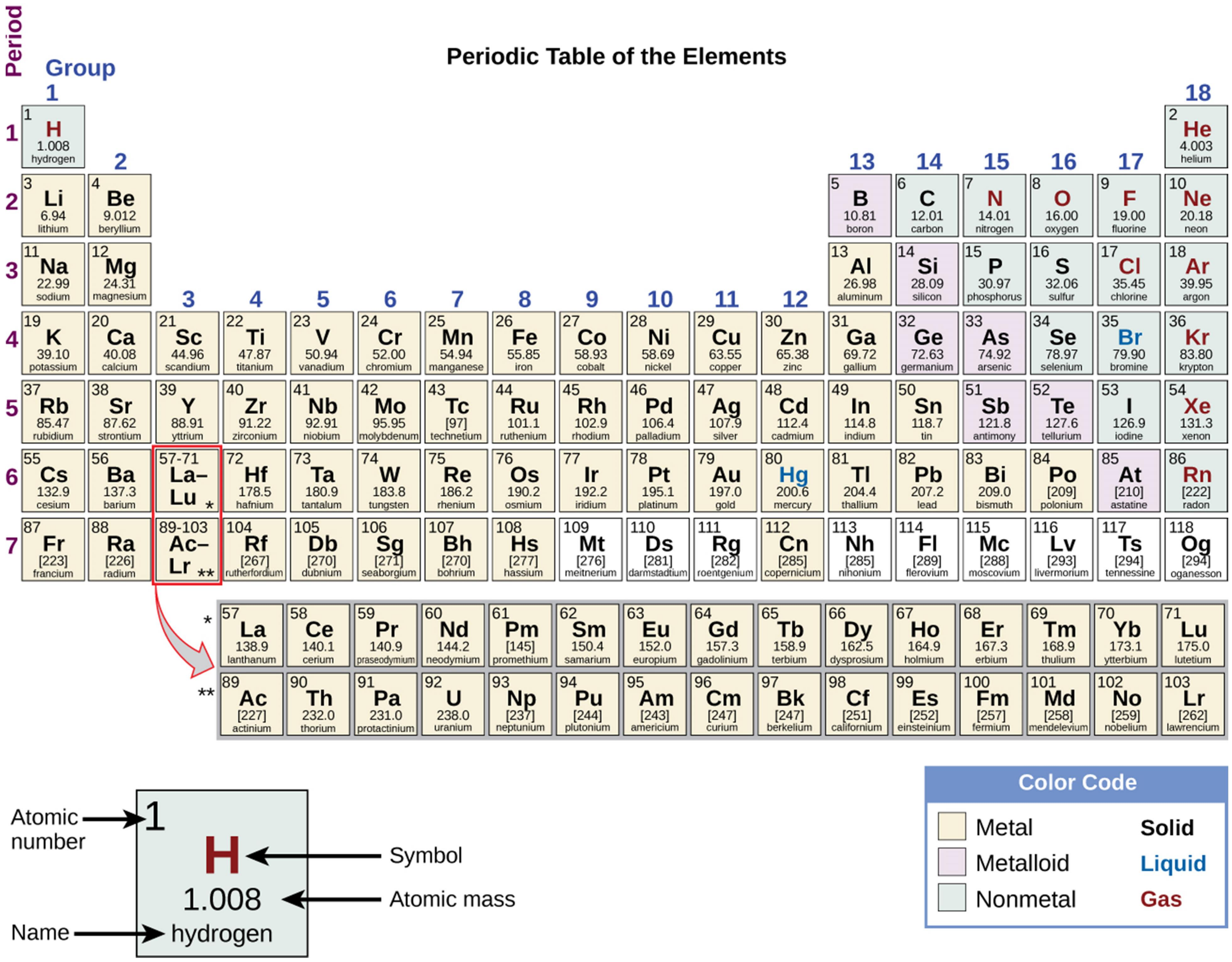


Figure 2.11: Elements in the periodic table are organized according to their properties.

2.3.2. Classification of elements in the periodic table

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

The elements can also be classified into the main-group elements (or representative elements) in the columns labeled 1, 2, and 13–18; the transition metals in the columns labeled 3–12; and inner transition metals in the two rows at the bottom of the table (the top-row elements are called lanthanides and the bottom-row elements are actinides; Figure 2.12). The elements can be subdivided further by more specific properties, such as the composition of the compounds they form. For example, the elements in group 1 (the first column) form compounds that consist of one atom of the element and one atom of hydrogen. These elements (except hydrogen) are known as alkali metals, and they all have similar chemical properties. The elements in group 2 (the second column) form compounds consisting of one atom of the element and two atoms of hydrogen: These are called alkaline earth metals, with similar properties among members of that group. Other groups with specific names are the pnictogens (group 15), chalcogens (group 16), halogens (group 17), and the noble gases (group 18, also known as inert gases). The groups can also be referred to by the first element of the group: For example, the chalcogens can be called the oxygen group or oxygen family. Hydrogen is a unique, nonmetallic element with properties similar to both group 1 and group 17 elements. For that reason, hydrogen may be shown at the top of both groups, or by itself.

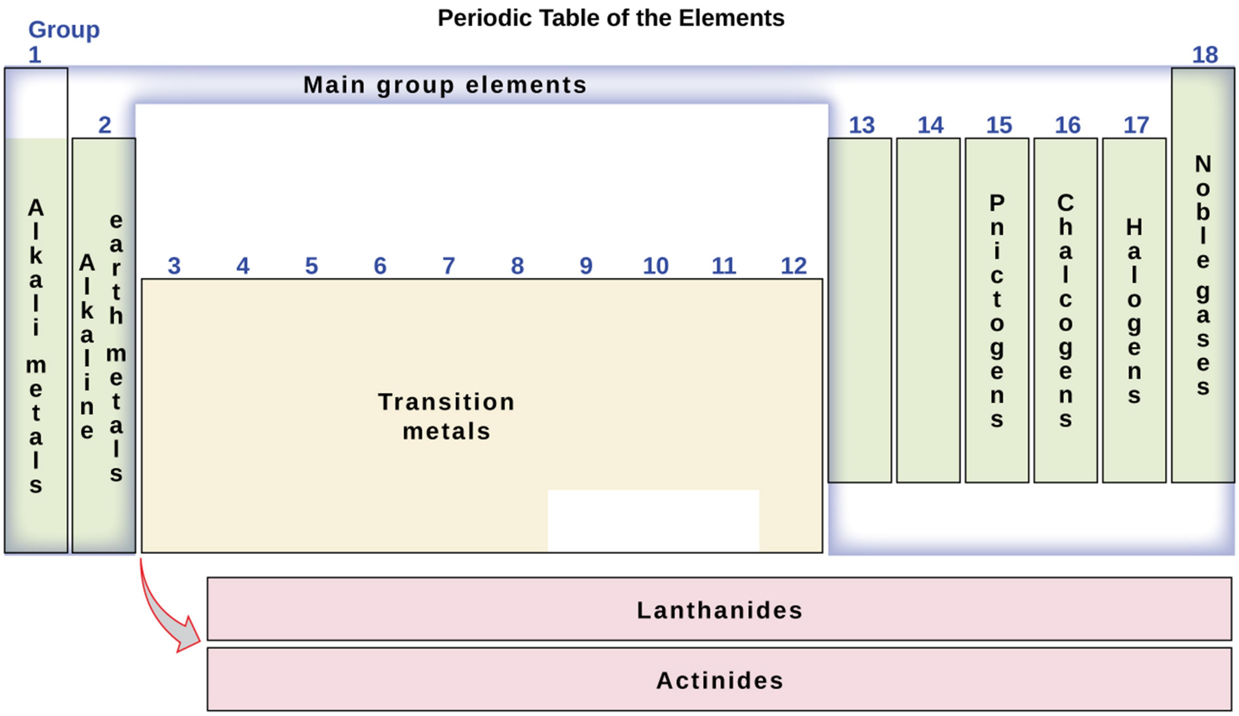


Figure 2.12: The periodic table organizes elements with similar properties into groups.

Example 2.5

Naming Groups of Elements

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

(a) Chlorine (c) Sodium

(b) Calcium

Solution: The family names are as follows:

(a) Halogen (c) Alkali metal

(b) Alkaline earth metal

✍**Check Your Learning**

Give the group name for each of the following elements:

(a) Krypton (b) selenium(c) lithium (d) barium

2.4. Ionic and Molecular Compounds

In ordinary chemical reactions, the nucleus of each atom (and thus the identity of the element) remains unchanged. Electrons, however, can be added to atoms by transfer from other atoms, lost by transfer to other atoms, or shared with other atoms. The transfer and sharing of electrons among atoms govern the chemistry of the elements. During the formation of some compounds, atoms gain or lose electrons, and form electrically charged particles called ions (Figure 2.13).

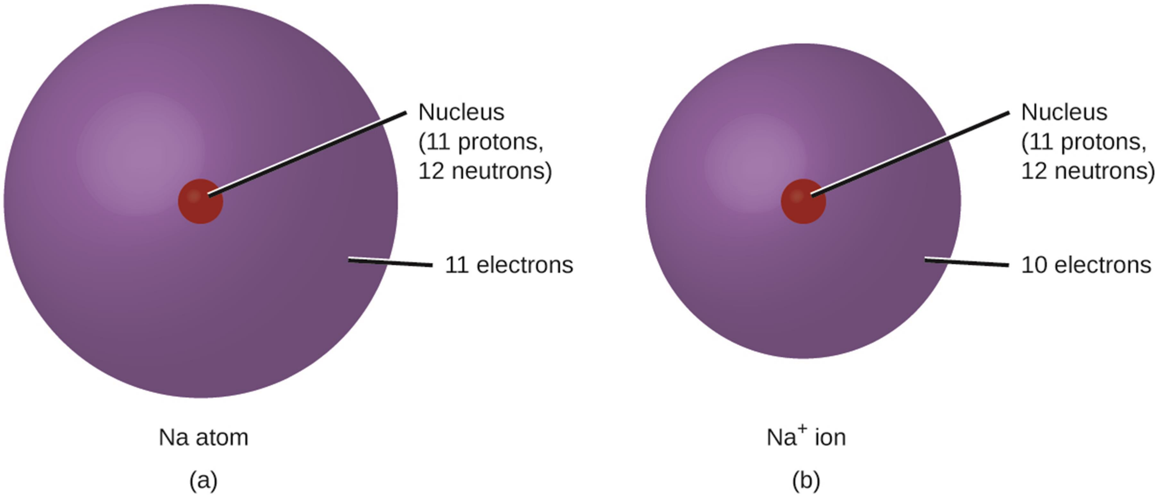


Figure 2.13: (a) A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. (b) A sodium cation (Na+) has lost an electron, so it has one more proton (11) than electrons (10), giving it an overall positive charge, signified by a superscripted plus sign. The

ion's electron cloud contains 10 electrons and is smaller than that of the sodium atom in figure "a".

You can use the periodic table to predict whether an atom will form an anion or a cation, and you can often predict the charge of the resulting ion. Atoms of many main-group metals lose enough electrons to leave them with the same number of electrons as an atom of the preceding noble gas. To illustrate, an atom of an alkali metal (group 1) loses one electron and forms a cation with a 1+ charge; an alkaline earth metal (group 2) loses two electrons and forms a cation with a 2+ charge, and so on. For example, a neutral calcium atom, with 20 protons and 20 electrons, readily loses two electrons. This results in a cation with 20 protons, 18 electrons, and a 2+ charge. It has the same number of electrons as atoms of the preceding noble gas, argon, and is symbolized Ca^{2+}. The name of a metal ion is the same as the name of the metal atom from which it forms, so Ca^{2+} is called a calcium ion.

When atoms of nonmetal elements form ions, they generally gain enough electrons to give them the same number of electrons as an atom of the next noble gas in the periodic table. Atoms of group 17 gain one electron and form anions with a 1− charge; atoms of group 16 gain two electrons and form ions with a 2− charge, and so on. For example, the neutral bromine atom, with 35 protons and 35 electrons, can gain one electron to provide it with 36 electrons. This results in an anion with 35 protons, 36 electrons, and a 1− charge. It has the same number of electrons as atoms of the next noble gas, krypton, and is symbolized Br−.

Note the usefulness of the periodic table in predicting likely ion formation and charge (Figure 2.14). Moving from the far left to the right on the periodic table, main-group elements tend to form cations with a charge equal to the group number. That is, group 1 elements form 1+ ions; group 2 elements form 2+ ions, and so on. Moving from the far right to the left on the periodic table, elements often form anions with a negative charge equal to the number of groups moved left from the noble gases. For example, group 17 elements (one group left of the noble gases) form 1− ions; group 16 elements (two groups left) form 2− ions, and so on. This trend can be used as a guide in many cases, but its predictive value decreases when moving toward the center of the periodic table. In fact, transition metals and some other metals often exhibit variable charges that are not predictable by their location in the table. For example, copper can form ions with a 1+ or 2+ charge, and iron can form ions with a 2+ or 3+ charge.

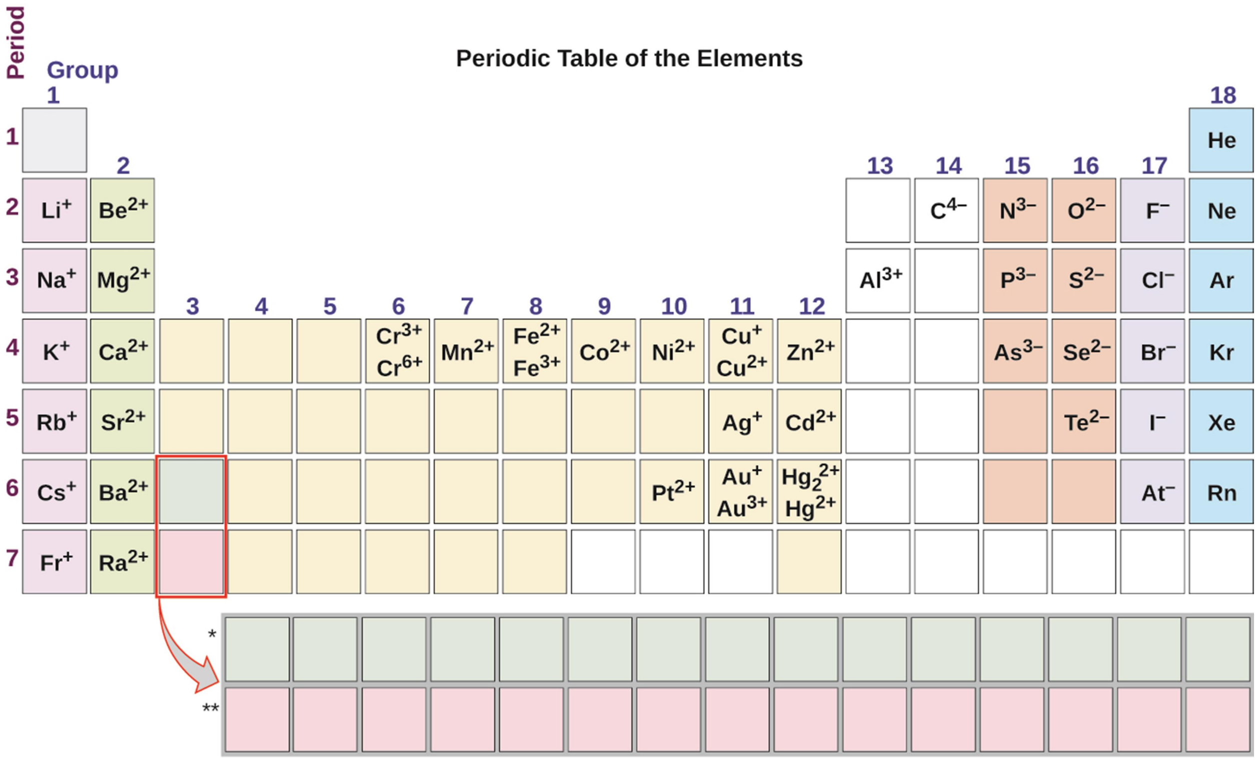


Figure 2.14**:** Some elements exhibit a regular pattern of ionic charge when they form ions.

Example 2.6

Composition of Ions

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

Solution

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

Example 2.7

Formation of Ions

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

Solution

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

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

Check Your Learning

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

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

The ions that we have discussed so far are called monatomic ions, that is, they are ions formed from only one atom. We also find many polyatomic ions. These ions, which act as discrete units, are electrically charged molecules (a group of bonded atoms with an overall charge). Some of the more important polyatomic ions are listed in Table 2.4. Oxyanions are polyatomic ions that contain one or more oxygen atoms. At this point in your study of chemistry, you should memorize the names, formulas, and charges of the most common polyatomic ions. Because you will use them repeatedly, they will soon become familiar.

Table 2.4: Common Polyatomic Ions

Name	Formula	Related Acid	Formula
Ammonium	NH_4^+		
Hydronium	H_3O^+		
Peroxide	O_2^{2-}		
Hydroxide	OH^-		
Acetate	CH_3COO^-	acetic acid	CH_3COOH
Cyanide	CN^-	hydrocyanic acid	HCN
Azide	N_3^-	hydrazoic acid	HN_3
Carbonate	CO_3^{2-}	carbonic acid	H_2CO_3
Bicarbonate	HCO_3^-		
Nitrate	NO_3^-	nitric acid	HNO_3
Nitrite	NO_2^-	nitrous acid	HNO_2
Sulfate	SO_4^{2-}	sulfuric acid	H_2SO_4
Hydrogen sulfate	HSO_4^-		
Sulfite	SO_3^{2-}	sulfurous acid	H_2SO_3
Hydrogen sulfite	HSO_3^-		
Phosphate	PO_4^{3-}	phosphoric acid	H_3PO_4
Hydrogen phosphate	HPO_4^{2-}		
Dihydrogen phosphate	$H_2PO_4^-$		
Perchlorate	ClO_4^-	perchloric acid	$HClO_4$
Chlorate	ClO_3^-	chloric acid	$HClO_3$
Chlorite	ClO_2^-	chlorous acid	$HClO_2$
Hypochlorite	ClO^-	hypochlorous acid	$HClO$
Chromate	CrO_4^{2-}	chromic acid	H_2CrO_4
Dichromate	$Cr_2O_7^{2-}$	dichromic acid	$H_2Cr_2O_7$
Permanganate	MnO_4^-	permanganic acid	$HMnO_4$

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

The nature of the attractive forces that hold atoms or ions together within a compound is the basis for classifying chemical bonding. When electrons are transferred and ions form, ionic bonds result. Ionic bonds are electrostatic forces of attraction, that is, the attractive forces experienced between objects of opposite electrical charge (in this case, cations and anions). When electrons are "shared" and molecules form, covalent bonds result. Covalent bonds are the attractive forces between the positively charged nuclei of the bonded atoms and one or more pairs of electrons that are located between the atoms. Compounds are classified as ionic or molecular (covalent) on the basis of the bonds present in them.

2.4.1. Formation of Ionic Compounds

When an element composed of atoms that readily lose electrons (a metal) reacts with an element composed of atoms that readily gain electrons (a nonmetal), a transfer of electrons usually occurs, producing ions. The compound formed by this transfer is stabilized by the electrostatic attractions (ionic bonds) between the ions of opposite charge present in the compound. For example, when each sodium atom in a sample of sodium metal (group 1) gives up one electron to form a sodium cation, Na^+, and each chlorine atom in a sample of chlorine gas (group 17) accepts one electron to form a chloride anion, Cl^-, the resulting compound, NaCl, is composed of sodium ions and chloride ions in the ratio of one Na^+ ion for each Cl^- ion. Similarly, each calcium atom (group 2) can give up two electrons and transfer one to each of two chlorine atoms to form $CaCl_2$, which is composed of Ca^{2+} and Cl^- ions in the ratio of one Ca^{2+} ion to two Cl^- ions.

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

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

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

Example 2.8

Predicting the Formula of an Ionic Compound

The gemstone sapphire (Figure 2.15) is mostly a compound of aluminum and oxygen that contains aluminum cations, Al^{3+}, and oxygen anions, O^{2-}. What is the formula of this compound?

Figure 2.15: Although pure aluminum oxide is colorless, trace amounts of iron and titanium give blue sapphire its characteristic color. This is a photograph of a ring with a sapphire set in it.

Solution

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

Many ionic compounds contain polyatomic ions (Table 2.4) as the cation, the anion, or both. As with simple ionic compounds, these compounds must also be electrically neutral, so their formulas can be predicted by treating the polyatomic ions as discrete units. We use parentheses in a formula to indicate a group of atoms that behave as a unit. For example, the formula for calcium phosphate, one of the minerals in our bones, is $Ca_3(PO_4)_2$. This formula indicates that there are three calcium ions (Ca^{2+}) for every two phosphate ($PO_4{}^{3-}$) groups. The $PO_4{}^{3-}$ groups are discrete units, each consisting of one phosphorus atom and four oxygen atoms, and having an overall charge of 3−. The compound is electrically neutral, and its formula shows a total count of three Ca, two P, and eight O atoms.

Example 2.9

Predicting the Formula of a Compound with a Polyatomic Anion

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

Solution

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

✍**Check Your Learning**

1. Predict the formula of the ionic compound formed between the lithium ion and the peroxide ion, $O_2{}^{2-}$ (Hint: Use the periodic table to predict the sign and the charge on the lithium ion.)
2. Predict the formula of the ionic compound formed between the sodium cation, Na^+, and the sulfide anion, S^{2-}.

Because an ionic compound is not made up of single, discrete molecules, it may not be properly symbolized using a molecular formula. Instead, ionic compounds must be symbolized by a formula indicating the relative numbers of its constituent ions. For compounds containing only monatomic ions (such as NaCl) and for many compounds containing polyatomic ions (such as $CaSO_4$), these formulas are just the empirical formulas introduced earlier in this chapter. However, the formulas for some ionic compounds containing polyatomic ions are not empirical formulas. For example, the ionic compound sodium oxalate is comprised of Na^+ and $C_2O_4^{2-}$ ions combined in a 2:1 ratio, and its formula is written as $Na_2C_2O_4$. The subscripts in this formula are not the smallest-possible whole numbers, as each can be divided by 2 to yield the empirical formula, $NaCO_2$. This is not the accepted formula for sodium oxalate, however, as it does not accurately represent the compound's polyatomic anion, $C_2O_4^{2-}$.

2.4.2. Formation of Molecular Compounds

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

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

Example 2.10

Predicting the Type of Bonding in Compounds

Predict whether the following compounds are ionic or molecular:

(a) KI, the compound used as a source of iodine in table salt

(b) H_2O_2, the bleach and disinfectant hydrogen peroxide

(c) $CHCl_3$, the anesthetic chloroform

(d) Li_2CO_3, a source of lithium in antidepressants

Solution

(a) Potassium (group 1) is a metal, and iodine (group 17) is a nonmetal; KI is predicted to be ionic.

(b) Hydrogen (group 1) is a nonmetal, and oxygen (group 16) is a nonmetal; H_2O_2 is predicted to be molecular.

(c) Carbon (group 14) is a nonmetal, hydrogen (group 1) is a nonmetal, and chlorine (group 17) is a nonmetal; $CHCl_3$ is predicted to be molecular.

(d) Lithium (group 1) is a metal, and carbonate is a polyatomic ion; Li_2CO_3 is predicted to be ionic.

✍**Check Your Learning**

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

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

2.5. Chemical Nomenclature

Nomenclature, a collection of rules for naming things, is important in science and in many other situations. This module describes an approach that is used to name simple ionic and molecular compounds, such as NaCl, $CaCO_3$, and N_2O_4. The simplest of these are **binary compounds**, those containing only two elements, but we will also consider how to name ionic compounds containing polyatomic ions, and one specific, very important class of compounds known as acids (subsequent chapters in this module will focus on these compounds in great detail). We will limit our attention here to inorganic compounds, compounds that are composed principally of elements other than carbon, and will follow the nomenclature guidelines proposed by IUPAC. The rules for organic compounds, in which carbon is the principle element, will be treated in a later chapter on organic chemistry.

2.5.1. Ionic compounds

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

2.5.1.1. Compounds Containing Only Monatomic Ions

The name of a binary compound containing monatomic ions consists of the name of the cation (the name of the metal) followed by the name of the anion (the name of the nonmetallic element with its ending replaced by the suffix -*ide*). Some examples are given in Table 2.5.

Table2.5: Names of Some Ionic Compounds

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

2.5.1.2. Compounds Containing Polyatomic Ions

Compounds containing polyatomic ions are named similarly to those containing only monatomic ions, i.e. by naming first the cation and then the anion. Examples are shown in Table 2.6.

Table2.6: Names of Some Polyatomic Ionic Compounds

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

CHEMISTRY IN EVERYDAY LIFE

Ionic Compounds in Your Cabinets

Every day you encounter and use a large number of ionic compounds. Some of these compounds, where they are found, and what they are used for are listed in Table 2.7. Look at the label or ingredients list on the various products that you use during the next few days, and see if you run into any of those in this table, or find other ionic compounds that you could now name or write as a formula.

Table 2.7: Everyday Ionic Compounds

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

2.5.1.3. Compounds Containing a Metal Ion with a Variable Charge

Most of the transition metals and some main group metals can form two or more cations with different charges. Compounds of these metals with nonmetals are named with the same method as compounds in the first category, except the charge of the metal ion is specified by a Roman numeral in parentheses after the name of the metal. The charge of the metal ion is determined from the formula of the compound and the charge of the anion. For example, consider binary ionic compounds of iron and chlorine. Iron typically exhibits a charge of either 2+ or 3+ (see Figure 2.14), and the two corresponding compound formulas are $FeCl_2$ and $FeCl_3$. The simplest name, "iron chloride," will, in this case, be ambiguous, as it does not distinguish between these two compounds. In cases like this, the charge of the metal ion is included as a Roman numeral in parentheses immediately following the metal name. These two compounds are then unambiguously named iron(II) chloride and iron(III) chloride, respectively. Other examples are provided in Table 2.8.

Table2.8: Some Ionic Compounds with Variably Charged Metal Ions

Compound	**Name**
$FeCl_2$	iron(II) chloride
$FeCl_3$	iron(III) chloride
Hg_2O	mercury(I) oxide
HgO	mercury(II) oxide
SnF_2	tin(II) fluoride
SnF_4	tin(IV) fluoride

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

2.5.1.4. Ionic Hydrates

Ionic compounds that contain water molecules as integral components of their crystals are called **hydrates**. The name for an ionic hydrate is derived by adding a term to the name for the anhydrous (meaning “not hydrated”) compound that indicates the number of water molecules associated with each formula unit of the compound. The added word begins with a Greek prefix denoting the number of water molecules (see Table 2.9) and ends with “hydrate.” For example, the anhydrous compound copper(II) sulfate also exists as a hydrate containing five water molecules and named copper(II) sulfate pentahydrate. Washing soda is the common name for a hydrate of sodium carbonate containing 10 water molecules; the systematic name is sodium carbonate decahydrate.

Formulas for ionic hydrates are written by appending a vertically centered dot, a coefficient representing the number of water molecules, and the formula for water. The two examples mentioned in the previous paragraph are represented by the formulas
Copper(II) sulfate pentahydrate $CuSO_4{\cdot}5H_2O$
Sodium carbonate decahydrate$Na_2CO_3{\cdot}10H_2O$

Table2.9: Nomenclature Prefixes

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

Example 2.11

Naming Ionic Compounds

Name the following ionic compounds

(a) Fe_2S_3 (b) CuSe (c) GaN (d) $MgSO_4{\cdot}7H_2O$ (e) $Ti_2(SO_4)_3$

Solution

The anions in these compounds have a fixed negative charge (S^{2-}, Se^{2-} , N^{3-}, Cl^{-}, and SO_4^{2-}),SO_4^{2-}), and the compounds must be neutral. Because the total number of positive charges in each compound must equal the total number of negative charges, the positive ions must be Fe^{3+}, Cu^{2+}, Ga^{3+}, Cr^{3+}, and Ti^{3+}. These charges are used in the names of the metal ions:

(a) iron(III) sulfide (b) copper(II) selenide (c) gallium(III) nitride
(d) magnesium sulfate heptahydrate (e) titanium(III) sulfate

✍**Check Your Learning**

Write the formulas of the following ionic compounds:

(a) Chromium(III) phosphide (d) copper(I) oxide
(b) Mercury(II) sulfide (e) iron(III) chloride dihydrate
(c) Manganese(II) phosphate

2.5.2. Molecular Compounds

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

2.5.2.1. Compounds Composed of Two Elements

When two nonmetallic elements form a molecular compound, several combination ratios are often possible. For example, carbon and oxygen can form the compounds CO and CO_2. Since these are different substances with different properties, they cannot both have the same name (they cannot both be called carbon oxide). To deal with this situation, we use a naming method that is somewhat similar to that used for ionic compounds, but with added prefixes to specify the numbers of atoms of each element. The name of the more metallic element (the one farther to the left and/or bottom of the periodic table) is first, followed by the name of the more nonmetallic element (the one farther to the right and/or top) with its ending changed to the suffix *–ide*. The numbers of atoms of each element are designated by the Greek prefixes shown in Table 2.10.

When only one atom of the first element is present, the prefix *mono-* is usually deleted from that part. Thus, CO is named carbon monoxide, and CO_2 is called carbon dioxide. When two vowels are adjacent, the *a* in the Greek prefix is usually dropped. Some other examples are shown in Table 2.10.

Table2.10: Names of Some Molecular Compounds Composed of Two Elements

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

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

Example 2.12

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

✍**Check Your Learning**

Write the formulas for the following compounds:

(a) phosphorus pentachloride (b) dinitrogen monoxide (c) iodine heptafluoride

(d) carbon tetrachloride

2.5.2.2. 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 module, but for now, it will suffice to note that many acids release hydrogen ions, H^+, when dissolved in water. To denote this distinct chemical property, a mixture of water with an acid is given a name derived from the compound's name. If the compound is a **binary acid** (comprised of hydrogen and one other nonmetallic element):

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

For example, when the gas HCl (hydrogen chloride) is dissolved in water, the solution is called *hydrochloric acid*. Several other examples of this nomenclature are shown in Table 2.11

Table2.11: 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

2.5.2.3. 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. 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 2.12. 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 sulfurous, acid).

Table 2.12: 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

Review Exercise

1. In what way are isotopes of a given element always different? In what way(s) are they always the same?
2. Write the symbol for each of the following ions:
    - (a) the ion with a 1+ charge, atomic number 55, and mass number 133
    - (b) the ion with 54 electrons, 53 protons, and 74 neutrons
    - (c) the ion with atomic number 15, mass number 31, and a 3− charge
    - (d) the ion with 24 electrons, 30 neutrons, and a 3+ charge
3. Write the symbol for each of the following ions:
4. Determine the number of protons, neutrons, and electrons in the following isotopes that are used in medical diagnoses:
    - (a) atomic number 9, mass number 18, charge of 1
    - (b) atomic number 43, mass number 99, charge of 7+
    - (c) atomic number 53, atomic mass number 131, charge of 1−
    - (d) atomic number 81, atomic mass number 201, charge of 1+
    - (e) Name the elements in parts (a), (b), (c), and (d).
5. The following are properties of isotopes of two elements that are essential in our diet. Determine the number of protons, neutrons and electrons in each and name them.
    - (a) atomic number 26, mass number 58, charge of 2+
    - (b) atomic number 53, mass number 127, charge of 1−
6. Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes:
    - (a) ${}^{10}{}_{5}\mathrm{B}$
    - (b) ${}^{199}{}_{80}\mathrm{Hg}$
    - (c) ${}^{63}{}_{29}\mathrm{Cu}$
    - (d) ${}^{77}{}_{34}\mathrm{Se}$
7. An element has the following natural abundances and isotopic masses: 90.92% abundance with 19.99 amu, 0.26% abundance with 20.99 amu, and 8.82% abundance with 21.99 amu. Calculate the average atomic mass of this element.
8. Average atomic masses listed by IUPAC are based on a study of experimental results. Bromine has two isotopes, ${}^{79}\mathrm{Br}$ and ${}^{81}\mathrm{Br}$, whose masses (78.9183 and 80.9163 amu, respectively) and abundances (50.69% and 49.31%, respectively) were determined in

earlier experiments. Calculate the average atomic mass of bromine based on these experiments.

9. Variations in average atomic mass may be observed for elements obtained from different sources. Lithium provides an example of this. The isotopic composition of lithium from naturally occurring minerals is 7.5% ^{6}Li and 92.5% ^{7}Li, which have masses of 6.01512 amu and 7.01600 amu, respectively. A commercial source of lithium, recycled from a military source, was 3.75% ^{6}Li (and the rest ^{7}Li). Calculate the average atomic mass values for each of these two sources.
10. The ^{18}O:^{16}O abundance ratio in some meteorites is greater than that used to calculate the average atomic mass of oxygen on earth. Is the average mass of an oxygen atom in these meteorites greater than, less than, or equal to that of a terrestrial oxygen atom?
11. Explain why the symbol for the element sulfur and the formula for a molecule of sulfur differ.
12. Determine the empirical formulas for the following compounds:
    - (a) caffeine, $C_8H_{10}N_4O_2$
    - (b) fructose, $C_{12}H_{22}O_{11}$
    - (c) hydrogen peroxide, H_2O_2
13. (d) ascorbic acid (vitamin C), $C_6H_8O_6$
14. Using the periodic table, identify the lightest member of each of the following groups:
    - (a) noble gases
    - (b) alkaline earth metals
    - (c) alkali metals
    - (d) chalcogens
15. Use the periodic table to give the name and symbol for each of the following elements:
    - (a) the noble gas in the same period as germanium
    - (b) the alkaline earth metal in the same period as selenium
    - (c) the halogen in the same period as lithium
    - (d) the chalcogen in the same period as cadmium
16. Using the periodic table, predict whether the following chlorides are ionic or covalent: KCl, NCl_3, ICl, $MgCl_2$, PCl_5, $SiCl_4$, PCl_3, $CaCl_2$, CsCl, $CuCl_2$, $CrCl_3$,and CCl_4.
17. For each of the following pairs of ions, write the formula of the compound they will form:
    - (a) Ca^{2+}, S^{2-}
    - (b) NH^{4+}, $SO4^{2-}$
    - (c) Na^{+}, $HPO4^{2-}$
    - (e) Mg^{2+}, $PO4^{3-}$
    - (d) Al^{3+}, Br^{-}
18. Write the formulas of the following compounds:

(a) rubidium bromide
(b) magnesium selenide
(c) sodium oxide
(d) calcium chloride
(e) hydrogen fluoride
(f) gallium phosphide
(g) aluminum bromide
(h) ammonium sulfate
(i) lithium carbonate
(j) sodium perchlorate
(k) barium hydroxide
(l) ammonium carbonate
(m) sulfuric acid
(n) calcium acetate
(o) magnesium phosphate
(p) sodium sulfite

19. Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:

(a) Cr_2O_3
(b) $FeCl_2$
(c) CrO_3
(d) $TiCl_4$
(e) $CoCl_2 \cdot 6H_2O$
(f) MoS_2

20. The following ionic compounds are found in common household products. Name each of the compounds:

(a) $Ca(H_2PO_4)_2$
(b) $FeSO_4$
(c) $CaCO_3$
(d) MgO
(e) $NaNO_2$
21. (f) K

22. What are the IUPAC names of the following compounds?

(a) manganese dioxide
(b) mercurous chloride (Hg_2Cl_2)
(c) ferric nitrate [$Fe(NO_3)_3$]
(d) titanium tetrachloride
(e) cupric bromide ($CuBr_2$)

CHAPTER THREE

Composition of Substances and Solutions

Introduction

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.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 on a frequent basis, 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. Quantitative aspects of the composition of substances (such as the calcium-containing compound) and mixtures (such as the pool water) are the subject of this chapter.

Perform computations relating a solution's concentration and its components' volumes and/or masses using these units.

Learning Objectives of the Chapter: At the end of this chapter you will be able to

- Define the amount unit mole and the related quantity Avogadro's number
- Explain the relation between mass, moles, and numbers of atoms or molecules, and perform calculations deriving these quantities from one another
- Compute the percent composition of a compound
- Determine the empirical and molecular formula of a compound
- Calculate solution concentrations using molarity
- Perform dilution calculations using the dilution equation
- Define the concentration units of mass percentage, volume percentage, mass-volume percentage, parts-per-million (ppm), and parts-per-billion (ppb)

3.1. Formula Mass and Mole Concept

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

3.1.1. Formula Mass

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

Formula Mass for Covalent Substances

For covalent substances, the formula represents the numbers and types of atoms composing a single molecule of the substance; therefore, the formula mass may be correctly referred to as a molecular mass. Consider chloroform ($CHCl_3$), a covalent compound once used as a surgical anesthetic and now primarily used in the production of tetrafluoroethylene, the building block for the "anti-stick" polymer, Teflon. The molecular formula of chloroform indicates that a single molecule contains one carbon atom, one hydrogen atom, and three chlorine atoms. The average molecular mass of a chloroform molecule is therefore equal to the sum of the average atomic masses of these atoms. Figure 3.1 outlines the calculations used to derive the molecular mass of chloroform, which is 119.37 amu.

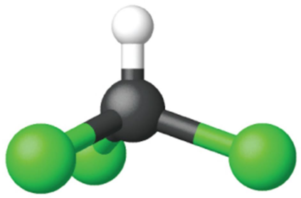
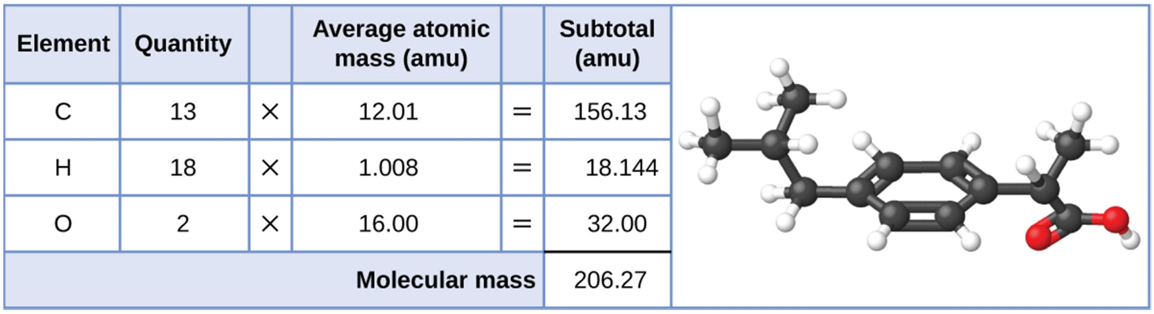
Element	Quantity		Average atomic mass (amu)		Subtotal (amu)	
C	1	×	12.01	=	12.01	
H	1	×	1.008	=	1.008	
Cl	3	×	35.45	=	106.35	
Molecular mass					119.37	

Figure 3.1: The average mass of a chloroform molecule, $CHCl_3$, is 119.37 amu, which is the sum of the average atomic masses of each of its constituent atoms. The model shows the molecular structure of chloroform.

Likewise, the molecular mass of an aspirin molecule, $C_9H_8O_4$, is the sum of the atomic masses of nine carbon atoms, eight hydrogen atoms, and four oxygen atoms, which amounts to 180.15 amu (Figure 3.2).



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

Figure 3.2: The average mass of an aspirin molecule is 180.15 amu. The model shows the molecular structure of aspirin, $C_9H_8O_4$.

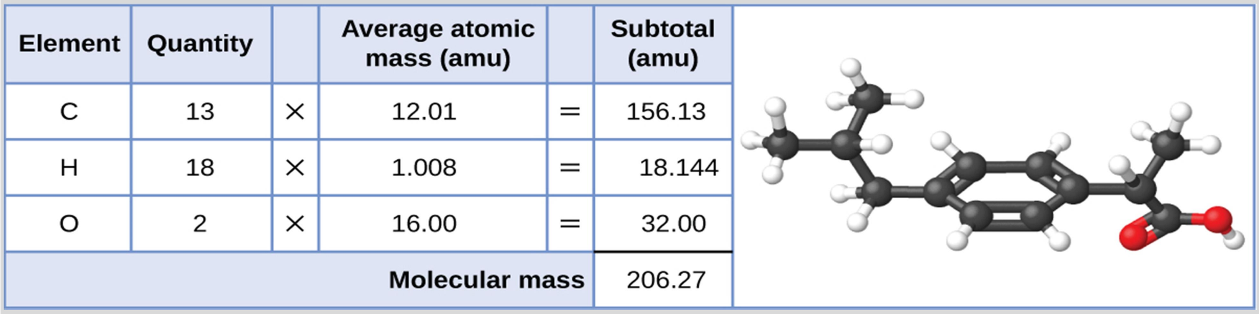
Example 3.1

Computing Molecular Mass for a Covalent Compound

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

Solution

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



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

Check Your Learning

Acetaminophen, $C_8H_9NO_2$, is a covalent compound and the active ingredient in several popular nonprescription pain medications, such as Tylenol. What is the molecular mass (amu) for this compound?

Formula Mass for Ionic Compounds

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

As an example, consider sodium chloride, NaCl, the chemical name for common table salt. Sodium chloride is an ionic compound composed of sodium cations, Na^+, and chloride anions, Cl^-, combined in a 1:1 ratio. The formula mass for this compound is computed as 58.44 amu (see Figure 3.3).

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

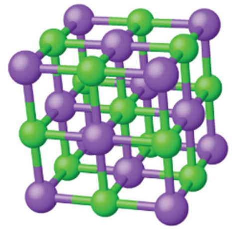


Figure 3.3: Table salt, NaCl, contains an array of sodium and chloride ions combined in a 1:1 ratio. Its formula mass is 58.44 amu.

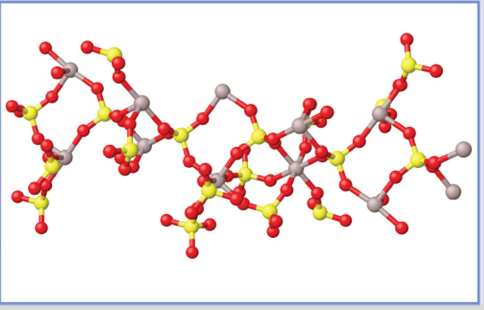
Example 3.2

Computing Formula Mass for an Ionic Compound

Aluminum sulfate, $Al_2(SO_4)_3$, is an ionic compound that is used in the manufacture of paper and in various water purification processes. What is the formula mass (amu) of this compound?

Solution

The formula for this compound indicates it contains Al^{3+} and SO_4^{2-} ions combined in a 2:3 ratio. For purposes of computing a formula mass, it is helpful to rewrite the formula in the simpler format, $Al_2S_3O_{12}$. Following the approach outlined above, the formula mass for this compound is calculated as follows:

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)	
Al	2	×	26.98	=	53.96	
S	3	×	32.06	=	96.18	
O	12	×	16.00	=	192.00	
				Molecular mass	342.14	

✍ Check Your Learning

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

3.1.2. The Mole Concept

The identity of a substance is defined not only by the types of atoms or ions it contains, but by the quantity of each type of atom or ion. For example, water, H_2O, and hydrogen peroxide, H_2O_2, are alike in that their respective molecules are composed of hydrogen and oxygen atoms. However, because a hydrogen peroxide molecule contains two oxygen atoms, as opposed to the water molecule, which has only one, the two substances exhibit very different properties. Today, sophisticated instruments allow the direct measurement of these defining microscopic traits; however, the same traits were originally derived from the measurement of macroscopic properties (the masses and volumes of bulk quantities of matter) using relatively simple tools (balances and volumetric glassware). This experimental approach required the introduction of a new unit for amount of substances, the mole, which remains indispensable in modern chemical science.

The mole is an amount unit similar to familiar units like pair, dozen, gross, etc. It provides a specific measure of the number of atoms or molecules in a sample of matter. One Latin connotation for the word “mole” is “large mass” or “bulk,” which is consistent with its use as the name for this unit. The mole provides a link between an easily measured macroscopic property, bulk mass, and an extremely important fundamental property, number of atoms, molecules, and so forth. A mole of substance is that amount in which there are 6.02214076 X 10^{23} discrete entities (atoms or molecules). This large number is a fundamental constant known as Avogadro's number (NA) or the Avogadro constant in honor of Italian scientist Amedeo Avogadro. This constant is properly reported with an explicit unit of "per mole," a conveniently rounded version being 6.022 X 10^{23}/mol.

Consistent with its definition as an amount unit, 1 mole of any element contains the same number of atoms as 1 mole of any other element. The masses of 1 mole of different elements, however, are different, since the masses of the individual atoms are drastically different. The molar mass of an element (or compound) is the mass in grams of 1 mole of that substance, a property expressed in units of grams per mole (g/mol) (see Figure 3.4).

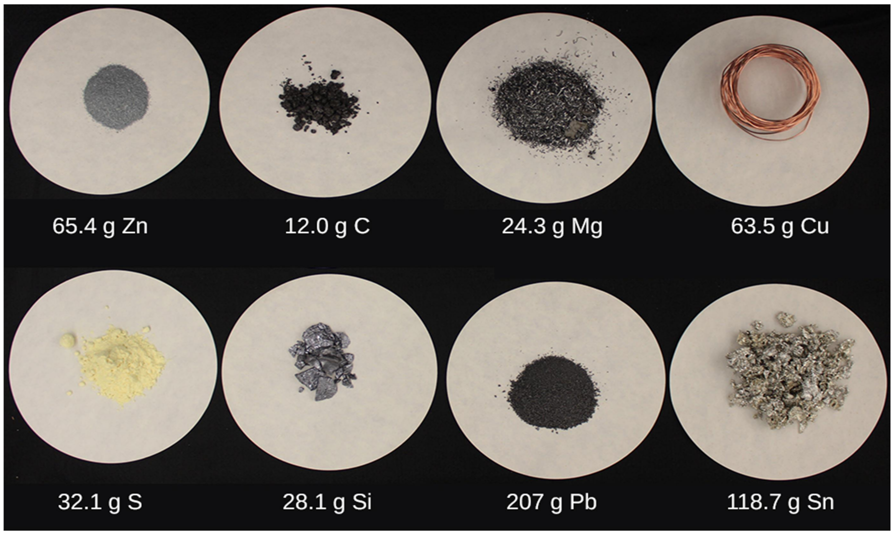


Figure 3.4: Each sample contains 6.022 X 10^{23} atoms 1.00 mol of atoms. From left to right (top row): 65.4 g zinc, 12.0 g carbon, 24.3 g magnesium, and 63.5 g copper. From left to right (bottom row): 32.1 g sulfur, 28.1 g silicon, 207 g lead, and 118.7 g tin.

This figure contains eight different substances displayed on white circles. The amount of each substance is visibly different.

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

Extending this principle, the molar mass of a compound in grams is likewise numerically equivalent to its formula mass in amu (Figure 3.5).

This photo shows two vials filled with a colorless liquid. It also shows two bowls: one filled with an off-white powder and one filled with a bright red powder.

Figure 3.5: Each sample contains 6.02 X 10^{23} molecules or formula units—1.00 mol of the compound or element. Clock-wise from the upper left: 130.2 g of $C_8H_{17}OH$ (1-octanol, formula mass 130.2 amu), 454.4 g of HgI_2 (mercury(II) iodide, formula mass 454.4 amu), 32.0 g of CH_3OH (methanol, formula mass 32.0 amu) and 256.5 g of S_8 (sulfur, formula mass 256.5 amu).

While atomic mass and molar mass are numerically equivalent, keep in mind that they are vastly different in terms of scale, as represented by the vast difference in the magnitudes of their respective units (amu versus g). To appreciate the enormity of the mole, consider a small drop of water weighing about 0.03 g (see Figure 3.6). Although this represents just a tiny fraction of 1 mole of water (~18 g), it contains more water molecules than can be clearly imagined. If the molecules were distributed equally among the roughly seven billion people on earth, each person would receive more than 100 billion molecules.

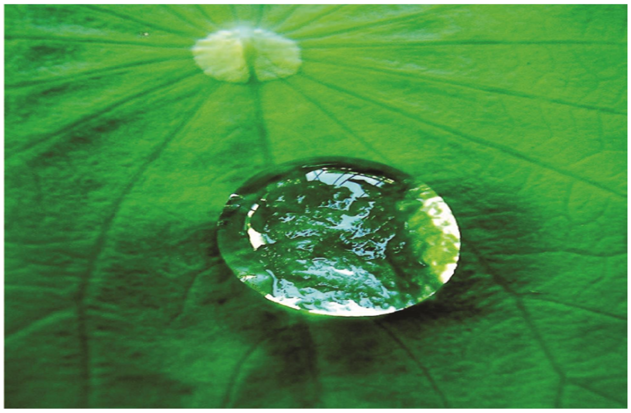


Figure 3.7**:** The number of molecules in a single droplet of water is roughly 100 billion times greater than the number of people on earth. A close-up photo of a water droplet on a leaf is shown. The water droplet is not perfectly spherical.

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

Example 3.3

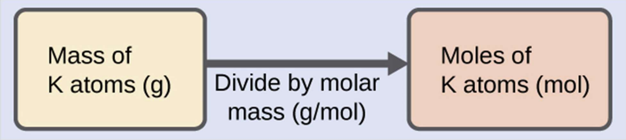
Deriving Moles from Grams for an Element

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

Solution

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

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



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

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

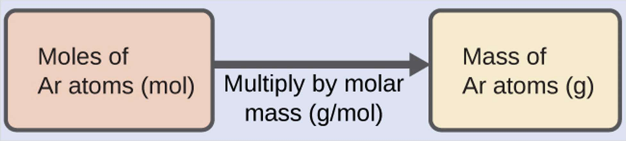
Example 3.4

Deriving Grams from Moles for an Element

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

Solution

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



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

$$9.2\ X\ 10^{-4} mol\ Ar \left(\frac{39.95g}{mol\ Ar}\right) = 0.037gAr$$

✍**Check Your Learning**

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

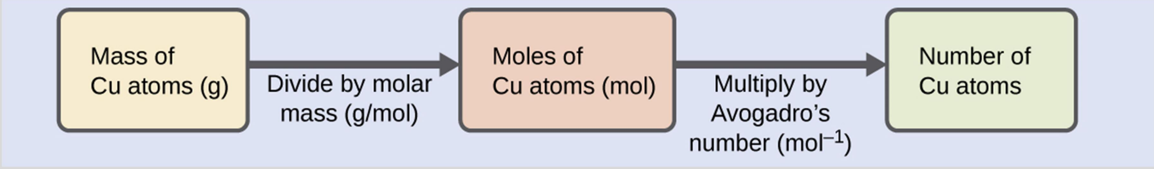
Example 3.5

Deriving Number of Atoms from Mass for an Element

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

Solution

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



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

$$5.00\cancel{g}\ Cu \left(\frac{\cancel{mol}\ Cu}{63.55\cancel{g}}\right)\left(\frac{6.022\ X10^{23}}{\cancel{mol}}\ atoms \qquad 4.74\ X10^{22}\ atoms\ of\ Copper$$

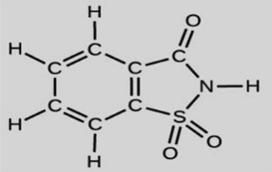
✍Check Your Learning

1. A prospector panning for gold in a river collects 15.00 g of pure gold. How many Au atoms are in this quantity of gold?
2. How many moles of sucrose, $C_{12}H_{22}O_{11}$, are in a 25-g sample of sucrose?
3. What is the mass of 0.443 mol of hydrazine, N_2H_4?

Example 3.6

Deriving the Number of Atoms and Molecules from the Mass of a Compound

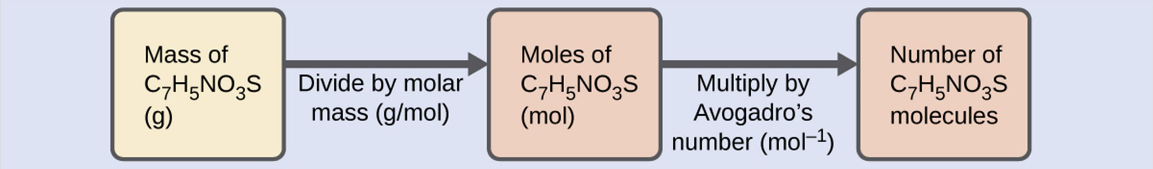
A packet of an artificial sweetener contains 40.0 mg of saccharin ($C_7H_5NO_3S$), which has the structural formula:



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

Solution

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



Using the provided mass and molar mass for saccharin yields:

$$0.0400g\ C_7H_5NO_3S\left(\frac{\cancel{mol}\ \ {}_7H_5NO_3S}{183.18\cancel{g}C_7H_5NO_3S}\right)\left(\frac{6.022\ X10^{23}C_7H_5NO_3S\ molecules}{1\cancel{mol}\ C_7H_5NO_3S}\right)=$$

$$=1.31X10^{20}C_7H_5NO_3S\ molecules$$

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

$$1.31X10^{20}C_7H_5NO_3S\ molecules\left(\frac{7\ C\ atoms}{1C_7H_5NO_3Smolecules}\right)==9.17X10^{20}\ C\ atom$$

✍**Check Your Learning**

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

3.2. Determining empirical and molecular formulas

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

3.2.1. Percent Composition

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

$$\boldsymbol{\%H=\frac{Mass\ of\ H}{Mass\ of\ compound}\ X\ 100\%}$$

$$\%\boldsymbol{C} = \frac{\boldsymbol{Mass\ of\ C}}{\boldsymbol{Mass\ of\ compound}}\ \boldsymbol{X}\ \mathbf{100\%}$$

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

$$\%H = \frac{2.5g\ H}{10.0g\ Compound}\ X\ 100\% = 25\%$$

$$\%C = \frac{7.5g\ C}{10.0g\ compound}\ X\ 100\% = 75\%$$

Example 3.7

Calculation of Percent Composition

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

Solution

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

$$\%H = \frac{1.85gH}{12.04g\ compound}\ X\ 100\% = 15.4\%$$

$$\%N = \frac{2.85gN}{12.04g\ compound}\ X\ 100\% = 23.7\%$$

$$\%C = \frac{7.34gC}{12.04g\ compound}\ X\ 100\% = 61.0\%$$

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

✍**Check Your Learning**

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

Determining Percent Composition from Molecular or Empirical Formulas

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

$$\%N = \frac{14.01 amuN}{17.03 amuNH_3} X\ 100\% = 82.27\%$$

$$\%H = \frac{3.024 amuH}{17.03 amuNH_3} X\ 100\% = 17.76\%$$

This same approach may be taken considering a pair of molecules, a dozen molecules, or a mole of molecules, etc. The latter amount is most convenient and would simply involve the use of molar masses instead of atomic and formula masses, as demonstrated Example 3.8. As long as the molecular or empirical formula of the compound in question is known, the percent composition may be derived from the atomic or molar masses of the compound's elements.

Example 3.8

Determining Percent Composition from a Molecular Formula

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

Solution

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

$$\%C = \frac{9molCx\ mola\ \ mass\ C}{molar\ massC_9H_8O_4} x\ 100 = \frac{9x12.01g/mol}{180.159g/mol} x100 = \frac{108.09g/mol}{180.159g/mol} x100$$

$$= 60.00\%$$

$$\%H = \frac{8molHx\ molar\ mass\ H}{molar\ mass\ \ _9H_8O_4} x\ 100 = \frac{8x1.008g/mol}{180.159g/mol} x100 = \frac{8.064g/mol}{180.159g/mol} x100$$

$$= 4.476\%$$

$$\%O = \frac{4mol\ Ox\ molar\ mass\ O}{molar\ mass\ \ _9H_8O_4}\ x\ 100 = \frac{4x16.00g/mol}{180.159g/mol}x100 = \frac{64.00g/mol}{180.159g/mol}x100$$

$$= 35.52\%$$

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

✍**Check Your Learning**

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

3.2.2. Determination of Empirical Formulas

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

$$1.71gC\ X\frac{1mol\ C}{12.01gC} = 0.142molC$$

$$0.287gH\ X\frac{1molH}{1.008gH} = 0.284molH$$

Thus, this compound may be represented by the formula $C_{0.142}H_{0.248}$. Per convention, formulas contain whole-number subscripts, which can be achieved by dividing each subscript by the smaller subscript:

$$C_{\frac{0.1420}{0.1420}}H_{\frac{0.284}{0.1420}} = CH_2$$

(Recall that subscripts of "1" are not written but rather assumed if no other number is present.) The empirical formula for this compound is thus CH_2. This may or not be the compound's molecular formula as well; however, additional information is needed to make that determination (as discussed later in this section).

Check Your Learning

A sample of compound determined to contain 5.31 g Cl and 8.40 g O. What is the empirical formula of the compound?

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

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

Figure 3.8 outlines this procedure in flow chart fashion for a substance containing elements A and X.

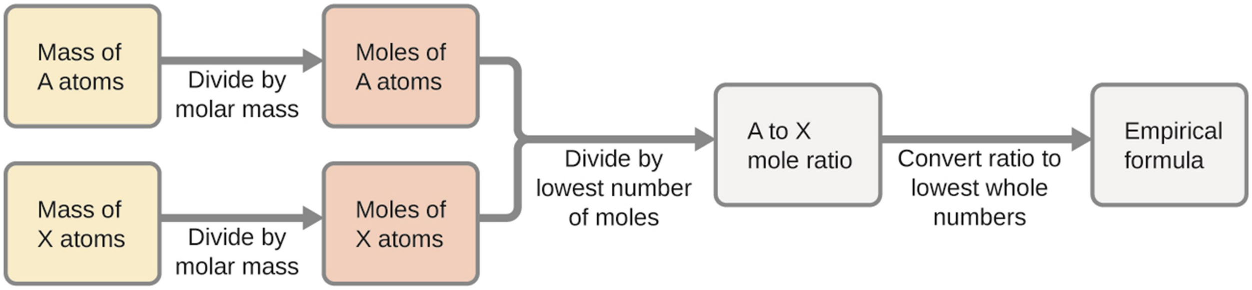


Figure 3.8: The empirical formula of a compound can be derived from the masses of all elements in the sample.

Example 3.9

Determining a Compound's Empirical Formula from the Masses of its Elements

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

Solution

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

$$34.97 gFe\left(\frac{molFe}{55.85g}\right) = 0.6261 mole\ Fe$$

$$15.03 gO\left(\frac{molO}{16.00g}\right) = 0.9394 mole\ O$$

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

$$\frac{0.6261}{0.6261} = 1.00 moleFe$$

$$\frac{0.9394}{0.6261} = 1.500 moleO$$

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

$$2(Fe_1O_{1.5})=Fe_2O_3$$

The empirical formula is Fe_2O_3.

✍**Check Your Learning**

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

Deriving Empirical Formulas from Percent Composition

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

Example 3.10

Determining an Empirical Formula from Percent Composition

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

Solution

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

$$27.29\%C = \frac{27.29gC}{100gcompound}$$

$$72.71\%O = \frac{72.71gO}{100g\ compound}$$

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

$$27.29gC\left(\frac{molC}{12.01g}\right) = 2.272mol\ C$$

$$72.71g\ O\left(\frac{molO}{16.00g}\right) = 4.544mol\ O$$

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

$$\frac{2.272\ mol\ C}{2.272} = 1$$

$$\frac{4.544\ mol\ O}{2.272} = 2$$

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

✍**Check Your Learning**

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

3.2.3. Determination 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. Molar mass can be measured by a number of experimental methods.

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

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

The molecular formula is then obtained by multiplying each subscript in the empirical formula by n, as shown by the generic empirical formula $\boldsymbol{AxBy}$:

$$(\boldsymbol{A_xB_y})_{\boldsymbol{n}} = \boldsymbol{A_{nx}B_{ny}}$$

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

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

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

$$(CH_2O)_6{=}C_6H_{12}O_6$$

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

Example 3.11

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:

$$74.02 gC \left(\frac{1 mol\ C}{12.01 g\ C}\right) = 6.163\ mol\ C$$

$$8.710\ g\ H \left(\frac{1 mol\ H}{1.01 gH}\right) = 8.624\ mol\ H$$

$$17.27 g\ N \left(\frac{1 mol\ N}{14.01 g\ N}\right) = 1.233\ mol\ N$$

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

6.163molC/1.233molN=5

8.264molH/1.233molN=7

1.233molN/1.233molN=1

$$\frac{1.233}{1.233} = 1.000 mol\ N$$

$$\frac{6.163}{1.233} = 4.998\ mol\ C$$

$$\frac{8.624}{1.233} = 6.994\ mol\ H$$

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

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

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

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

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

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

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

✍ **Check Your Learning**

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?

3.3. Molarity and Other Concentration Units

Preceding sections of this chapter focused on the composition of substances: samples of matter that contain only one type of element or compound. However, mixtures—samples of matter containing two or more substances physically combined—are more commonly encountered in nature than are pure substances. Similar to a pure substance, the relative composition of a mixture plays an important role in determining its properties. The relative amount of oxygen in a planet's atmosphere determines its ability to sustain aerobic life. The relative amounts of iron, carbon, nickel, and other elements in steel (a mixture known as an "alloy") determine its physical strength and resistance to corrosion. The relative amount of the active ingredient in a medicine determines its effectiveness in achieving the desired pharmacological effect. The relative amount of sugar in a beverage determines its sweetness. This section will describe one of the most common ways in which the relative compositions of mixtures may be quantified.

3.3.1. Molarity

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

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

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

Concentrations may be quantitatively assessed using a wide variety of measurement units, each convenient for particular applications.

Molarity (M) is a useful concentration unit for many applications in chemistry. **Molarity** is defined as the number of moles of solute in exactly 1 liter (1 L) of the solution:

$$Molarity = \frac{Mole\ of\ Solute}{L\ of\ Solution}$$

Example 3.12

Calculating Molar Concentrations

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

Solution

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

$Molarity = \frac{0.133\ mol}{355 ml \frac{1L}{1000ml}}$ =0.375 mol

Check Your Learning

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

Example 3.13

Calculating Molar Concentrations from the Mass of Solute

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

Solution

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

$$\frac{25.2gC\,H_3COOH\ \ X\ \frac{1\,mol\ \ C\,H_3COOH}{60.052gC\,H_3COOH}}{0.500L\ solution} = 0.839\ M$$

✍**Check Your Learning**

1. Calculate the molarity of 6.52 g of $CoCl_2$ (128.9 g/mol) dissolved in an aqueous solution with a total volume of 75.0 mL.
2. How many grams of NaCl are contained in 0.250 L of a 5.30-*M* solution?
3. The concentration of acetic acid in white vinegar was determined to be 0.839 *M*. What volume of vinegar contains 75.6 g of acetic acid?

3.3.2. Dilution of Solutions

Dilution is the process whereby the concentration of a solution is lessened by the addition of solvent. For example, a glass of iced tea becomes increasingly diluted as the ice melts. The water from the melting ice increases the volume of the solvent (water) and the overall volume of the solution (iced tea), thereby reducing the relative concentrations of the solutes that give the beverage its taste (Figure 3.9).

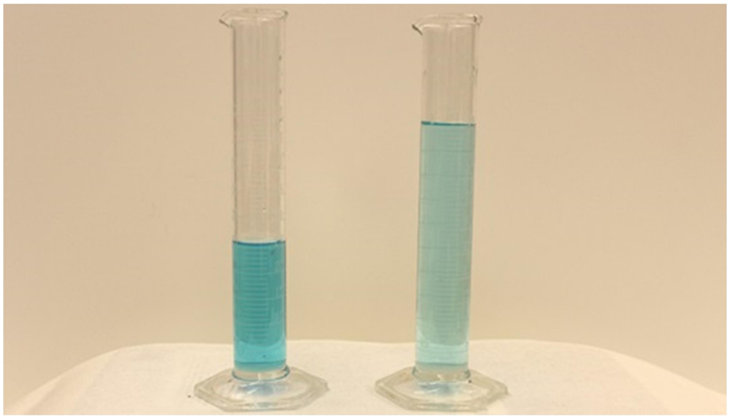


Figure 3.9: This figure shows two graduated cylinders side-by-side.Both solutions contain the same mass of copper nitrate. The solution on the right is more dilute because the copper nitrate is dissolved in more solvent. The first has about half as much blue liquid as the second. The blue liquid is darker in the first cylinder than in the second.

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

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

$$n = ML$$

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

$$\boldsymbol{n_1 = M_1L_1}$$

$$\boldsymbol{n_2 = M_2L_2}$$

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

$$\boldsymbol{M_1L_1 = M_2L_2}$$

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

$$\mathbf{C_1V_1=C_2V_2}$$

Where, *C* and *V* are concentration and volume, respectively.

Example 3.14

Determining the Concentration of a Diluted Solution

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

Solution

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

$$\mathbf{C_1V_1=C_2V_2C_2=C_1V_1/\ V_2}$$

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

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

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

✍ **Check Your Learning**

1. What is the concentration of the solution that results from diluting 25.0 mL of a 2.04-*M* solution of CH_3OH to 500.0 mL?
2. What volume of 0.12 *M* HBr can be prepared from 11 mL (0.011 L) of 0.45 *M* HBr?
3. A laboratory experiment calls for 0.125 *M* HNO_3. What volume of 0.125 *M* HNO_3 can be prepared from 0.250 L of 1.88 *M* HNO_3?
4. What volume of 1.59 *M* KOH is required to prepare 5.00 L of 0.100 *M* KOH?
5. What volume of a 0.575-*M* solution of glucose, $C_6H_{12}O_6$, can be prepared from 50.00 mL of a 3.00-*M* glucose solution?

3.3.3. Percentage (W/W, W/V and V/V)

The previous section introduced molarity, a very useful measurement unit for evaluating the concentration of solutions. However, molarity is only one measure of concentration. This section will describe some other units of concentration that are commonly used in various applications, either for convenience or by convention.

3.3.3.1. Mass Percentage

Earlier in this chapter, percent composition was introduced as a measure of the relative amount of a given element in a compound. Percentages are also commonly used to express the composition of mixtures, including solutions. The **mass percentage** of a solution component is defined as the ratio of the component's mass to the solution's mass, expressed as a percentage:

$$Mass\ Percentage = \frac{mass\ of\ component}{mass\ of\ solution}\ X\ 100\%$$

Mass percentage is also referred to by similar names such as *percent mass, percent weight, weight/weight percent*, and other variations on this theme. The most common symbol for mass percentage is simply the percent sign, %, although more detailed symbols are often used including %mass, %weight, and (w/w)%. Use of these more detailed symbols can prevent confusion of mass percentages with other types of percentages, such as volume percentages (to be discussed later in this section).

Mass percentages are popular concentration units for consumer products. For example the label of typical liquid bleach,an aqueous solution of sodium hypochlorite (NaOCl),bottle cites the concentration of its active ingredient, sodium hypochlorite (NaOCl), as being 7.4%. A 100.0-g sample of bleach would therefore contain 7.4 g of NaOCl.

Example 3.15

Calculation of Percent by Mass

A 5.0-g sample of spinal fluid contains 3.75 mg (0.00375 g) of glucose. What is the percent by mass of glucose in spinal fluid?

Solution

The spinal fluid sample contains roughly 4 mg of glucose in 5000 mg of fluid, so the mass fraction of glucose should be a bit less than one part in 1000, or about 0.1%. Substituting the given masses into the equation defining mass percentage yields:

$$\%\ glucose = \frac{3.75mg\ glucose\ \frac{1g}{1000mg}}{5.0g\ spinal\ fluid} = 0.075\%$$

The computed mass percentage agrees with our rough estimate (it's a bit less than 0.1%).

Note that while any mass unit may be used to compute a mass percentage (mg, g, kg, oz, and so on), the same unit must be used for both the solute and the solution so that the mass units cancel, yielding a dimensionless ratio. In this case, the solute mass unit in the numerator was converted from mg to g to match the units in the denominator. Alternatively, the spinal fluid mass unit in the denominator could have been converted from g to mg instead. As long as identical mass units are used for both solute and solution, the computed mass percentage will be correct.

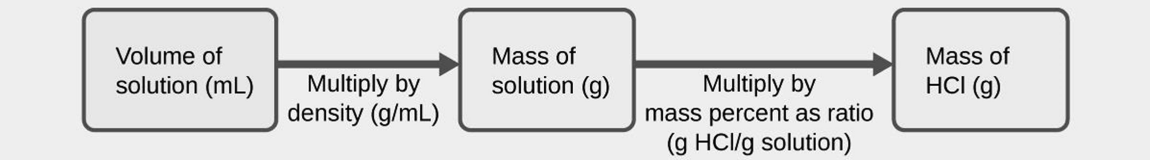
Example 3.16

Calculations using Mass Percentage

“Concentrated” hydrochloric acid is an aqueous solution of 37.2% HCl that is commonly used as a laboratory reagent. The density of this solution is 1.19 g/mL. What mass of HCl is contained in 0.500 L of this solution?

Solution

The HCl concentration is near 40%, so a 100-g portion of this solution would contain about 40 g of HCl. Since the solution density isn’t greatly different from that of water (1 g/mL), a reasonable estimate of the HCl mass in 500 g (0.5 L) of the solution is about five times greater than that in a 100 g portion, or 5 ×40 = 200 g. In order to derive the mass of solute in a solution from its mass percentage, the mass of the solution must be known. Using the solution density given, convert the solution’s volume to mass, and then use the given mass percentage to calculate the solute mass. This mathematical approach is outlined in this flowchart:



For proper unit cancellation, the 0.500-L volume is converted into 500 mL, and the mass percentage is expressed as a ratio, 37.2 g HCl/g solution:

$$500ml\ solution \left(\frac{1.19g\ solution}{ml\ solution}\right)\left(\frac{37.2g\ HCl}{100g\ solution}\right) = 221\ g\ HCl$$

This mass of HCl is consistent with our rough estimate of approximately 200 g.

Check Your Learning

1. A bottle of a tile cleanser contains 135 g of HCl and 775 g of water. What is the percent by mass of HCl in this cleanser?
2. What volume of concentrated HCl solution contains 125 g of HCl?

3.3.3.2. Volume Percentage

Liquid volumes over a wide range of magnitudes are conveniently measured using common and relatively inexpensive laboratory equipment. The concentration of a solution formed by dissolving a liquid solute in a liquid solvent is therefore often expressed as a **volume percentage**, %vol or (v/v)%:

$$\text{Volume percentage} = \frac{\text{Volume solute}}{Volume\ of\ solution}\ X\ 100\%$$

Example 3.17

Calculations using Volume Percentage

Rubbing alcohol (isopropanol) is usually sold as a 70%vol aqueous solution. If the density of isopropyl alcohol is 0.785 g/mL, how many grams of isopropyl alcohol are present in a 355 mL bottle of rubbing alcohol?

Solution

Per the definition of volume percentage, the isopropanol volume is 70% of the total solution volume. Multiplying the isopropanol volume by its density yields the requested mass:

$$(355ml\ solution)\left(\frac{70ml\ isopropyl\ acohol}{100ml\ solution}\right)\left(\frac{0.785g\ isopropyl\ alcohol}{1mL\ isopropyl\ alcohol}\right)$$

$$= 195g\ isopropyl\ alcohol$$

✍**Check Your Learning**

Wine is approximately 12% ethanol (CH_3CH_2OH) by volume. Ethanol has a molar mass of 46.06 g/mol and a density 0.789 g/mL. How many moles of ethanol are present in a 750-mL bottle of wine?

3.3.3.3. Mass-Volume Percentage

“Mixed” percentage units, derived from the mass of solute and the volume of solution, are popular for certain biochemical and medical applications. A **mass-volume percent** is a ratio of a solute’s mass to the solution’s volume expressed as a percentage. The specific units used for solute mass and solution volume may vary, depending on the solution. For example, physiological saline solution, used to prepare intravenous fluids, has a concentration of 0.9% mass/volume (m/v), indicating that the composition is 0.9 g of solute per 100 mL of solution. The concentration of glucose in blood (commonly referred to as “blood sugar”) is also typically expressed in terms of a mass-volume ratio. Though not expressed explicitly as a percentage, its concentration is usually given in milligrams of glucose per deciliter (100 mL) of blood (Figure 3.10).

Figure 3.10: "Mixed" mass-volume units are commonly encountered in medical settings. (a) The NaCl concentration of physiological saline is 0.9% (m/v). (b) This device measures glucose levels in a sample of blood. The normal range for glucose concentration in blood (fasting) is around 70–100 mg/dL.

3.3.4. Parts per million (ppm) and Part per billion (ppb)

Very low solute concentrations are often expressed using appropriately small units such as **parts per million (ppm)** or **parts per billion (ppb)**. Like percentage ("part per hundred") units, ppm and ppb may be defined in terms of masses, volumes, or mixed mass-volume units. There are also ppm and ppb units defined with respect to numbers of atoms and molecules.

The mass-based definitions of ppm and ppb are given here:

$$ppm \quad \frac{mass\ solute}{mass\ solution}\ X10^6 ppm$$

$$ppb = \frac{mass\ solute}{mass\ solution}\ X10^9 ppb$$

Both ppm and ppb are convenient units for reporting the concentrations of pollutants and other trace contaminants in water. Concentrations of these contaminants are typically very low in treated and natural waters, and their levels cannot exceed relatively low concentration thresholds without causing adverse effects on health and wildlife. For example, the Environmental Protection Agency (EPA) has identified the maximum safe level of fluoride ion in tap water to be 4 ppm. Inline water filters are designed to reduce the concentration of fluoride and several other trace-level contaminants in tap water.

Example 3.18

Calculation of Parts per Million and Parts per Billion Concentrations

According to the EPA, when the concentration of lead in tap water reaches 15 ppb, certain remedial actions must be taken. What is this concentration in ppm? At this concentration, what mass of lead (µg) would be contained in a typical glass of water (300 mL)?

Solution

The definitions of the ppm and ppb units may be used to convert the given concentration from ppb to ppm. Comparing these two unit definitions shows that ppm is 1000 times greater than ppb (1 ppm = 10^3 ppb). Thus:

$$15ppb\ X\ \frac{1ppm}{10^3 ppb} = 0.015ppm$$

The definition of the ppb unit may be used to calculate the requested mass if the mass of the solution is provided. Since the volume of solution (300 mL) is given, its density must be used to derive the corresponding mass. Assume the density of tap water to be roughly the same as that of pure water (~1.00 g/mL), since the concentrations of any dissolved substances should not be very large. Rearranging the equation defining the ppb unit and substituting the given quantities yields:

$$ppb = \frac{mass\ solute}{mass\ solution}\ X 10^9 ppb$$

$$mass\ of\ solute = \frac{ppb\ X\ mass\ solution}{10^9 ppb}$$

$$mass\ solute = \frac{15ppb\ X\ 300mL\ X\ \frac{1.00g}{ml}}{10^9 ppb} = 4.5\ X\ 10^{-6} g$$

Finally, convert this mass to the requested unit of micrograms:

$$4.4\ X\ 10^{-6} g\ X\ \frac{1\mu g}{10^{-6g}} = 4.5\mu g$$

Check Your Learning

A 50.0-g sample of industrial wastewater was determined to contain 0.48 mg of mercury. Express the mercury concentration of the wastewater in ppm and ppb units.

Review Exercises

1. What is the total mass (amu) of carbon in each of the following molecules?
   a. CH_4
   b. $CHCl_3$
   c. $C_{12}H_{10}O_6$
   d. $CH_3CH_2CH_2CH_2CH_3$
2. What is the total mass of hydrogen in each of the molecules?
   a. CH_4
   b. $CHCl_3$
   c. $C_{12}H_{10}O_6$
   d. $CH_3CH_2CH_2CH_2CH_3$
3. Calculate the molecular or formula mass of each of the following:
   a. P_4 b. H_2O c) $Ca(NO_3)_2$ d) CH_3CO_2H (acetic acid) e) $C_{12}H_{22}O_{11}$ (sucrose, cane sugar)
4. Compare 1 mole of H_2, 1 mole of O_2, and 1 mole of F_2.
   a. Which has the largest number of molecules? Explain why.
   b. Which has the greatest mass? Explain why
5. Which contains the greatest mass of oxygen: 0.75 mol of ethanol (C_2H_5OH), 0.60 mol of formic acid (HCO_2H), or 1.0 mol of water (H_2O)? Explain why.
6. Which contains the greatest number of moles of oxygen atoms: 1 mol of ethanol (C_2H_5OH), 1 mol of formic acid (HCO_2H), or 1 mol of water (H_2O)? Explain why.
7. Calculate the empirical or molecular formula mass and the molar mass of each of the following minerals:
   a. turquoise, $CuAl_6(PO_4)_4(OH)_8(H_2O)_4$
   b. limestone, $CaCO_3$
   c. halite, NaCl
   d. beryl, $Be_3Al_2Si_6O_{18}$
   e. malachite, $Cu_2(OH)_2CO_3$
8. Determine the number of moles of compound and the number of moles of each type of atom in each of the following:
   a. 25.0 g of propylene, C_3H_6
   b. 3.06 ×× 10^{-3} g of the amino acid glycine, $C_2H_5NO_2$
   c. 25 lb of the herbicide Treflan, $C_{13}H_{16}N_2O_4F$ (1 lb = 454 g)
   d. 0.125 kg of the insecticide Paris Green, $Cu_4(AsO_3)_2(CH_3CO_2)_2$
   e. 325 mg of aspirin, $C_6H_4(CO_2H)(CO_2CH_3)$
9. Determine the mass of each of the following:
   a. 0.0146 mol KOH
   b. 10.2 mol ethane, C_2H_6

c. 1.6×10^{-3} mol Na_2SO_4

d. 6.854×10^{3} mol glucose, $C_6H_{12}O_6$

e. 2.86 mol $Co(NH_3)_6Cl_3$

10. A 55-kg woman has 7.5×10^{-3} mol of hemoglobin (molar mass = 64,456 g/mol) in her blood. How many hemoglobin molecules is this? What is this quantity in grams?
11. Determine the number of atoms and the mass of zirconium, silicon, and oxygen found in 0.3384 mol of zircon, $ZrSiO_4$, a semiprecious stone.
12. Diamond is one form of elemental carbon. An engagement ring contains a diamond weighing 1.25 carats (1 carat = 200 mg). How many atoms are present in the diamond?
13. A tube of toothpaste contains 0.76 g of sodium monofluorophosphate (Na_2PO_3F) in 100 mL.
    a. What mass of fluorine atoms in mg was present?
    b. How many fluorine atoms were present?
14. Determine the percent ammonia, NH_3, in $Co(NH_3)_6Cl_3$, to three significant figures.
15. Determine the percent water in $CuSO_4 \cdot 5H_2O$ to three significant figures.
16. Determine the empirical formulas for compounds with the following percent compositions:
    a. 15.8% carbon and 84.2% sulfur
    b. 40.0% carbon, 6.7% hydrogen, and 53.3% oxygen
    c. Lucite (Plexiglas); 59.9% C, 8.06% H, 32.0% O
    d. Saran; 24.8% C, 2.0% H, 73.1% Cl
    e. polyethylene; 86% C, 14% H
    f. polystyrene; 92.3% C, 7.7% H
    g. Orlon; 67.9% C, 5.70% H, 26.4% N
17. A compound of carbon and hydrogen contains 92.3% C and has a molar mass of 78.1 g/mol. What is its molecular formula?
18. Dichloroethane, a compound that is often used for dry cleaning, contains carbon, hydrogen, and chlorine. It has a molar mass of 99 g/mol. Analysis of a sample shows that it contains 24.3% carbon and 4.1% hydrogen. What is its molecular formula?
19. Determine the empirical and molecular formula for chrysotile asbestos. Chrysotile has the following percent composition: 28.03% Mg, 21.60% Si, 1.16% H, and 49.21% O. The molar mass for chrysotile is 520.8 g/mol.
20. **20.** Explain what changes and what stays the same when 1.00 L of a solution of NaCl is diluted to 1.80 L.

21. A 200-mL sample and a 400-mL sample of a solution of salt have the same molarity. In what ways are the two samples identical? In what ways are these two samples different?
22. Determine the molarity for each of the following solutions:
    a. 0.444 mol of $CoCl_2$ in 0.654 L of solution
    b. 98.0 g of phosphoric acid, H_3PO_4, in 1.00 L of solution
    c. 0.2074 g of calcium hydroxide, $Ca(OH)_2$, in 40.00 mL of solution
    d. 10.5 kg of $Na_2SO_4 \cdot 10H_2O$ in 18.60 L of solution
    e. 7.0 ×× 10^{-3} mol of I_2 in 100.0 mL of solution
    f. 1.8 ×× 10^4 mg of HCl in 0.075 L of solution
23. Calculate the number of moles and the mass of the solute in each of the following solutions:
    a. 2.00 L of 18.5 *M* H_2SO_4, concentrated sulfuric acid
    b. 100.0 mL of 3.8 ×× 10^{-5} *M* NaCN, the minimum lethal concentration of sodium cyanide in blood serum
    c. 5.50 L of 13.3 *M* H_2CO, the formaldehyde used to “fix” tissue samples
    d. 325 mL of 1.8 ×× 10^{-6} *M* $FeSO_4$, the minimum concentration of iron sulfate detectable by taste in drinking water
24. Calculate the molarity of each of the following solutions:
    a. 0.195 g of cholesterol, $C_{27}H_{46}O$, in 0.100 L of serum, the average concentration of cholesterol in human serum
    b. 4.25 g of NH_3 in 0.500 L of solution, the concentration of NH_3 in household ammonia
    c. 1.49 kg of isopropyl alcohol, C_3H_7OH, in 2.50 L of solution, the concentration of isopropyl alcohol in rubbing alcohol
    d. 0.029 g of I_2 in 0.100 L of solution, the solubility of I_2 in water at 20 °C
25. There is about 1.0 g of calcium, as Ca^{2+}, in 1.0 L of milk. What is the molarity of Ca^{2+} in milk?
26. What volume of a 1.00-*M* $Fe(NO_3)_3$ solution can be diluted to prepare 1.00 L of a solution with a concentration of 0.250 *M*?
27. If 0.1718 L of a 0.3556-*M* C_3H_7OH solution is diluted to a concentration of 0.1222 *M*, what is the volume of the resulting solution?

28. What is the concentration of the NaCl solution that results when 0.150 L of a 0.556-*M* solution is allowed to evaporate until the volume is reduced to 0.105 L?

29. What is the molarity of the diluted solution when each of the following solutions is diluted to the given final volume?

    a. 1.00 L of a 0.250-*M* solution of $Fe(NO_3)_3$ is diluted to a final volume of 2.00 L

    b. 0.5000 L of a 0.1222-*M* solution of C_3H_7OH is diluted to a final volume of 1.250 L

    c. 2.35 L of a 0.350-*M* solution of H_3PO_4 is diluted to a final volume of 4.00 L

    d. 22.50 mL of a 0.025-*M* solution of $C_{12}H_{22}O_{11}$ is diluted to 100.0 mL

30. What volume of a 0.20-*M* K_2SO_4 solution contains 57 g of K_2SO_4?

31. What mass of a concentrated solution of nitric acid (68.0% HNO_3 by mass) is needed to prepare 400.0 g of a 10.0% solution of HNO_3 by mass?

32. What mass of a 4.00% NaOH solution by mass contains 15.0 g of NaOH?

33. What mass of solid NaOH (97.0% NaOH by mass) is required to prepare 1.00 L of a 10.0% solution of NaOH by mass? The density of the 10.0% solution is 1.109 g/mL.

34. What mass of HCl is contained in 45.0 mL of an aqueous HCl solution that has a density of 1.19 g cm^{-3} and contains 37.21% HCl by mass?

35. The hardness of water (hardness count) is usually expressed in parts per million (by mass) of $CaCO_3$, which is equivalent to milligrams of $CaCO_3$ per liter of water. What is the molar concentration of Ca^{2+} ions in a water sample with a hardness count of 175 mg $CaCO_3$/L?

36. In Canada and the United Kingdom, devices that measure blood glucose levels provide a reading in millimoles per liter. If a measurement of 5.3 m*M* is observed, what is the concentration of glucose ($C_6H_{12}O_6$) in mg/dL?

37. A throat spray is 1.40% by mass phenol, C_6H_5OH, in water. If the solution has a density of 0.9956 g/mL, calculate the molarity of the solution.

38. A cough syrup contains 5.0% ethyl alcohol, C_2H_5OH, by mass. If the density of the solution is 0.9928 g/mL, determine the molarity of the alcohol in the cough syrup.

39. Find the molarity of a 40.0% by mass aqueous solution of sulfuric acid, H_2SO_4, for which the density is 1.3057 g/mL.

CHAPTER FOUR

Stoichiometry of Chemical Reaction

Introduction

Many modern rocket fuels are solid mixtures of substances combined in carefully measured amounts and ignited to yield a thrust-generating chemical reaction. The engines of these rockets rely on carefully prepared solid mixtures of chemicals combined in precisely measured amounts. Igniting the mixture initiates a vigorous chemical reaction that rapidly generates large amounts of gaseous products. These gases are ejected from the rocket engine through its nozzle, providing the thrust needed to propel heavy payloads into space. Both the nature of this chemical reaction and the relationships between the amounts of the substances being consumed and produced by the reaction are critically important considerations that determine the success of the technology. This chapter will describe how to symbolize chemical reactions using chemical equations, how to classify some common chemical reactions by identifying patterns of reactivity, and how to determine the quantitative relations between the amounts of substances involved in chemical reactions-that is, the reaction *stoichiometry*.

Learning Objective of the Chapter: At the end of this chapter you will be able to

- Write and balance chemical equations in molecular, total ionic, and net ionic formats
- Classify chemical reactions as one of these three types given appropriate descriptions or chemical equations
- Predict the solubility of common inorganic compounds by using solubility rules
- Perform stoichiometric calculations involving mass, moles, and solution molarity
- Explain the concepts of theoretical yield and limiting reactants/reagents
- Derive the theoretical yield and percent yield for a reaction under specified conditions
- Describe the fundamental aspects of titrations and gravimetric analysis.
- Determine the concentration of a sample using acid-base titration

4.1. Writing and Balancing Chemical Equations

4.1.1. Writing Chemical Equations

An earlier chapter of this module introduced the use of element symbols to represent individual atoms. When atoms gain or lose electrons to yield ions, or combine with other atoms to form molecules, their symbols are modified or combined to generate chemical formulas that appropriately represent these species. Extending this symbolism to represent both the identities and the relative quantities of substances undergoing a chemical (or physical) change involves writing and balancing a **chemical equation**. Consider as an example the reaction between one methane molecules (CH_4) and two diatomic oxygen molecules (O_2) to produce one carbon dioxide molecule (CO_2) and two water molecules (H_2O). The chemical equation representing this process is provided in the upper half of Figure 4.1, with space-filling molecular models shown in the lower half of the figure.

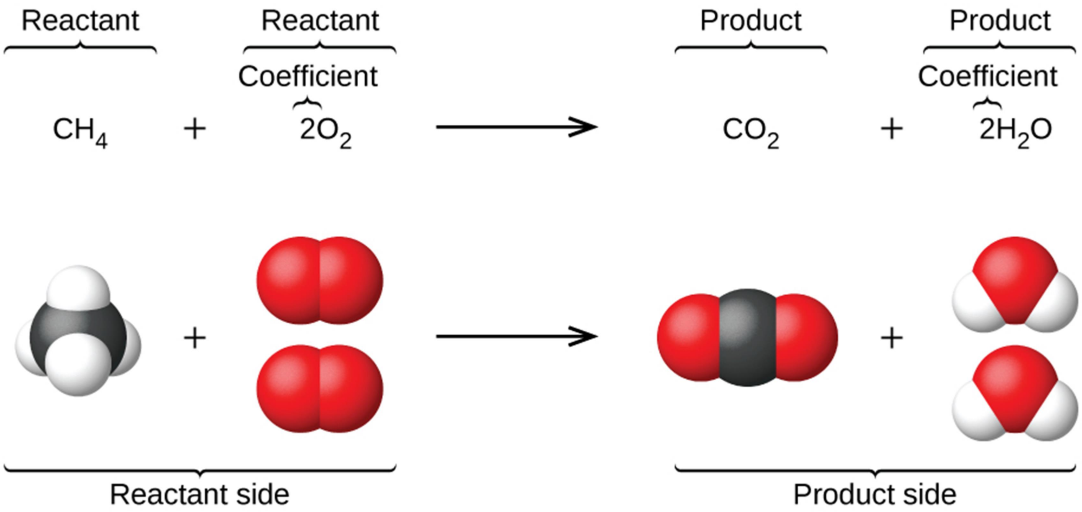


Figure 4.1: The reaction between methane and oxygen to yield carbon dioxide and water (shown at bottom) may be represented by a chemical equation using formulas (top).

This example illustrates the fundamental aspects of any chemical equation:

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

It is common practice to use the smallest possible whole-number coefficients in a chemical equation, as is done in this example. Realize, however, that these coefficients represent the *relative* numbers of reactants and products, and, therefore, they may be correctly interpreted as ratios. Methane and oxygen react to yield carbon dioxide and water in a 1:2:1:2 ratio. This ratio is satisfied if the numbers of these molecules are, respectively, 1-2-1-2, or 2-4-2-4, or 3-6-3-6, and so on (Figure 4.2). Likewise, these coefficients may be interpreted with regard to any amount (number) unit, and so this equation may be correctly read in many ways, including:

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

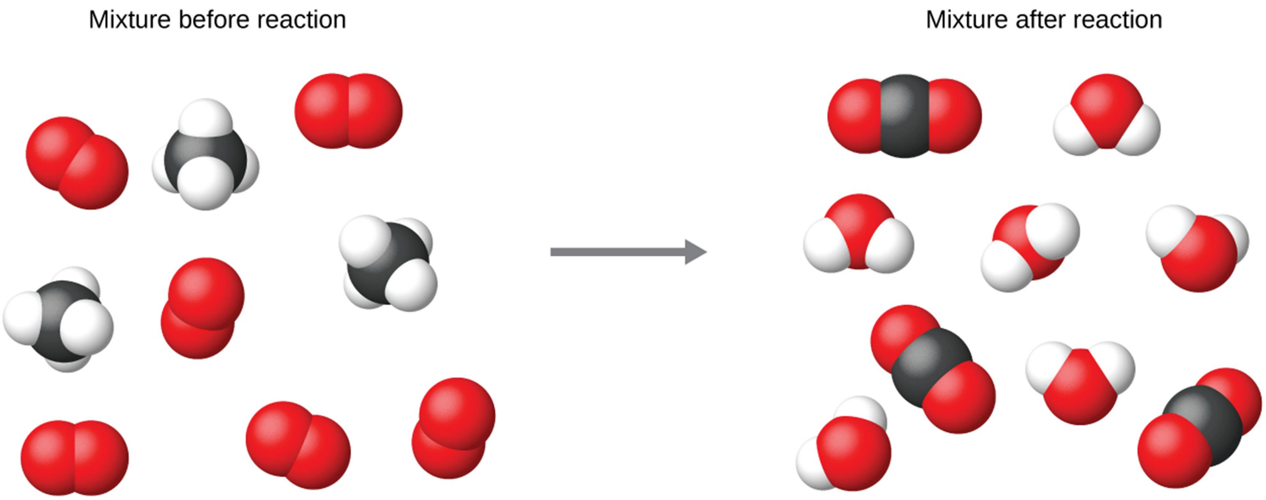


Figure 4.2: Regardless of the absolute numbers of molecules involved, the ratios between numbers of molecules of each species that react (the reactants) and molecules of each species that form (the products) are the same and are given by the chemical reaction equation.

4.1.2. Balancing Chemical Equations

The chemical equation described in section 4.1 is **balanced**, meaning that equal numbers of atoms for each element involved in the reaction are represented on the reactant and product sides. This is a requirement the equation must satisfy to be consistent with the law of conservation of matter. It may be confirmed by simply summing the numbers of atoms on either side of the arrow and comparing these sums to ensure they are equal. Note that the number of atoms for a given element is calculated by multiplying the coefficient of any formula containing that element by the element's subscript in the formula. If an element appears in more than one formula on a given side of the equation, the number of atoms represented in each must be computed and then added together. For example, both product species in the example reaction, CO_2 and H_2O, contain the element oxygen, and so the number of oxygen atoms on the product side of the equation is

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

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

$$\mathbf{CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O}$$

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

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

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

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

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

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

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

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

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

$$\mathbf{2H_2O} \longrightarrow 2H2 _{+} \mathbf{O2} \text{ (balanced)}$$

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

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

$$\mathbf{2H_2O \longrightarrow 2H_2 + O_2}$$

Example 4.1

Balancing Chemical Equations

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

Solution

First, write the unbalanced equation.

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

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

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

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

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

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

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

$$2N_2 + 5O_2 \longrightarrow 2N_2O_5$$

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

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

✍**Check Your Learning**

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

It is sometimes convenient to use fractions instead of integers as intermediate coefficients in the process of balancing a chemical equation. When balance is achieved, all the equation's coefficients may then be multiplied by a whole number to convert the fractional coefficients to integers without upsetting the atom balance. For example, consider the reaction of ethane (C_2H_6) with oxygen to yield H_2O and CO_2, represented by the unbalanced equation:

$$C_2H_6 + O_2 \longrightarrow H_2O + CO_2 \text{ (unbalanced)}$$

Following the usual inspection approach, one might first balance C and H atoms by changing the coefficients for the two product species, as shown:

$$C_2H_6 + O_2 \longrightarrow 3H_2O + 2CO_2 \text{ (unbalanced)}$$

This results in seven O atoms on the product side of the equation, an odd number—no integer coefficient can be used with the O_2 reactant to yield an odd number, so a fractional coefficient, 7/2, is used instead to yield a provisional balanced equation:

$$C_2H_6 + 7/2O_2 \longrightarrow 3H_2O + 2CO_2$$

A conventional balanced equation with integer-only coefficients is derived by multiplying each coefficient by 2:

$$2C_2H_6 + 7O_2 \longrightarrow 6H_2O + 4CO_2$$

Finally with regard to balanced equations, recall that convention dictates use of the *smallest whole-number coefficients*. Although the equation for the reaction between molecular nitrogen and molecular hydrogen to produce ammonia is, indeed, balanced,

$$3N_2 + 9H_2 \longrightarrow 6NH_3$$

the coefficients are not the smallest possible integers representing the relative numbers of reactant and product molecules. Dividing each coefficient by the greatest common factor, 3, gives the preferred equation:

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

Additional Information in Chemical Equations

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

$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$$

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

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

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

4.1.3. Equations for Ionic Reactions

Given the abundance of water on earth, it stands to reason that a great many chemical reactions take place in aqueous media. When ions are involved in these reactions, the chemical equations may be written with various levels of detail appropriate to their intended use. To illustrate this, consider a reaction between ionic compounds taking place in an aqueous solution. When aqueous solutions of $CaCl_2$ and $AgNO_3$ are mixed, a reaction takes place producing aqueous $Ca(NO_3)_2$ and solid AgCl:

$$CaCl_2(aq) + 2AgNO_3(aq) \longrightarrow Ca(NO_3)_2(aq) + 2AgCl(s)$$

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

$$CaCl_2(aq) \longrightarrow Ca^{2+}(aq) + 2Cl^-(aq)$$

$$2AgNO_3(aq) \longrightarrow 2Ag^+(aq) + 2NO_3^-(aq)$$

$$Ca(NO_3)_2(aq) \longrightarrow Ca^{2+}(aq) + 2NO_3^-(aq)$$

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

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

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

Examining this equation shows that two chemical species are present in identical form on both sides of the arrow, $Ca^{2+}(aq)$ and $NO_3^{-}(aq)$. These **spectator ions**—ions whose presence is required to maintain charge neutrality—are neither chemically nor physically changed by the process, and so they may be eliminated from the equation to yield a more succinct representation called a **net ionic equation**:

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

$$\mathbf{2Cl^{-}(aq) + 2Ag^{+}(aq) \longrightarrow 2AgCl(s)}$$

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

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

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

Example 4.2

Molecular and Ionic Equations

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

Solution

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

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

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

$$CO_2(aq) + 2NaOH(aq) \longrightarrow Na_2CO_3(aq) + H_2O(l)$$

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

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

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

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

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

✍**Check Your Learning**

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

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

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

4.2. Classification of chemical reactions

Humans interact with one another in various and complex ways, and we classify these interactions according to common patterns of behavior. When two humans exchange information, we say they are communicating. When they exchange blows with their fists or feet, we say they are fighting. Faced with a wide range of varied interactions between chemical substances, scientists have likewise found it convenient (or even necessary) to classify chemical interactions by identifying common patterns of reactivity. This module will provide an introduction to three of the most prevalent types of chemical reactions: acid-base, precipitation, and oxidation-reduction.

4.2.1. Acid-base reactions

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

For purposes of this brief introduction, we will consider only the more common types of acid-base reactions that take place in aqueous solutions. In this context, an **acid** is a substance that will dissolve in water to yield hydronium ions, H_3O^+. As an example, consider the equation shown here:

$$HCl(aq) + H_2O(aq) \longrightarrow Cl^-(aq) + H_3O^+(aq)$$

The process represented by this equation confirms that hydrogen chloride is an acid. When dissolved in water, H_3O^+ ions are produced by a chemical reaction in which H^+ ions are transferred from HCl molecules to H_2O molecules (Figure 4.3).

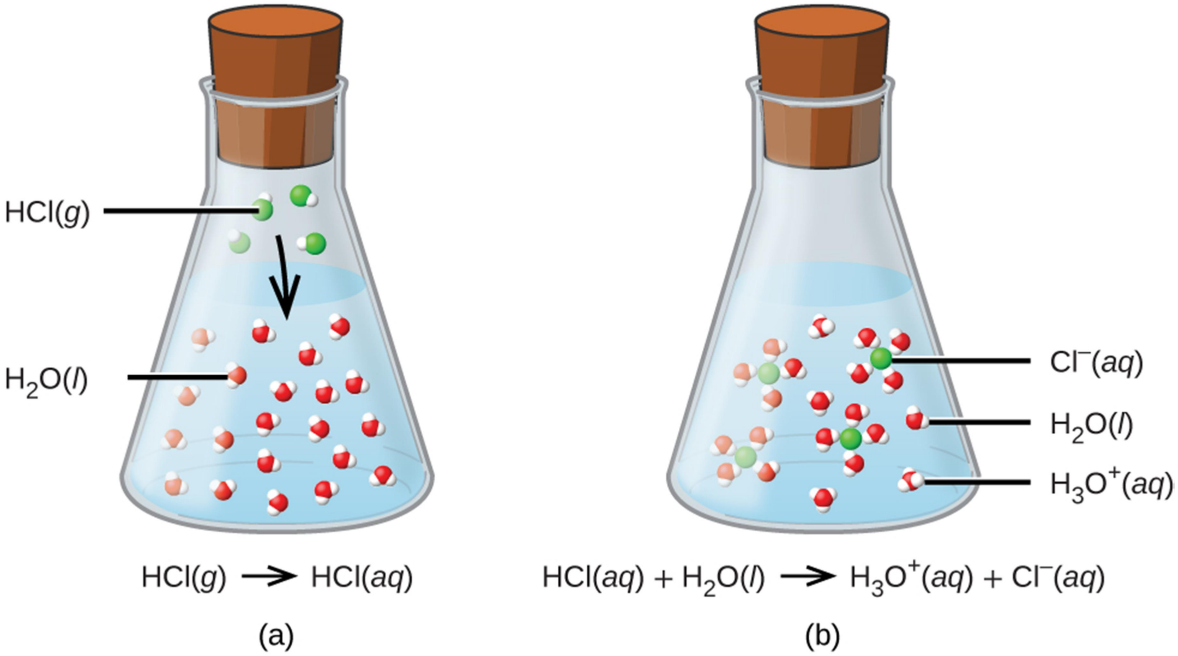


Figure 4.3: When hydrogen chloride gas dissolves in water, (a) it reacts as an acid, transferring protons to water molecules to yield (b) hydronium ions (and solvated chloride ions).

The nature of HCl is such that its reaction with water as just described is essentially 100% efficient: Virtually every HCl molecule that dissolves in water will undergo this reaction. Acids that completely react in this fashion are called **strong acids**, and HCl is one among just a handful of common acid compounds that are classified as strong (Table 4.1). A far greater number of compounds behave as **weak acids** and only partially react with water, leaving a large majority of dissolved molecules in their original form and generating a relatively small amount of hydronium ions. Weak acids are commonly encountered in nature, being the substances partly responsible for the tangy taste of citrus fruits, the stinging sensation of insect bites, and the unpleasant smells associated with body odor. A familiar example of a weak acid is acetic acid, the main ingredient in food vinegars:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^{-}(aq) + H_3O^{+}(aq)$$

When dissolved in water under typical conditions, only about 1% of acetic acid molecules are present in the ionized form, CH_3COO^{-} (Figure 4.4). (The use of a double-arrow in the equation above denotes the partial reaction aspect of this process, a concept addressed fully in the chapters on chemical equilibrium.)

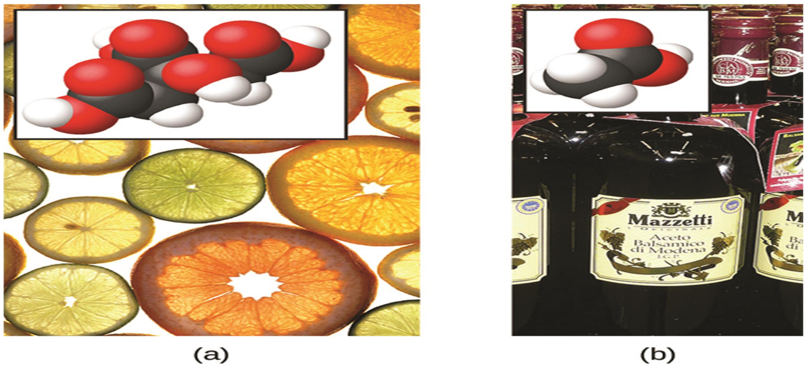


Figure 4.4: (a) Fruits such as oranges, lemons, and grapefruit contain the weak acid citric acid. (b) Vinegars contain the weak acid acetic acid.

Table4.1: Common Strong Acids

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

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

Consider as an example the dissolution of lye (sodium hydroxide) in water:

$$NaOH(s) \longrightarrow Na^+(aq) + OH^-(aq)$$

This equation confirms that sodium hydroxide is a base. When dissolved in water, NaOH dissociates to yield Na^+ and OH^- ions. This is also true for any other ionic compound containing hydroxide ions. Since the dissociation process is essentially complete when ionic compounds dissolve in water under typical conditions, NaOH and other ionic hydroxides are all classified as strong bases.

Unlike ionic hydroxides, some compounds produce hydroxide ions when dissolved by chemically reacting with water molecules. In all cases, these compounds react only partially and so are classified as **weak bases**. These types of compounds are also abundant in nature and important commodities in various technologies. For example, global production of the weak base ammonia is typically well over 100 metric tons annually, being widely used as an agricultural fertilizer, a raw material for chemical synthesis of other compounds, and an active ingredient in household cleaners (Figure 4.5). When dissolved in water, ammonia reacts partially to yield hydroxide ions, as shown here:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

This is, by definition, an acid-base reaction, in this case involving the transfer of H^+ ions from water molecules to ammonia molecules. Under typical conditions, only about 1% of the dissolved ammonia is present as NH_4^+ ions.

Figure 4.5: Ammonia is a weak base used in a variety of applications. (a) Pure ammonia is commonly applied as an agricultural fertilizer. (b) Dilute solutions of ammonia are effective household cleansers.

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

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

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

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

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

Example 4.3

Writing Equations for Acid-Base Reactions

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

(a) The weak acid hydrogen hypochlorite reacts with water

(b) A solution of barium hydroxide is neutralized with a solution of nitric acid

Solution

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

$$HOCl(aq) + H_2O(l) \rightleftharpoons OCl^-(aq) + H_3O^+(aq)$$

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

(b) The two reactants are provided, $Ba(OH)_2$ and HNO_3. Since this is a neutralization reaction, the two products will be water and a salt composed of the cation of the ionic hydroxide (Ba^{2+}) and the anion generated when the acid transfers its hydrogen ion (NO_3^-).

$$Ba(OH)_2(aq) + 2HNO_3(aq) \longrightarrow Ba(NO_3)_2(aq) + 2H_2O(l)$$

✍Check Your Learning

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

CHEMISTRY IN EVERYDAY LIFE

Stomach Antacids

Our stomachs contain a solution of roughly 0.03 *M* HCl, which helps us digest the food we eat. The burning sensation associated with heartburn is a result of the acid of the stomach leaking through the muscular valve at the top of the stomach into the lower reaches of the esophagus. The lining of the esophagus is not protected from the corrosive effects of stomach acid the way the lining of the stomach is, and the results can be very painful. When we have heartburn, it feels better if we reduce the excess acid in the esophagus by taking an antacid. As you may have guessed, antacids are bases. One of the most common antacids is calcium carbonate, $CaCO_3$. The reaction,

$$CaCO_3(s)+2HCl(aq)\rightleftharpoons CaCl_2(aq)+H_2O(l)+CO_2(g)$$

not only neutralizes stomach acid, it also produces $CO_2(g)$, which may result in a satisfying belch. Milk of Magnesia is a suspension of the sparingly soluble base magnesium hydroxide, $Mg(OH)_2$. It works according to the reaction:

$$Mg(OH)_2(s)\rightleftharpoons Mg^{2+}(aq)+2OH^-(aq)$$

The hydroxide ions generated in this equilibrium then go on to react with the hydronium ions from the stomach acid, so that:

$$H_3O^++OH^-\rightleftharpoons 2H_2O(l)$$

This reaction does not produce carbon dioxide, but magnesium-containing antacids can have a laxative effect. Several antacids have aluminum hydroxide, $Al(OH)_3$, as an active ingredient. The aluminum hydroxide tends to cause constipation, and some antacids use aluminum hydroxide in concert with magnesium hydroxide to balance the side effects of the two substances.

4.2.2. Precipitation reactions and solubility rules

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

The extent to which a substance may be dissolved in water, or any solvent, is quantitatively expressed as its **solubility**, defined as the maximum concentration of a substance that can be achieved under specified conditions. Substances with relatively large solubility are said to be **soluble**. A substance will **precipitate** when solution conditions are such that its concentration exceeds its solubility. Substances with relatively low solubility are said to be **insoluble**, and these are the substances that readily precipitate from solution. For purposes of predicting the identities of solids formed by precipitation reactions, one may simply refer to patterns of solubility that have been observed for many ionic compounds (Table 4.2).

Table4.2: patterns of solubility of some ionic compounds

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

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

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

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

The net ionic equation representing this reaction is:

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

Lead iodide is a bright yellow solid that was formerly used as an artist's pigment known as iodine yellow (Figure 4.6). The properties of pure PbI_2 crystals make them useful for fabrication of X-ray and gamma ray detectors.

Figure 4.6: A precipitate of PbI_2 forms when solutions containing Pb^{2+} and I^- are mixed.

The solubility guidelines in Table 4.2 may be used to predict whether a precipitation reaction will occur when solutions of soluble ionic compounds are mixed together. One merely needs to identify all the ions present in the solution and then consider if possible cation/anion pairing could result in an insoluble compound. For example, mixing solutions of silver nitrate and sodium fluoride will yield a solution containing Ag^+, NO_3^-, Na^+, and F^- ions. Aside from the two ionic compounds originally present in the solutions, $AgNO_3$ and NaF, two additional ionic compounds may be derived from this collection of ions: $NaNO_3$ and AgF. The solubility guidelines indicate all nitrate salts are soluble but that AgF is one of the exceptions to the general solubility of fluoride salts. A precipitation reaction, therefore, is predicted to occur, as described by the following equations:

$$NaF(aq) + AgNO_3(aq) \longrightarrow AgF(s) + NaNO_3(aq) \text{ (molecular)}$$
$$Ag^+(aq) + F^-(aq) \longrightarrow AgF(s) \text{ (net ionic)}$$

Example 4.4

Predicting Precipitation Reactions

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

(a) potassium sulfate and barium nitrate

(b) lithium chloride and silver acetate

(c) lead nitrate and ammonium carbonate

Solution

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

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

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

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

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

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

✍ **Check Your Learning**

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

4.2.3. Oxidation-Reduction Reactions

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

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

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

It is helpful to view the process with regard to each individual reactant, that is, to represent the fate of each reactant in the form of an equation called a **half-reaction**:

$$\mathbf{2Na(s) \longrightarrow 2Na^{+}(s) + 2e-}$$

$$\mathbf{Cl_2(g) + 2e^- \longrightarrow 2Cl^-(s)}$$

These equations show that Na atoms *lose electrons* while Cl atoms (in the Cl_2 molecule) *gain electrons*, the "*s*" subscripts for the resulting ions signifying they are present in the form of a solid ionic compound. For redox reactions of this sort, the loss and gain of electrons define the complementary processes that occur:

Oxidation = loss of electrons
Reduction = gain of electrons

In this reaction, then, sodium is *oxidized* and chlorine undergoes **reduction**. Viewed from a more active perspective, sodium functions as a **reducing agent (reductant)**, since it provides electrons to (or reduces) chlorine. Likewise, chlorine functions as an **oxidizing agent (oxidant)**, as it effectively removes electrons from (oxidizes) sodium.

reducing agent = species that is oxidized
oxidizing agent = species that is reduced

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

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

The product of this reaction is a covalent compound, so transfer of electrons in the explicit sense is not involved. To clarify the similarity of this reaction to the previous one and permit an unambiguous definition of redox reactions, a property called *oxidation number* has been defined. The **oxidation number** (or **oxidation state**) of an element in a compound is the charge its atoms would possess *if the compound was ionic*. The following guidelines are used to assign oxidation numbers to each element in a molecule or ion.

1. The oxidation number of an atom in an elemental substance is zero.
2. The oxidation number of a monatomic ion is equal to the ion's charge.
3. Oxidation numbers for common nonmetals are usually assigned as follows:
   - Hydrogen: +1 when combined with nonmetals, −1 when combined with metals
   - Oxygen: −2 in most compounds, sometimes −1 (so-called peroxides, O_2^{2-}), very rarely −1/2 (so-called superoxides, O_2^-), positive values when combined with F (values vary)

- Halogens: −1 for F always, −1 for other halogens except when combined with oxygen or other halogens (positive oxidation numbers in these cases, varying values)

4. The sum of oxidation numbers for all atoms in a molecule or polyatomic ion equals the charge on the molecule or ion.

Note: The proper convention for reporting charge is to write the number first, followed by the sign (e.g., 2+), while oxidation number is written with the reversed sequence, sign followed by number (e.g., +2). This convention aims to emphasize the distinction between these two related properties.

Example 4.5

Assigning Oxidation Numbers

Follow the guidelines in this section of the text to assign oxidation numbers to all the elements in the following species:

(a) H_2S (b) SO_3^{2-} (c) Na_2SO_4

Solution

(a) According to guideline 1, the oxidation number for H is +1.

Using this oxidation number and the compound's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:

charge on $H_2S = 0 = (2\times+1)+(1\times x)$

$x = 0 - (2\times+1) = -2$

(b) Guideline 3 suggests the oxidation number for oxygen is −2.

Using this oxidation number and the ion's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:

charge on $SO_3^{2-} = -2 = (3\times-2)+(1\times x) x = -2-(3\times-2) = +4$

(c) For ionic compounds, it's convenient to assign oxidation numbers for the cation and anion separately.

According to guideline 2, the oxidation number for sodium is +1.

Assuming the usual oxidation number for oxygen (−2 per guideline 3), the oxidation number for sulfur is calculated as directed by guideline 4:

charge on $SO_4^{2-} = -2 = (4\times-2)+(1\times x)$

$x = -2-(4\times-2) = +6$

Check Your Learning

Assign oxidation states to the elements whose atoms are underlined in each of the following compounds or ions:

(a) KNO_3 (b) AlH_3(c) NH_4^+(d) $H_2PO_4^-$

Using the oxidation number concept, an all-inclusive definition of redox reaction has been established. **Oxidation-reduction (redox) reactions** are those in which one or more elements involved undergo a change in oxidation number. (While the vast majority of redox reactions involve changes in oxidation number for two or more elements, a few interesting exceptions to this rule do exist Example 4.5.) Definitions for the complementary processes of this reaction class are correspondingly revised as shown here:

$$\text{Oxidation} = \text{increase in oxidation number}$$
$$\text{Reduction} = \text{decrease in oxidation number}$$

Returning to the reactions used to introduce this topic, they may now both be identified as redox processes. In the reaction between sodium and chlorine to yield sodium chloride, sodium is oxidized (its oxidation number increases from 0 in Na to +1 in NaCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_2 to −1 in NaCl). In the reaction between molecular hydrogen and chlorine, hydrogen is oxidized (its oxidation number increases from 0 in H_2 to +1 in HCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_2 to −1 in HCl).

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

$$\mathbf{10Al(s) + 6NH_4ClO_4(s) \longrightarrow 4Al_2O_3(s) + 2AlCl_3(s) + 12H_2O(g) + 3N_2(g)}$$

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

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

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

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

This reaction may be observed by placing copper wire in a solution containing a dissolved silver salt. Silver ions in solution are reduced to elemental silver at the surface of the copper wire, and the resulting Cu^{2+} ions dissolve in the solution to yield a characteristic blue color (Figure 4.8).

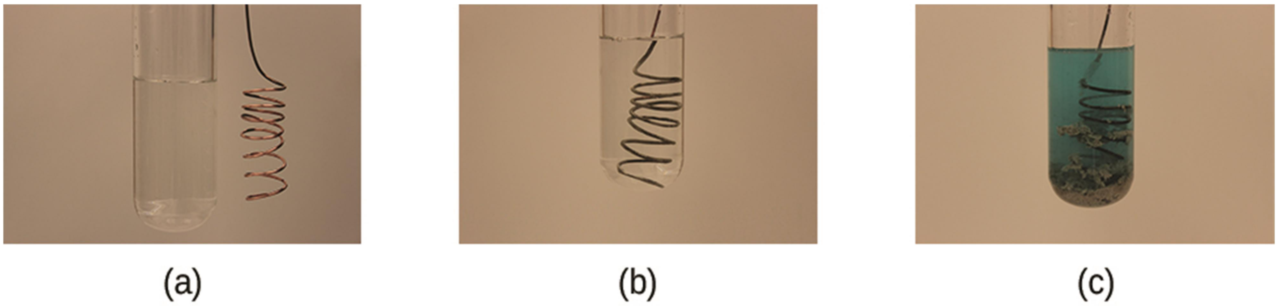


Figure 4.8: (a) A copper wire is shown next to a solution containing silver(I) ions. (b) Displacement of dissolved silver ions by copper ions results in (c) accumulation of gray-colored silver metal on the wire and development of a blue color in the solution, due to dissolved copper ions.

Example 4.6

Describing Redox Reactions

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

(a) $ZnCO_3(s) \longrightarrow ZnO(s) + CO_2(g)$

(b) $2Ga(l) + 3Br_2(l) \longrightarrow 2GaBr_3(s)$

(c) $2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$

(d) $BaCl_2(aq) + K_2SO_4(aq) \longrightarrow BaSO_4(s) + 2KCl(aq)$

(e) $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$

Solution

(a) This is not a redox reaction, since oxidation numbers remain unchanged for all elements.

(b) This is a redox reaction. Gallium is oxidized, its oxidation number increasing from 0 in $Ga(l)$ to +3 in $GaBr_3(s)$. The reducing agent is $Ga(l)$. Bromine is reduced, its oxidation number decreasing from 0 in $Br_2(l)$ to −1 in $GaBr_3(s)$. The oxidizing agent is $Br_2(l)$.

(c) This is a redox reaction. It is a particularly interesting process, as it involves the same element, oxygen, undergoing both oxidation and reduction (a so-called *disproportionation reaction)*. Oxygen is oxidized, its oxidation number increasing from −1 in $H_2O_2(aq)$ to 0 in $O_2(g)$. Oxygen is also reduced, its oxidation number decreasing from −1 in $H_2O_2(aq)$ to −2 in $H_2O(l)$. For disproportionation reactions, the same substance functions as an oxidant and a reductant.

(d) This is not a redox reaction, since oxidation numbers remain unchanged for all elements.

(e) This is a redox reaction (combustion). Carbon is oxidized, its oxidation number increasing from −2 in $C_2H_4(g)$ to +4 in $CO_2(g)$. The reducing agent (fuel) is $C_2H_4(g)$. Oxygen is reduced, its oxidation number decreasing from 0 in $O_2(g)$ to −2 in $H_2O(l)$. The oxidizing agent is $O_2(g)$.

✍**Check Your Learning**

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

$Sn(s)+2HCl(g)\longrightarrow SnCl_2(s)+H_2(g)$

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

Balancing Redox Reactions via the Half-Reaction Method

Redox reactions that take place in aqueous media often involve water, hydronium ions, and hydroxide ions as reactants or products. Although these species are not oxidized or reduced, they do participate in chemical change in other ways (e.g., by providing the elements required to form oxyanions). Equations representing these reactions are sometimes very difficult to balance by inspection, so systematic approaches have been developed to assist in the process. One very useful approach is to use the method of half-reactions, which involves the following steps:

1. Write the two half-reactions representing the redox process.
2. Balance all elements except oxygen and hydrogen.
3. Balance oxygen atoms by adding H_2O molecules.
4. Balance hydrogen atoms by adding H^+ ions.
5. Balance charge by adding electrons.
6. If necessary, multiply each half-reaction's coefficients by the smallest possible integers to yield equal numbers of electrons in each.

7. Add the balanced half-reactions together and simplify by removing species that appear on both sides of the equation.
8. For reactions occurring in basic media (excess hydroxide ions), carry out these additional steps:
    a. Add OH^- ions to both sides of the equation in numbers equal to the number of H^+ ions.
    b. On the side of the equation containing both H^+ and OH^- ions, combine these ions to yield water molecules.
    c. Simplify the equation by removing any redundant water molecules.
9. Finally, check to see that both the number of atoms and the total charges[1] are balanced.

Example 4.7

Balancing Redox Reactions in Acidic Solution

Write a balanced equation for the reaction between dichromate ion and iron(II) to yield iron(III) and chromium(III) in acidic solution.

$$Cr_2O_7^{2-} + Fe^{2+} \longrightarrow Cr^{3+} + Fe^{3+}$$

Solution

Step 1: *Write the two half-reactions*.

Each half-reaction will contain one reactant and one product with one element in common.

$Fe^{2+} \longrightarrow Fe^{3+}$

$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$

Step 2: *Balance all elements except oxygen and hydrogen*.

The iron half-reaction is already balanced, but the chromium half-reaction shows two Cr atoms on the left and one Cr atom on the right. Changing the coefficient on the right side of the equation to 2 achieves balance with regard to Cr atoms.

$Fe^{2+} \longrightarrow Fe^{3+}$

$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$

Step 3: *Balance oxygen atoms by adding* H_2O *molecules*.

The iron half-reaction does not contain O atoms. The chromium half-reaction shows seven O atoms on the left and none on the right, so seven water molecules are added to the right side.

$Fe^{2+} \longrightarrow Fe^{3+}$

$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$

Step 4: *Balance hydrogen atoms by adding* H^+ *ions*.

The iron half-reaction does not contain H atoms. The chromium half-reaction shows 14 H atoms on the right and none on the left, so 14 hydrogen ions are added to the left side.

$Fe^{2+} \longrightarrow Fe^{3+}$

$Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$

Step 5: *Balance charge by adding electrons*.

The iron half-reaction shows a total charge of 2+ on the left side (1 Fe^{2+} ion) and 3+ on the right side (1 Fe^{3+} ion). Adding one electron to the right side brings that side's total charge to (3+) + (1−) = 2+, and charge balance is achieved.

The chromium half-reaction shows a total charge of (1 × 2−) + (14 × 1+) = 12+ on the left side (1 $Cr_2O_7^{2-}$ ion and 14 H^+ ions). The total charge on the right side is (2 × 3+) = 6 + (2 Cr^{3+} ions). Adding six electrons to the left side will bring that side's total charge to (12+ + 6−) = 6+, and charge balance is achieved.

$Fe^{2+} \longrightarrow Fe^{3+} + e-$

$Cr_2O_7^{2-} + 14H^+ + 6e- \longrightarrow 2Cr^{3+} + 7H_2O$

Step 6: *Multiply the two half-reactions so the number of electrons in one reaction equals the number of electrons in the other reaction*.

To be consistent with mass conservation, and the idea that redox reactions involve the transfer (not creation or destruction) of electrons, the iron half-reaction's coefficient must be multiplied by 6.

$6Fe^{2+} \longrightarrow 6Fe^{3+} + 6e-$

$Cr_2O_7^{2-} + 6e- + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$

Step 7: *Add the balanced half-reactions and cancel species that appear on both sides of the equation*.

$Cr_2O_7^{2-} + 6e- + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 6e- + 7H_2O$

Only the six electrons are redundant species. Removing them from each side of the equation yields the simplified, balanced equation here:

$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

A final check of atom and charge balance confirms the equation is balanced.

	Reactants	Products
Fe	6	6

Cr	2	2
O	7	7
H	14	14
Charge	24+	24+

Check Your Learning

In basic solution, molecular chlorine, Cl_2, reacts with hydroxide ions, OH^-, to yield chloride ions, Cl^- and chlorate ions, ClO_4^-. HINT: This is a *disproportionation reaction* in which the element chlorine is both oxidized and reduced. Write a balanced equation for this reaction.

4.3. Reaction stoichiometry

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

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

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

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

$$\frac{2NH_3molecules}{3H_2molecules} \quad or \quad \frac{2\ dozNH_3molecules}{3doz\ \ {}_2molecules} \quad \text{or} \frac{2molN\ \ {}_3molecules}{3molH_2molecules}$$

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

Example 4.8

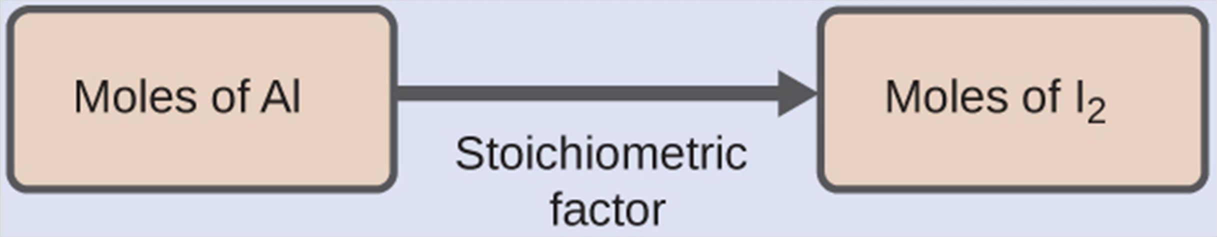
Moles of Reactant Required in a Reaction

How many moles of I_2 are required to react with 0.429 mol of Al according to the following equation ?

$$2Al + 3I_2 \longrightarrow 2AlI_3$$

Solution

Referring to the balanced chemical equation, the stoichiometric factor relating the two substances of interest is $3molI_2/\ 2mol\ Al$. The molar amount of iodine is derived by multiplying the provided molar amount of aluminum by this factor:



$$mol\ I_2 = 0.429mol\ Al \times 3\ molI_2/2mol\ Al = 0.644\ molI_2mol$$

Example 4.9

Number of Product Molecules Generated by a Reaction

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

$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$$

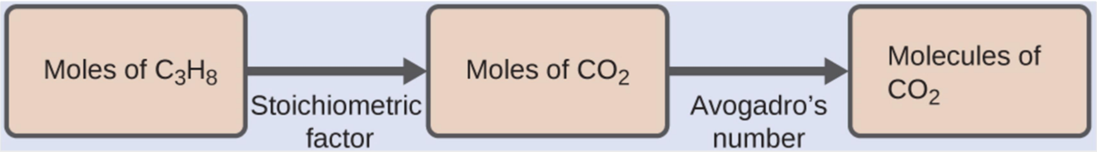
Solution

The approach here is the same as for Example 4.8, though the absolute number of molecules is requested, not the number of moles of molecules. This will simply require use of the moles-to-numbers conversion factor, Avogadro's number.

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

$$3\ molCO_2/1\ molC_3H_8$$

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



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

✍Check Your Learning

1. How many moles of $Ca(OH)_2$ are required to react with 1.36 mol of H_3PO_4 to produce $Ca_3(PO_4)_2$ according to the equation $3Ca(OH)_2 + 2H_3PO_4 \longrightarrow Ca_3(PO_4)_2 + 6H_2O$?
2. How many NH3 molecules are produced by the reaction of 4.0 mol of Ca(OH)2 according to the following equation:
   $(NH_4)_2SO_4 + Ca(OH)_2 \longrightarrow 2NH_3 + CaSO_4 + 2H_2O$

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

Example 4.10

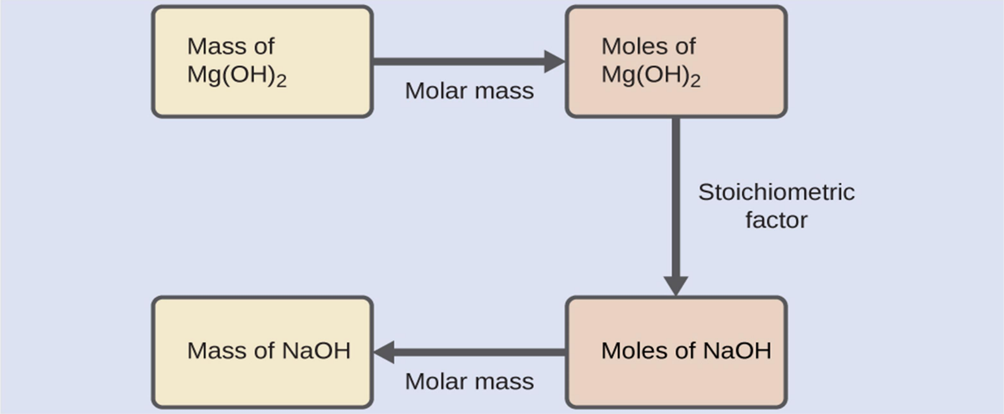
Relating Masses of Reactants and Products

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

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

Solution

The approach used previously in Example 4.8 and Example 4.9 is likewise used here; that is, we must derive an appropriate stoichiometric factor from the balanced chemical equation and use it to relate the amounts of the two substances of interest. In this case, however, masses (not molar amounts) are provided and requested, so additional steps of the sort learned in the previous chapter are required. The calculations required are outlined in this flowchart:



16g $Mg(OH)_2$×1mol $Mg(OH)_2$/58.3g $Mg(OH)_2$×2mol NaOH/1mol $Mg(OH)_2$×40.0 g NaOH/mol NaOH=22 g NaOH

Example 4.11

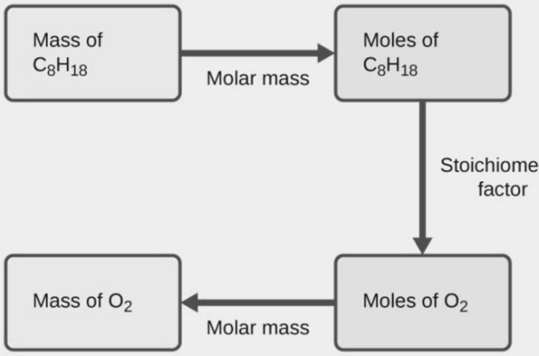
Relating Masses of Reactants

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

$$2C_8H_{18} + 25O_2 \longrightarrow 16CO_2 + 18H_2O_2$$

Solution

The approach required here is the same as for the Example 4.10, differing only in that the provided and requested masses are both for reactant species.



702gC_8H_{18}×1molC_8H_{18} /114.23gC_8H_{18}×25molO_2/2molC_8H_{18}×32.00 gO_2/molO_2=$2.46×10^3$gO_2

✍**Check Your Learning**

1. What mass of gallium oxide, Ga_2O_3, can be prepared from 29.0 g of gallium metal? The equation for the reaction is $4Ga+3O_2 \longrightarrow 2Ga_2O_3$.
2. What mass of CO is required to react with 25.13 g of Fe_2O_3 according to the equation $Fe_2O_3+3CO \longrightarrow 2Fe+3CO_2$?

These examples illustrate just a few instances of reaction stoichiometry calculations. Numerous variations on the beginning and ending computational steps are possible depending upon what particular quantities are provided and sought (volumes, solution concentrations, and so forth). Regardless of the details, all these calculations share a common essential component: the use of stoichiometric factors derived from balanced chemical equations. Figure 4.9 provides a general outline of the various computational steps associated with many reaction stoichiometry calculations.

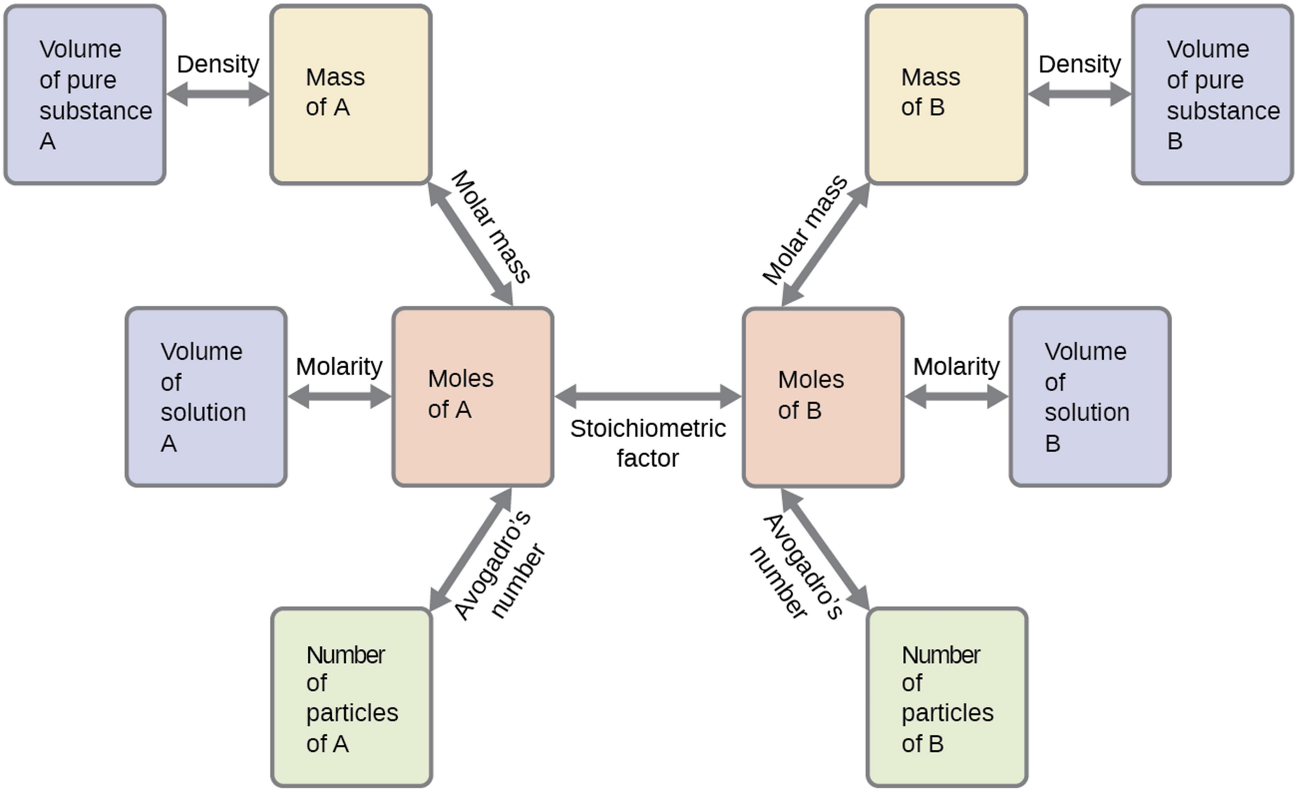


Figure 4.9: The flowchart depicts the various computational steps involved in most reaction stoichiometry calculations.

CHEMISTRY IN EVERYDAY LIFE

Airbags

Airbags (Figure 4.10) are a safety feature provided in most automobiles since the 1990s. The effective operation of an airbag requires that it be rapidly inflated with an appropriate amount (volume) of gas when the vehicle is involved in a collision. This requirement is satisfied in many automotive airbag systems through use of explosive chemical reactions, one common choice being the decomposition of sodium azide, NaN_3. When sensors in the vehicle detect a collision, an electrical current is passed through a carefully measured amount of NaN_3 to initiate its decomposition:

$$2NaN_3(s) \longrightarrow 3N_2(g) + 2Na(s)$$

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

Figure **4.10:** Airbags deploy upon impact to minimize serious injuries to passengers.

4.4. Reaction Yield

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

4.4.1. Limiting Reactant

Consider another food analogy, making grilled cheese sandwiches (Figure 4.11):

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

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

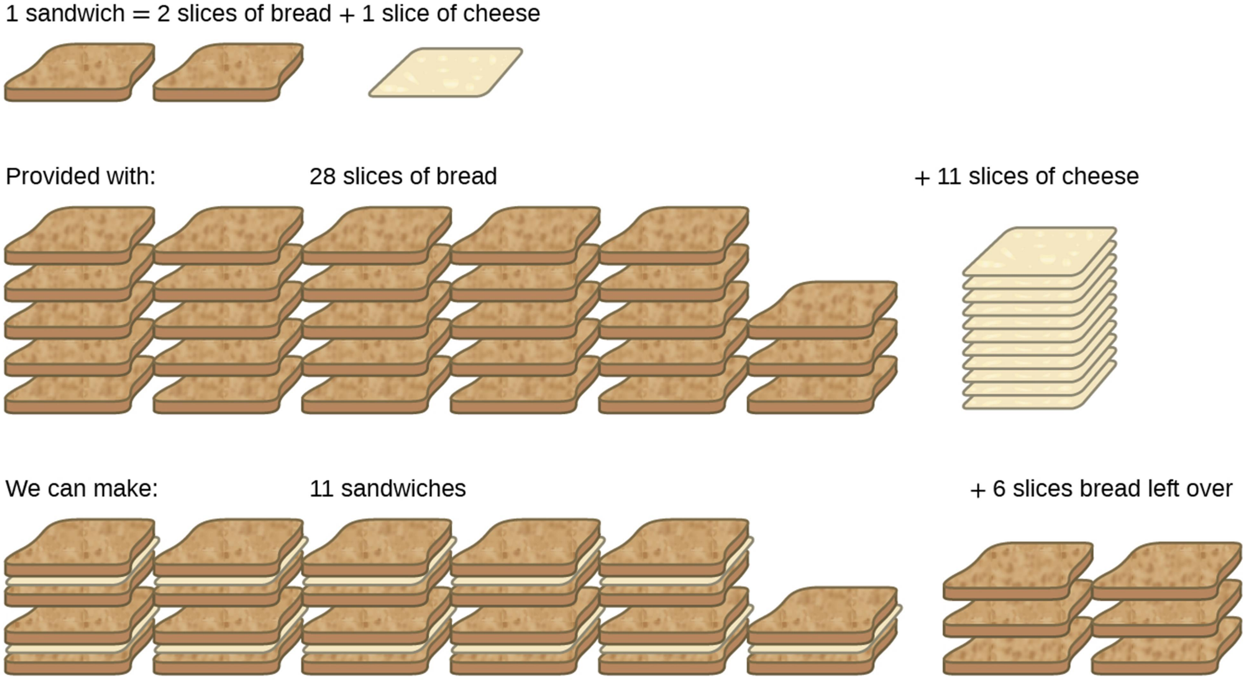


Figure 4.11: Sandwich making can illustrate the concepts of limiting and excess reactants.

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

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

The balanced equation shows the hydrogen and chlorine react in a 1:1 stoichiometric ratio. If these reactants are provided in any other amounts, one of the reactants will nearly always be entirely consumed, thus limiting the amount of product that may be generated. This substance is the **limiting reactant**, and the other substance is the **excess reactant**. Identifying the limiting and excess reactants for a given situation requires computing the molar amounts of each reactant provided and comparing them to the stoichiometric amounts represented in the balanced chemical equation. For example, imagine combining 3 moles of H_2 and 2 moles of Cl_2. This represents a 3:2 (or 1.5:1) ratio of hydrogen to chlorine present for reaction, which is greater than the stoichiometric ratio of 1:1. Hydrogen, therefore, is present in excess, and chlorine is the limiting reactant. Reaction of all the provided chlorine (2 mol) will consume 2 mol of the 3 mol of hydrogen provided, leaving 1 mol of hydrogen unreacted.

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

$$\text{mol HCl produced} = 3\text{mol}H_2 \times 2\text{ mol HCl}/1\text{ mol}H_2 = 6\text{ mol HCl}$$

Complete reaction of the provided chlorine would produce

$$\text{mol HCl produced} = 2\text{ mol}Cl_2 \times 2\text{ mol HCl}/1\text{ mol}Cl_2 = 4\text{ mol HCl}$$

The chlorine will be completely consumed once 4 moles of HCl have been produced. Since enough hydrogen was provided to yield 6 moles of HCl, there will be unreacted hydrogen remaining once this reaction is complete. Chlorine, therefore, is the limiting reactant and hydrogen is the excess reactant (Figure 4.12).

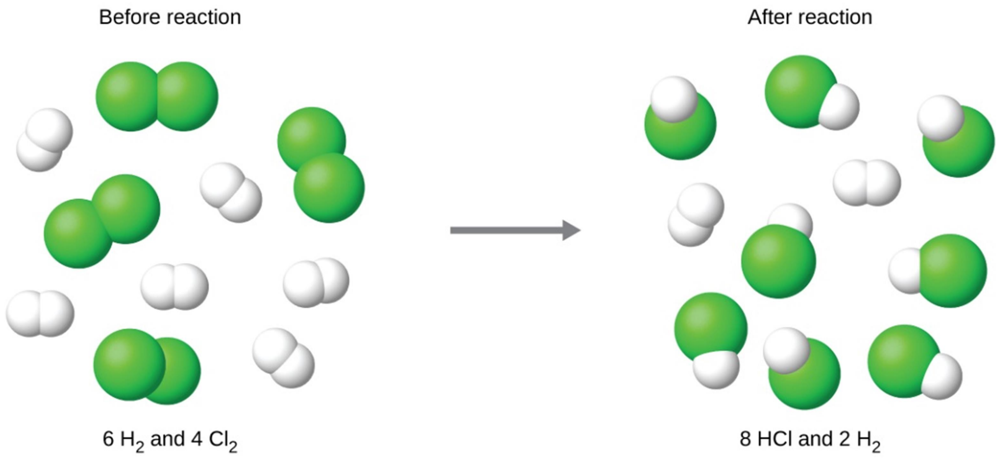


Figure 4.12**:** This illustration shows a reaction in which hydrogen is present in excess and chlorine is the limiting reactant. When H_2 and Cl_2 are combined in nonstoichiometric amounts, one of these reactants will limit the amount of HCl that can be produced.

Example 4.12

Identifying the Limiting Reactant

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

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

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

Solution

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

$$\text{mol Si}=2.00\text{g Si}\times 1\text{ mol Si}/28.09\text{g Si} = 0.0712\text{ mol Si}$$

$$\text{mol}N_2=1.50\text{g}N_2\times 1\text{mol}N_2/28.02\text{g}N_2=0.0535\text{ mol}N_2$$

The provided Si:N_2 molar ratio is:

$0.0712\text{ mol Si}/0.0535\text{ mol}N_2=1.33\text{ mol Si}/1\text{mol}N_2$

The stoichiometric Si:N_2 ratio is:

$$3\text{ mol Si}/2\text{ mol}N_2=1.5\text{ mol Si}/1\text{ mol}N_2$$

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

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

$$\text{mol}Si_3N_4\text{ produced} = 0.0712\text{ mol Si} \times 1\text{mol}Si_3N_4/3\text{molSi}=0.0237\text{ mol}Si_3N_4$$

while the 0.0535 moles of nitrogen would produce

$$\text{mol}Si_3N_4\text{produced}=0.0535\text{mol}N_2\times 1\text{mol}Si_3N_4/2\text{mol}N_2=0.0268\text{ mol}Si_3N_4$$

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

✍**Check Your Learning**

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

4.4.2. Percent Yield

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

$$\textbf{percent yield} = \frac{\textbf{actual yield}}{\textbf{theoretical yield}}\ \boldsymbol{x}\ \mathbf{100\%}$$

Actual and theoretical yields may be expressed as masses or molar amounts (or any other appropriate property; e.g., volume, if the product is a gas). As long as both yields are expressed using the same units, these units will cancel when percent yield is calculated.

Example 4.13

Calculation of Percent Yield

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

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

What is the percent yield?

Solution

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

$1.274 g CuSO_4 \times 1 mol CuSO_4/159.62 g CuSO_4 \times 1 mol\ Cu/1 mol CuSO_4 \times 63.55 g\ Cu/1 mol\ Cu = 0.5072\ g\ Cu$

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

$$\text{percent yield} = (\text{actual yield}/\text{theoretical yield}) \times 100$$

Percent yield = (0.392 g Cu/ 0.5072 g Cu)×100=77.3%

✍ **Check Your Learning**

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

$$CCl_4+2HF \longrightarrow CF_2Cl_2+2HCl$$

4.5. Quantitative Chemical Analysis

In the 18th century, the strength (actually the concentration) of vinegar samples was determined by noting the amount of potassium carbonate, K_2CO_3, which had to be added, a little at a time, before bubbling ceased. The greater the weight of potassium carbonate added to reach the point where the bubbling ended, the more concentrated the vinegar.

We now know that the effervescence that occurred during this process was due to reaction with acetic acid, CH_3CO_2H, the compound primarily responsible for the odor and taste of vinegar. Acetic acid reacts with potassium carbonate according to the following equation:

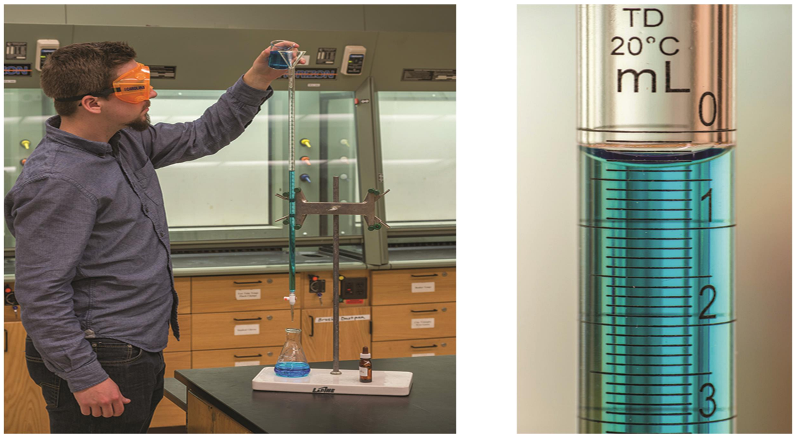
$$\mathbf{2CH_3CO_2H(aq) + K_2CO_3(s) \longrightarrow 2CH_3CO_2K(aq) + CO_2(g) + H_2O(l)}$$

The bubbling was due to the production of CO_2.

The test of vinegar with potassium carbonate is one type of **quantitative analysis**-the determination of the amount or concentration of a substance in a sample. In the analysis of vinegar, the concentration of the solute (acetic acid) was determined from the amount of reactant that combined with the solute present in a known volume of the solution. In other types of chemical analyses, the amount of a substance present in a sample is determined by measuring the amount of product that results.

4.5.1. Acid-base Titration

The described approach to measuring vinegar strength was an early version of the analytical technique known as **titration analysis**. A typical titration analysis involves the use of a **buret** (Figure 4.13) to make incremental additions of a solution containing a known concentration of some substance (the **titrant**) to a sample solution containing the substance whose concentration is to be measured (the **analyte**). The titrant and analyte undergo a chemical reaction of known stoichiometry, and so measuring the volume of titrant solution required for complete reaction with the analyte (the **equivalence point** of the titration) allows calculation of the analyte concentration. The equivalence point of a titration may be detected visually if a distinct change in the appearance of the sample solution accompanies the completion of the reaction. The halt of bubble formation in the classic vinegar analysis is one such example, though, more commonly, special dyes called **indicators** are added to the sample solutions to impart a change in color at or very near the equivalence point of the titration. Equivalence points may also be detected by measuring some solution property that changes in a predictable way during the course of the titration. Regardless of the approach taken to detect a titration’s equivalence point, the volume of titrant actually measured is called the **end point**. Properly designed titration methods typically ensure that the difference between the equivalence and end points is negligible. Though any type of chemical reaction may serve as the basis for a titration analysis, precipitation, acid-base, and redox titrations are the most common. In this topic the titration of strong acid-strong base will be discussed.



(a) (b)

Figure 4.13: (a) A student fills a buret in preparation for a titration analysis. (b) A typical buret permits volume measurements to the nearest 0.01 mL.

Example 4.14

Titration Analysis

The end point in a titration of a 50.00-mL sample of aqueous HCl was reached by addition of 35.23 mL of 0.250 M NaOH titrant. The titration reaction is:

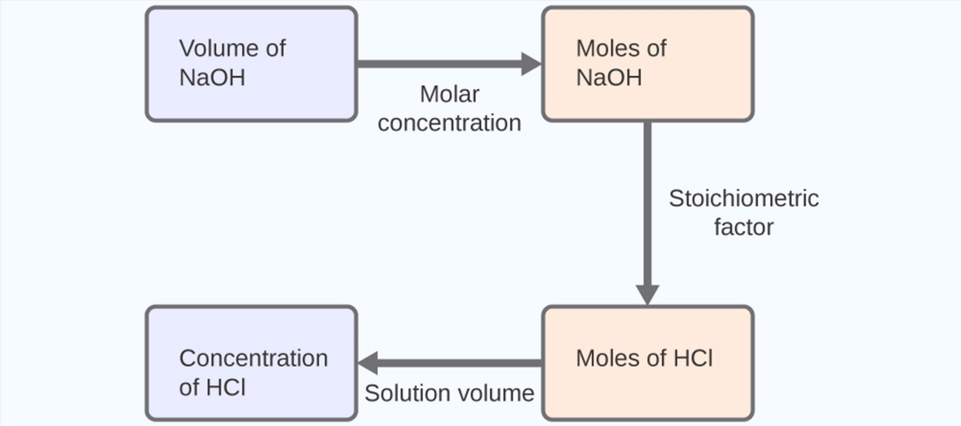
$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

What is the molarity of the HCl?

Solution

As for all reaction stoichiometry calculations, the key issue is the relation between the molar amounts of the chemical species of interest as depicted in the balanced chemical equation. The approach outlined in previous modules of this chapter is followed, with additional considerations required, since the amounts of reactants provided and requested are expressed as solution concentrations.

For this exercise, the calculation will follow the following outlined steps:



The molar amount of HCl is calculated to be:

$35.23 \text{mL NaOH} \times 1 \text{L}/1000 \text{mL} \times 0.250 \text{mol NaOH}/1 \text{L} \times 1 \text{ mol HCl}/1 \text{mol NaOH} = 8.81 \times 10^{-3} \text{mol HCl}$

Using the provided volume of HCl solution and the definition of molarity, the HCl concentration is:

$$M = \text{mol HCl} / \text{L solution}$$

$$M = 8.81 \times 10^{-3} \text{molHCl} / 50.00 \text{mL} \times 1 \text{L} / 1000 \text{mL}$$

$$M = 0.176 M$$

Note: For these types of titration calculations, it is convenient to recognize that solution molarity is also equal to the number of *milli*moles of solute per *milli*liter of solution:

$$M = \frac{mol\ solute}{L\ solution}\ X\ \frac{\frac{10^3 mmol}{mol}}{\frac{10^3 mL}{L}} = \frac{mmol\ solute}{mL\ solution}$$

Using this version of the molarity unit will shorten the calculation by eliminating two conversion factors:

$$\frac{35.23 mL\ NaOH\ X\ \frac{0.250 mmol\ NaOH}{mL\ NaOH}\ X\ \frac{1 mmolHCl}{1 mmol\ NaOH}}{50.00 mL\ solution} = 0.176 MHCl$$

Check Your Learning

A 20.00-mL sample of aqueous oxalic acid, $H_2C_2O_4$, was titrated with a 0.09113-*M* solution of potassium permanganate, $KMnO_4$.

$2MnO_4-(aq)+5H_2C_2O_4(aq)+6H^+(aq)\longrightarrow 10CO_2(g)+2Mn^{2+}(aq)+8H_2O(l)$

A volume of 23.24 mL was required to reach the end point. What is the oxalic acid

4.5.2. Gravimetric Analysis

A **gravimetric analysis** is one in which a sample is subjected to some treatment that causes a change in the physical state of the analyte that permits its separation from the other components of the sample. Mass measurements of the sample, the isolated analyte, or some other component of the analysis system, used along with the known stoichiometry of the compounds involved, permit calculation of the analyte concentration. Gravimetric methods were the first techniques used for quantitative chemical analysis, and they remain important tools in the modern chemistry laboratory.

The required change of state in a gravimetric analysis may be achieved by various physical and chemical processes. For example, the moisture (water) content of a sample is routinely determined by measuring the mass of a sample before and after it is subjected to a controlled heating process that evaporates the water. Also common are gravimetric techniques in which the analyte is subjected to a precipitation reaction of the sort described earlier in this chapter. The precipitate is typically isolated from the reaction mixture by filtration, carefully dried, and then weighed (Figure 4.13). The mass of the precipitate may then be used, along with relevant stoichiometric relationships, to calculate analyte concentration.

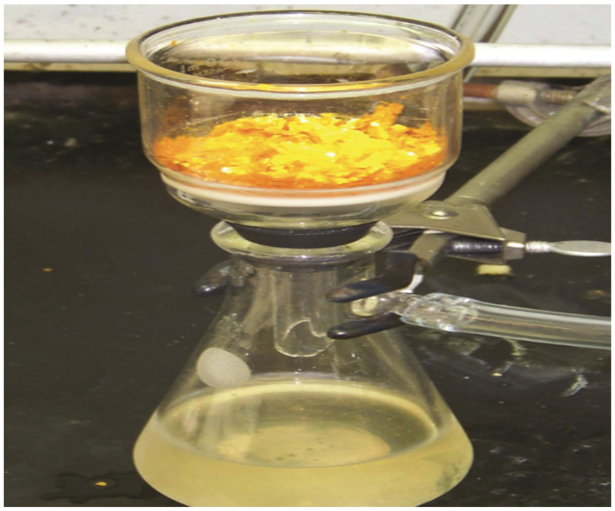


Figure 4.13: Precipitate may be removed from a reaction mixture by filtration.

Example 4.15

Gravimetric Analysis

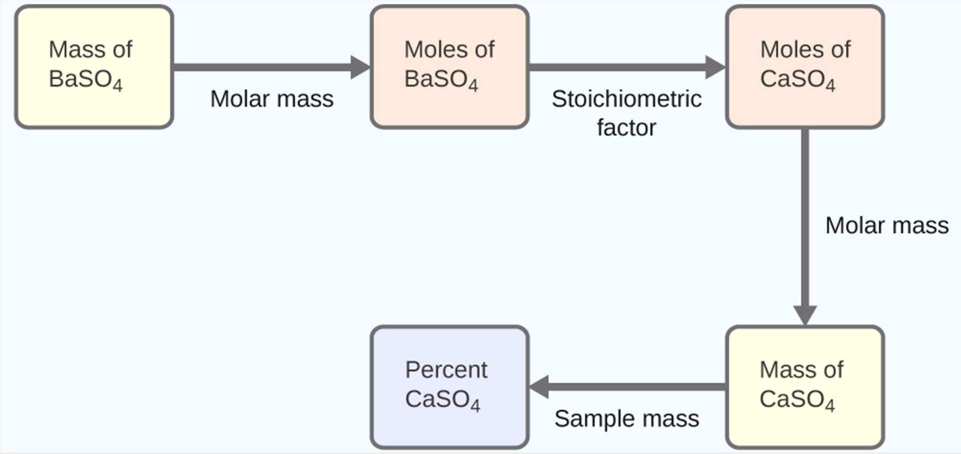
A 0.4550-g solid mixture containing $MgSO_4$ is dissolved in water and treated with an excess of $Ba(NO_3)_2$, resulting in the precipitation of 0.6168 g of $BaSO_4$.

$$MgSO_4(aq) + Ba(NO_3)_2(aq) \longrightarrow BaSO_4(s) + Mg(NO_3)_2(aq)$$

What is the concentration (mass percent) of $MgSO_4$ in the mixture?

Solution

The plan for this calculation is similar to others used in stoichiometric calculations, the central step being the connection between the moles of $BaSO_4$ and $MgSO_4$ through their stoichiometric factor. Once the mass of $MgSO_4$ is computed, it may be used along with the mass of the sample mixture to calculate the requested percentage concentration.



The mass of $MgSO_4$ that would yield the provided precipitate mass is

$0.6168 g\ BaSO_4 \times 1 mol\ BaSO_4 / 233.43 g\ BaSO_4 \times 1 mol\ MgSO_4 / 1 mol\ BaSO_4 \times 120.37 g\ MgSO_4 / 1 mol\ MgSO_4 = 0.3181 g\ MgSO_4$

The concentration of $MgSO_4$ in the sample mixture is then calculated to be

$$\text{Percent } MgSO_4 = \text{mass } MgSO_4 / \text{mass sample} \times 100\%$$

$$0.3181 g / 0.4550 g \times 100\% = 69.91\%$$

✍Check Your Learning

What is the percent of chloride ion in a sample if 1.1324 g of the sample produces 1.0881 g of AgCl when treated with excess Ag^+?

$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$

The elemental composition of hydrocarbons and related compounds may be determined via a gravimetric method known as **combustion analysis**. In a combustion analysis, a weighed sample of the compound is heated to a high temperature under a stream of oxygen gas, resulting in its complete combustion to yield gaseous products of known identities. The complete combustion of hydrocarbons, for example, will yield carbon dioxide and water as the only products. The gaseous combustion products are swept through separate, preweighed collection devices containing compounds that selectively absorb each product (Figure 4.14). The mass increase of each device corresponds to the mass of the absorbed product and may be used in an appropriate stoichiometric calculation to derive the mass of the relevant element.

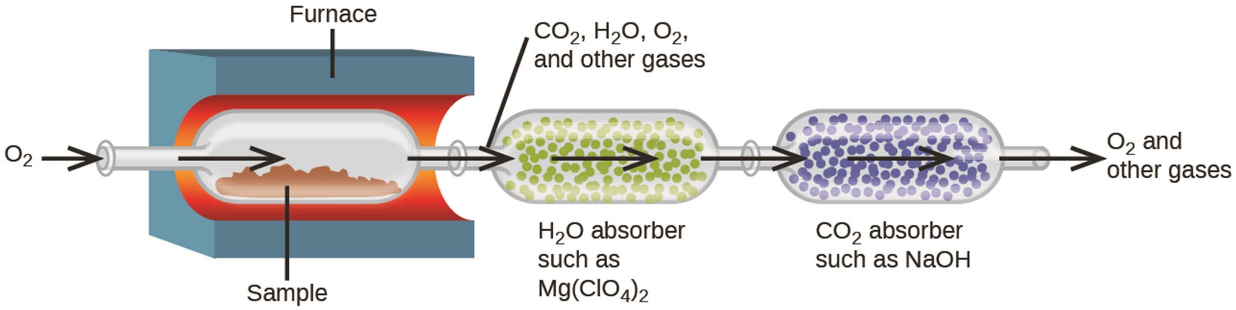


Figure 4.14: This schematic diagram illustrates the basic components of a combustion analysis device for determining the carbon and hydrogen content of a sample.

Example 4.16

Combustion Analysis

Polyethylene is a hydrocarbon polymer used to produce food-storage bags and many other flexible plastic items. A combustion analysis of a 0.00126-g sample of polyethylene yields 0.00394 g of CO_2 and 0.00161 g of H_2O. What is the empirical formula of polyethylene?

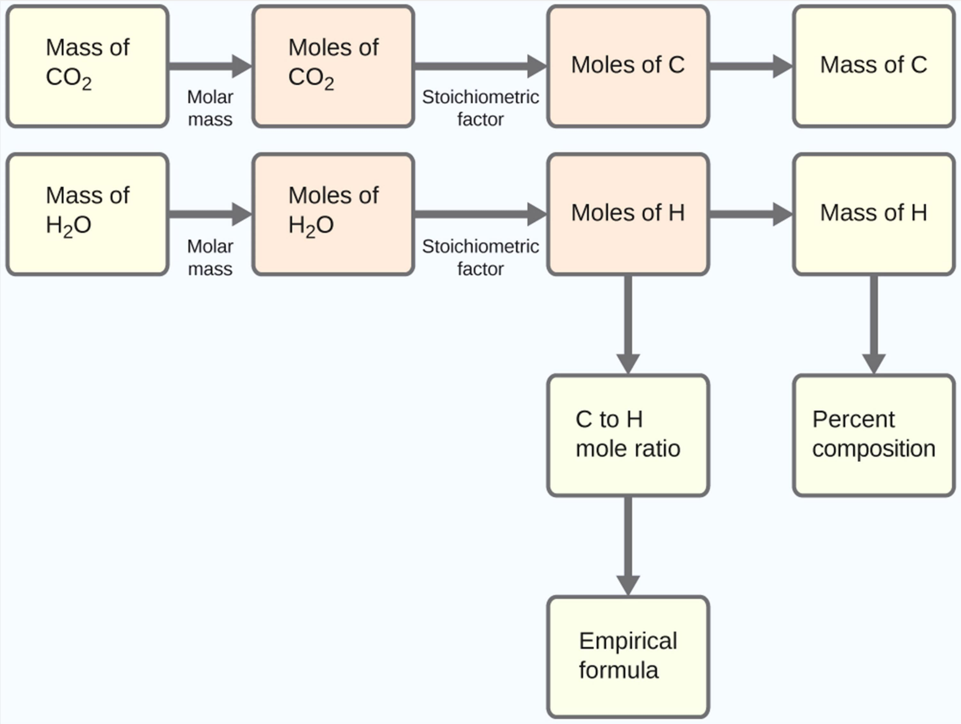
Solution

The primary assumption in this exercise is that all the carbon in the sample combusted is converted to carbon dioxide, and all the hydrogen in the sample is converted to water:

$$C_xH_y(s) + \text{excess } O_2(g) \longrightarrow xCO_2(g) + y2H_2O(g)$$

Note that a balanced equation is not necessary for the task at hand. To derive the empirical formula of the compound, only the subscripts *x* and *y* are needed.

First, calculate the molar amounts of carbon and hydrogen in the sample, using the provided masses of the carbon dioxide and water, respectively. With these molar amounts, the empirical formula for the compound may be written as described in the previous chapter of this text. An outline of this approach is given in the following flow chart:



$$\text{mol C} = 0.00394\text{g } CO_2 \times 1\text{mol } CO_2/44.01\text{ g} \times 1\text{mol C}/1\text{mol } CO_2 = 8.95\times10^{-5}\text{molC}$$

$$\text{mol H} = 0.00161\text{g } H_2O \times 1\text{mol } H_2O/18.02\text{g} \times 2\text{mol H}/1\text{mol } H_2O = 1.79\times10^{-4}\text{molH}$$

The empirical formula for the compound is then derived by identifying the smallest whole-number multiples for these molar amounts. The H-to-C molar ratio is molH / mol C =

1.79×10^{-4}mol H / 8.95×10^{-5}mol C = 2mol H / 1molC and the empirical formula for polyethylene is CH_2.

✍Check Your Learning

A 0.00215-g sample of polystyrene, a polymer composed of carbon and hydrogen, produced 0.00726 g of CO_2 and 0.00148 g of H_2O in a combustion analysis. What is the empirical formula for polystyrene?

Review Exercises

1. Balance the following equations:
   (b) $PCl_5(s) + H_2O(l) \longrightarrow POCl_3(l) + HCl(aq)$
   (c) $Cu(s) + HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + H_2O(l) + NO(g)$
   (d) $H_2(g) + I_2(s) \longrightarrow HI(s)$
   (e) $Fe(s) + O_2(g) \longrightarrow Fe_2O_3(s)$
   (f) $Na(s) + H_2O(l) \longrightarrow NaOH(aq) + H_2(g)$
   (g) $(NH_4)_2Cr_2O_7(s) \longrightarrow Cr_2O_3(s) + N_2(g) + H_2O(g)$
   (h) $P_4(s) + Cl_2(g) \longrightarrow PCl_3(l)$
   (i) $PtCl_4(s) \longrightarrow Pt(s) + Cl_2(g)$
2. Write a balanced molecular equation describing each of the following chemical reactions.
   (a) Solid calcium carbonate is heated and decomposes to solid calcium oxide and carbon dioxide gas.
   (b) Gaseous butane, C_4H_{10}, reacts with diatomic oxygen gas to yield gaseous carbon dioxide and water vapor.
   (c) Aqueous solutions of magnesium chloride and sodium hydroxide react to produce solid magnesium hydroxide and aqueous sodium chloride.
   (d) Water vapor reacts with sodium metal to produce solid sodium hydroxide and hydrogen gas.
3. Colorful fireworks often involve the decomposition of barium nitrate and potassium chlorate and the reaction of the metals magnesium, aluminum, and iron with oxygen.
   (a) Write the formulas of barium nitrate and potassium chlorate.

(b) The decomposition of solid potassium chlorate leads to the formation of solid potassium chloride and diatomic oxygen gas. Write an equation for the reaction.

(c) The decomposition of solid barium nitrate leads to the formation of solid barium oxide, diatomic nitrogen gas, and diatomic oxygen gas. Write an equation for the reaction.

(d) Write separate equations for the reactions of the solid metals magnesium, aluminum, and iron with diatomic oxygen gas to yield the corresponding metal oxides. (Assume the iron oxide contains Fe^{3+} ions.)

4. A novel process for obtaining magnesium from sea water involves several reactions. Write a balanced chemical equation for each step of the process.

   (a) The first step is the decomposition of solid calcium carbonate from seashells to form solid calcium oxide and gaseous carbon dioxide.

   (b) The second step is the formation of solid calcium hydroxide as the only product from the reaction of the solid calcium oxide with liquid water.

   (c) Solid calcium hydroxide is then added to the seawater, reacting with dissolved magnesium chloride to yield solid magnesium hydroxide and aqueous calcium chloride.

   (d) The solid magnesium hydroxide is added to a hydrochloric acid solution, producing dissolved magnesium chloride and liquid water.

   (e) Finally, the magnesium chloride is melted and electrolyzed to yield liquid magnesium metal and diatomic chlorine gas.

5. From the balanced molecular equations, write the complete ionic and net ionic equations for the following:

   (a) $K_2C_2O_4(aq) + Ba(OH)_2(aq) \longrightarrow 2KOH(aq) + BaC_2O_4(s)$

   (b) $Pb(NO_3)_2(aq) + H_2SO_4(aq) \longrightarrow PbSO_4(s) + 2HNO_3(aq)$

   (c) $CaCO_3(s) + H_2SO_4(aq) \longrightarrow CaSO_4(s) + CO_2(g) + H_2O(l)$

6. Use the following equations to answer the next four questions:

   (a) $H_2O(s) \longrightarrow H_2O(l)$

   (b) $Na^+(aq) + Cl^-(aq) + Ag^+(aq) + NO_3^-(aq) \longrightarrow AgCl(s) + Na^+(aq) + NO_3^-(aq)$

   (c) $CH_3OH(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$

   (d) $2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$

   (e) $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$

(f) Which equation describes a physical change?

(g) Which equation identifies the reactants and products of a combustion reaction?

(h) Which equation is not balanced?

(i) Which is a net ionic equation?

7. Silver can be separated from gold because silver dissolves in nitric acid while gold does not. Is the dissolution of silver in nitric acid an acid-base reaction or an oxidation-reduction reaction?
8. Determine the oxidation states of the elements in the compounds listed. None of the oxygen-containing compounds are peroxides or superoxides.

(a) H_2SO_4

(b) $Ca(OH)_2$

(c) BrOH

(d) $ClNO_2$

(e) $TiCl_4$

(f) NaH

9. Classify the following as acid-base reactions or oxidation-reduction reactions:

(a) $Na_2S(aq) + 2HCl(aq) \longrightarrow 2NaCl(aq) + H_2S(g)$

(b) $2Na(s) + 2HCl(aq) \longrightarrow 2NaCl(aq) + H_2(g)$

(c) $Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$

(d) $MgO(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2O(l)$

(e) $K_3P(s) + 2O_2(g) \longrightarrow K_3PO_4(s)$

(f) $3KOH(aq) + H_3PO_4(aq) \longrightarrow K_3PO_4(aq) + 3H_2O(l)$

10. Identify the atoms that are oxidized and reduced, the change in oxidation state for each, and the oxidizing and reducing agents in each of the following equations:

(a) $Mg(s) + NiCl_2(aq) \longrightarrow MgCl_2(aq) + Ni(s)$

(b) $PCl_3(l) + Cl_2(g) \longrightarrow PCl_5(s)$

(c) $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(g)$

(d) $Zn(s) + H_2SO_4(aq) \longrightarrow ZnSO_4(aq) + H_2(g)$

(e) $2K_2S_2O_3(s) + I_2(s) \longrightarrow K_2S_4O_6(s) + 2KI(s)$

(f) $3Cu(s) + 8HNO_3(aq) \longrightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$

11. Complete and balance the following acid-base equations:

(a) HCl gas reacts with solid $Ca(OH)_2(s)$.

(b) A solution of $Sr(OH)_2$ is added to a solution of HNO_3.

12. Complete and balance the following oxidation-reduction reactions, which give the highest possible oxidation state for the oxidized atoms.

(a) $K(s) + H_2O(l) \longrightarrow$

(b) $Ba(s) + HBr(aq) \longrightarrow$

(c) $Sn(s) + I_2(s) \longrightarrow$

13. When heated to 700–800 °C, diamonds, which are pure carbon, are oxidized by atmospheric oxygen. (They burn!) Write the balanced equation for this reaction.
14. The military has experimented with lasers that produce very intense light when fluorine combines explosively with hydrogen. What is the balanced equation for this reaction?
15. Write the molecular, total ionic, and net ionic equations for the following reactions:
    (a) $Ca(OH)_2(aq) + HC_2H_3O_2(aq) \longrightarrow$
    (b) $H_3PO_4(aq) + CaCl_2(aq) \longrightarrow$
16. In a common experiment in the general chemistry laboratory, magnesium metal is heated in air to produce MgO. MgO is a white solid, but in these experiments it often looks gray, due to small amounts of Mg_3N_2, a compound formed as some of the magnesium reacts with nitrogen. Write a balanced equation for each reaction.
17. Lithium hydroxide may be used to absorb carbon dioxide in enclosed environments, such as manned spacecraft and submarines. Write an equation for the reaction that involves 2 mol of LiOH per 1 mol of CO_2. (Hint: Water is one of the products.)
18. Calcium propionate is sometimes added to bread to retard spoilage. This compound can be prepared by the reaction of calcium carbonate, $CaCO_3$, with propionic acid, $C_2H_5CO_2H$, which has properties similar to those of acetic acid. Write the balanced equation for the formation of calcium propionate.
19. Copper(II) sulfide is oxidized by molecular oxygen to produce gaseous sulfur trioxide and solid copper(II) oxide. The gaseous product then reacts with liquid water to produce liquid hydrogen sulfate as the only product. Write the two equations which represent these reactions.
20. Write the balanced equation, then outline the steps necessary to determine the information requested in each of the following:
    (a) The number of moles and the mass of Mg required to react with 5.00 g of HCl and produce $MgCl_2$ and H_2.
    (b) The number of moles and the mass of oxygen formed by the decomposition of 1.252 g of silver (I) oxide.
    (c) The number of moles and the mass of magnesium carbonate, $MgCO_3$, required to produce 283 g of carbon dioxide. (MgO is the other product.)

(d) The number of moles and the mass of water formed by the combustion of 20.0 kg of acetylene, C_2H_2, in an excess of oxygen.

(e) The number of moles and the mass of barium peroxide, BaO_2, needed to produce 2.500 kg of barium oxide, BaO (O_2 is the other product.)

21. I_2 is produced by the reaction of 0.4235 mol of $CuCl_2$ according to the following equation: $2CuCl_2 + 4KI \longrightarrow 2CuI + 4KCl + I_2$.

(a) How many molecules of I_2 are produced?

(b) What mass of I_2 is produced?

22. Silver is often extracted from ores such as $K[Ag(CN)_2]$ and then recovered by the reaction: $2K[Ag(CN)_2](aq) + Zn(s) \longrightarrow 2Ag(s) + Zn(CN)_2(aq) + 2KCN(aq)$

(a) How many molecules of $Zn(CN)_2$ are produced by the reaction of 35.27 g of $K[Ag(CN)_2]$?

(b) What mass of $Zn(CN)_2$ is produced?

23. What mass of silver oxide, Ag_2O, is required to produce 25.0 g of silver sulfadiazine, $AgC_{10}H_9N_4SO_2$, from the reaction of silver oxide and sulfadiazine?

$$2C_{10}H_{10}N_4SO_2 + Ag_2O \longrightarrow 2AgC_{10}H_9N_4SO_2 + H_2O$$

24. Automotive air bags inflate when a sample of sodium azide, NaN_3, is very rapidly decomposed.

$$2NaN_3(s) \longrightarrow 2Na(s) + 3N_2(g)$$

What mass of sodium azide is required to produce 2.6 ft^3 (73.6 L) of nitrogen gas with a density of 1.25 g/L?

25. Urea, $CO(NH_2)_2$, is manufactured on a large scale for use in producing urea-formaldehyde plastics and as a fertilizer. What is the maximum mass of urea that can be manufactured from the CO_2 produced by combustion of 1.00×10^3kg of carbon followed by the reaction?

$$CO_2(g) + 2NH_3(g) \longrightarrow CO(NH_2)_2(s) + H_2O(l)$$

26. In an accident, a solution containing 2.5 kg of nitric acid was spilled. Two kilograms of Na_2CO_3 was quickly spread on the area and CO_2 was released by the reaction. Was sufficient Na_2CO_3 used to neutralize all of the acid?

27. What volume of 0.750 M hydrochloric acid solution can be prepared from the HCl produced by the reaction of 25.0 g of NaCl with excess sulfuric acid?

$$NaCl(s) + H_2SO_4(l) \longrightarrow HCl(g) + NaHSO_4(s)$$

28. What volume of a 0.2089 *M* KI solution contains enough KI to react exactly with the $Cu(NO_3)_2$ in 43.88 mL of a 0.3842 *M* solution of $Cu(NO_3)_2$?

$$2Cu(NO_3)_2+4KI\longrightarrow 2CuI+I_2+4KNO_3$$

29. What mass of $Ca(OH)_2$ is required to react with the acetic acid in 25.0 mL of a solution having a density of 1.065 g/mL and containing 58.0% acetic acid by mass?

30. The toxic pigment called white lead, $Pb_3(OH)_2(CO_3)_2$, has been replaced in white paints by rutile, TiO_2. How much rutile (g) can be prepared from 379 g of an ore that contains 88.3% ilmenite ($FeTiO_3$) by mass?

$$2FeTiO_3 + 4HCl + Cl_2 \longrightarrow 2FeCl_3 + 2TiO_2 + 2H_2O$$

31. The following quantities are placed in a container: 1.5×10^{24} atoms of hydrogen, 1.0 mol of sulfur, and 88.0 g of diatomic oxygen.
    (a) What is the total mass in grams for the collection of all three elements?
    (b) What is the total number of moles of atoms for the three elements?
    (c) If the mixture of the three elements formed a compound with molecules that contain two hydrogen atoms, one sulfur atom, and four oxygen atoms, which substance is consumed first?
    (d) How many atoms of each remaining element would remain unreacted in the change described in (c)?

32. What is the limiting reactant in a reaction that produces sodium chloride from 8 g of sodium and 8 g of diatomic chlorine?

33. A student isolated 25 g of a compound following a procedure that would theoretically yield 81 g. What was his percent yield?

34. A sample of 0.53 g of carbon dioxide was obtained by heating 1.31 g of calcium carbonate. What is the percent yield for this reaction?

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(s)$$

35. Freon-12, CCl_2F_2, is prepared from CCl_4 by reaction with HF. The other product of this reaction is HCl. Outline the steps needed to determine the percent yield of a reaction that produces 12.5 g of CCl_2F_2 from 32.9 g of CCl_4. Freon-12 has been banned and is no longer used as a refrigerant because it catalyzes the decomposition of ozone and has a very long lifetime in the atmosphere. Determine the percent yield.

36. Citric acid, $C_6H_8O_7$, a component of jams, jellies, and fruity soft drinks, is prepared industrially via fermentation of sucrose by the mold *Aspergillus niger*. The equation representing this reaction is

$$\mathbf{C_{12}H_{22}O_{11} + H_2O + 3O_2 \longrightarrow 2C_6H_8O_7 + 4H_2O}$$

37. What mass of citric acid is produced from exactly 1 metric ton (1.000×10^3 kg) of sucrose if the yield is 92.30%?

38. Toluene, $C_6H_5CH_3$, is oxidized by air under carefully controlled conditions to benzoic acid, $C_6H_5CO_2H$, which is used to prepare the food preservative sodium benzoate, $C_6H_5CO_2Na$. What is the percent yield of a reaction that converts 1.000 kg of toluene to 1.21 kg of benzoic acid?

$$\mathbf{2C_6H_5CH_3 + 3O_2 \longrightarrow 2C_6H_5CO_2H + 2H_2O}$$

39. Outline the steps needed to determine the limiting reactant when 30.0 g of propane, C_3H_8, is burned with 75.0 g of oxygen. Determine the limiting reactant.

40. The phosphorus pentoxide used to produce phosphoric acid for cola soft drinks is prepared by burning phosphorus in oxygen.
    (a) What is the limiting reactant when 0.200 mol of P_4 and 0.200 mol of O_2 react according to $P_4 + 5O_2 \longrightarrow P_4O_{10}$
    (b) Calculate the percent yield if 10.0 g of P_4O_{10} is isolated from the reaction.

41. What volume of 0.0105-M HBr solution is required to titrate 125 mL of a 0.0100 M $Ca(OH)_2$ solution?

$$Ca(OH)_2(aq) + 2HBr(aq) \longrightarrow CaBr_2(aq) + 2H_2O(l)$$

42. Potatoes can be peeled commercially by soaking them in a 3-M to 6-M solution of sodium hydroxide, then removing the loosened skins by spraying them with water. Does a sodium hydroxide solution have a suitable concentration if titration of 12.00 mL of the solution requires 30.6 mL of 1.65 M HCI to reach the end point?

43. The principal component of mothballs is naphthalene, a compound with a molecular mass of about 130 amu, containing only carbon and hydrogen. A 3.000-mg sample of naphthalene burns to give 10.3 mg of CO_2. Determine its empirical and molecular formulas.

44. A 0.025-g sample of a compound composed of boron and hydrogen, with a molecular mass of ~28 amu, burns spontaneously when exposed to air, producing 0.063 g of B_2O_3. What are the empirical and molecular formulas of the compound?

45. What volume of 0.08892 *M* HNO_3 is required to react completely with 0.2352 g of potassium hydrogen phosphate?

$$2HNO_3(aq) + K_2HPO_4(aq) \longrightarrow H_2PO_4(aq) + 2KNO_3(aq)$$

46. What mass of $Ca(OH)_2$ will react with 25.0 g of butanoic to form the preservative calcium butanoate according to the equation?

CHAPTER FIVE

Electronic Structure and Periodic Properties of Elements

Introduction

In 1054, Chinese astronomers recorded the appearance of a “guest star” in the sky, visible even during the day, which then disappeared slowly over the next two years. The sudden appearance was due to a supernova explosion, which was much brighter than the original star. Even though this supernova was observed almost a millennium ago, the remaining Crab Nebula continues to release energy today. It emits not only visible light but also infrared light, X-rays, and other forms of electromagnetic radiation. The nebula emits both continuous spectra (the blue-white glow) and atomic emission spectra (the colored filaments). In this chapter, we will discuss light and other forms of electromagnetic radiation and how they are related to the electronic structure of atoms and the periodic properties of the elements.

Learning Objectives of the Chapter: At the end of this chapter you will be able to

- Explain the wave and particle nature of light
- Describe the Bohr model of the hydrogen atom
- Extend the concept of wave–particle duality that was observed in electromagnetic radiation to matter as well
- List and differentiate the four quantum numbers that form the basis for completely specifying the state of an electron in an atom
- Relate electron configurations to element classifications in the periodic table
- Describe and explain the observed trends in atomic size, ionization energy, and electron affinity of the elements

5.1. Electromagnetic energy

The nature of light has been a subject of inquiry since antiquity. In the seventeenth century, Isaac Newton performed experiments with lenses and prisms and was able to demonstrate that white light consists of the individual colors of the rainbow combined together. Newton explained his optics findings in terms of a "corpuscular" view of light, in which light was composed of streams of extremely tiny particles travelling at high speeds according to Newton's laws of motion.

Others in the seventeenth century, such as Christiaan Huygens, had shown that optical phenomena such as reflection and refraction could be equally well explained in terms of light as waves travelling at high speed through a medium called "luminiferous aether" that was thought to permeate all space. Early in the nineteenth century, Thomas Young demonstrated that light passing through narrow, closely spaced slits produced interference patterns that could not be explained in terms of Newtonian particles but could be easily explained in terms of waves. Later in the nineteenth century, after James Clerk Maxwell developed his theory of **electromagnetic radiation** and showed that light was the visible part of a vast spectrum of electromagnetic waves, the particle view of light became thoroughly discredited. By the end of the nineteenth century, scientists viewed the physical universe as roughly comprising two separate domains: matter composed of particles moving according to Newton's laws of motion, and electromagnetic radiation consisting of waves governed by Maxwell's equations. Today, these domains are referred to as classical mechanics and classical electrodynamics (or classical electromagnetism). Although there were a few physical phenomena that could not be explained within this framework, scientists at that time were so confident of the overall soundness of this framework that they viewed these aberrations as puzzling paradoxes that would ultimately be resolved somehow within this framework. As we shall see, these paradoxes led to a contemporary framework that intimately connects particles and waves at a fundamental level called wave-particle duality, which has superseded the classical view.

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

5.1.1. Characteristics of Light

Waves

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

Waves need not be restricted to travel through matter. As Maxwell showed, electromagnetic waves consist of an electric field oscillating in step with a perpendicular magnetic field, both of which are perpendicular to the direction of travel. These waves can travel through a vacuum at a constant speed of 2.998×10^8 m/s, the speed of light (denoted by c).

All waves, including forms of **electromagnetic radiation**, are characterized by, a wavelength (denoted by λ, the lowercase Greek letter lambda), a frequency (denoted by ν, the lowercase Greek letter nu), and an amplitude. As can be seen in Figure 5.1, the **wavelength** is the distance between two consecutive peaks or troughs in a wave (measured in meters in the SI system). Electromagnetic waves have wavelengths that fall within an enormous range-wavelengths of kilometers (10^3 m) to picometers (10^{-12} m) have been observed. The **frequency** is the number of wave cycles that pass a specified point in space in a specified amount of time (in the SI system, this is measured in seconds). A cycle corresponds to one complete wavelength. The unit for frequency, expressed as cycles per second [s^{-1}], is the hertz (Hz). Common multiples of this unit are megahertz, ($1 \text{ MHz} = 1 \times 10^6 \text{ Hz}$) and gigahertz ($1 \text{ GHz} = 1 \times 10^9 \text{ Hz}$). The **amplitude** corresponds to the magnitude of the wave's displacement and so, in Figure 5.1, this corresponds to one-half the height between the peaks and troughs. The amplitude is related to the intensity of the wave, which for light is the brightness, and for sound is the loudness.

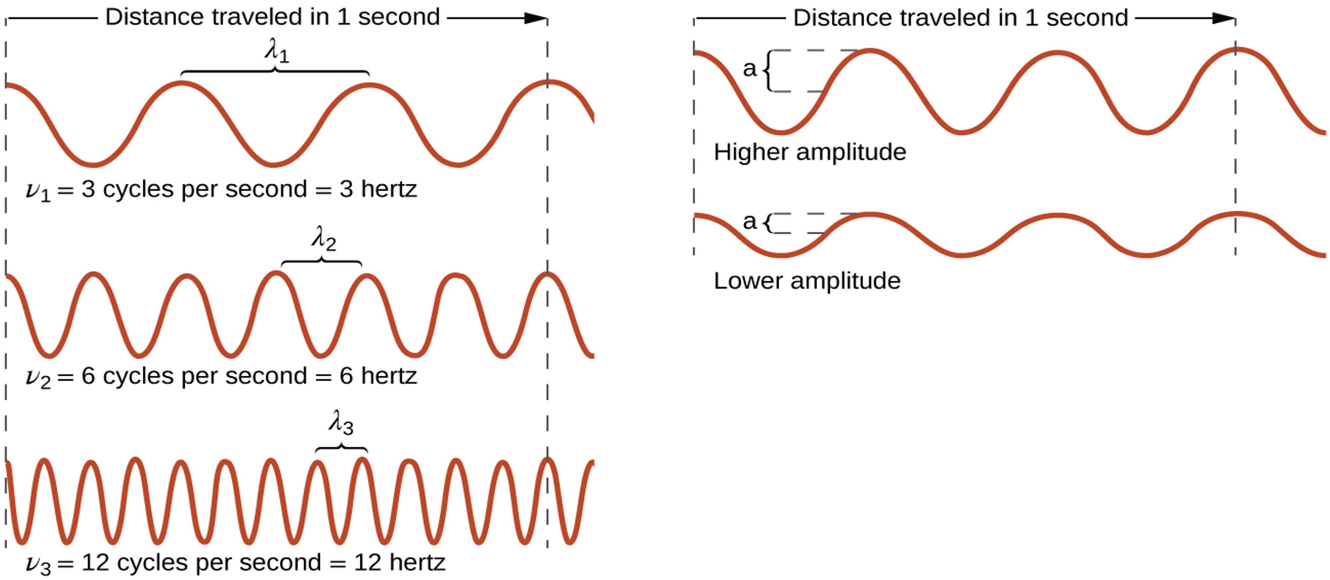


Figure 5.1: One-dimensional sinusoidal waves show the relationship among wavelength, frequency, and speed. The wave with the shortest wavelength has the highest frequency. Amplitude is one-half the height of the wave from peak to trough.

The product of a wave's wavelength (λ) and its frequency (ν), $\lambda\nu$, is the speed of the wave. Thus, for electromagnetic radiation in a vacuum, speed is equal to the fundamental constant, *c*:

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

Wavelength and frequency are inversely proportional: As the wavelength increases, the frequency decreases. The inverse proportionality is illustrated in Figure 5.2. This figure also shows the electromagnetic spectrum, the range of all types of electromagnetic radiation. Each of the various colors of visible light has specific frequencies and wavelengths associated with them, and you can see that visible light makes up only a small portion of the electromagnetic spectrum. Because the technologies developed to work in various parts of the electromagnetic spectrum are different, for reasons of convenience and historical legacies, different units are typically used for different parts of the spectrum. For example, radio waves are usually specified as frequencies (typically in units of MHz), while the visible region is usually specified in wavelengths (typically in units of nm or angstroms).

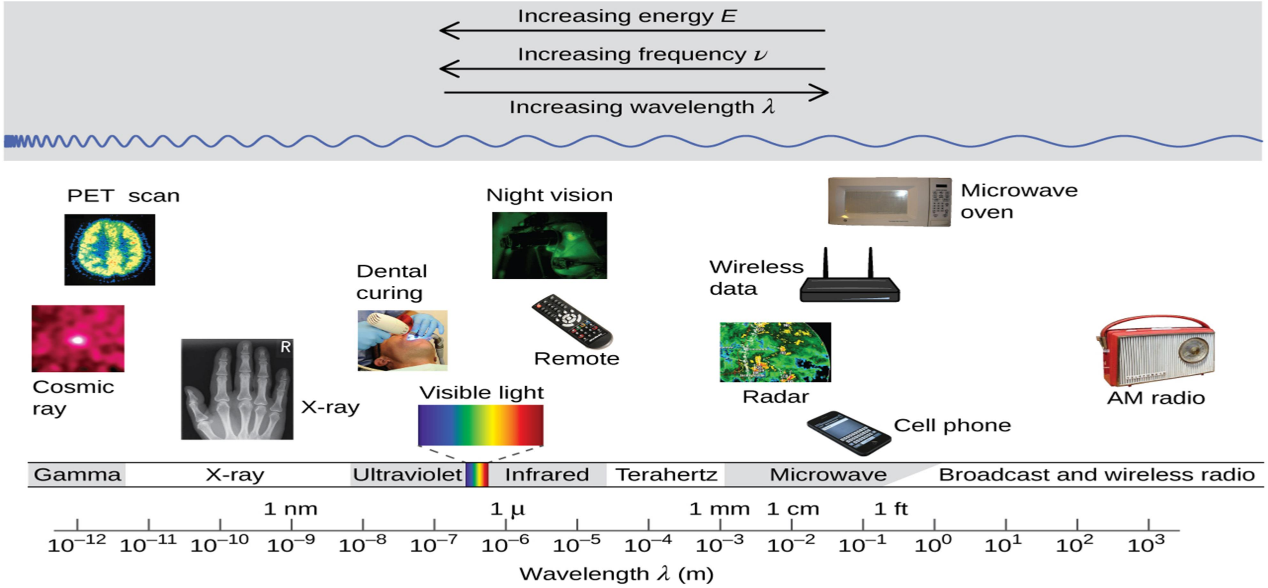


Figure 5.2: Portions of the electromagnetic spectrum are shown in order of decreasing frequency and increasing wavelength.

Example 5.1

Determining the Frequency and Wavelength of Radiation

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

Solution

We can rearrange the equation $c = \lambda v$ to solve for the frequency:

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

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

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

✍ Check Your Learning

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

5.1.2. Quantization and Photons

The Photoelectric Effect

The next paradox in the classical theory to be resolved concerned the photoelectric effect (Figure 5.3). It had been observed that electrons could be ejected from the clean surface of a metal when light having a frequency greater than some threshold frequency was shone on it. Surprisingly, the kinetic energy of the ejected electrons did not depend on the brightness of the light, but increased with increasing frequency of the light. Since the electrons in the metal had a certain amount of binding energy keeping them there, the incident light needed to have more energy to free the electrons. According to classical wave theory, a wave's energy depends on its intensity (which depends on its amplitude), not its frequency. One part of these observations was that the number of electrons ejected within in a given time period was seen to increase as the brightness increased. In 1905, Albert Einstein was able to resolve the paradox by incorporating Planck's quantization findings into the discredited particle view of light (Einstein actually won his Nobel Prize for this work, and not for his theories of relativity for which he is most famous).

Einstein argued that the quantized energies that Planck had postulated in his treatment of blackbody radiation could be applied to the light in the photoelectric effect so that the light striking the metal surface should not be viewed as a wave, but instead as a stream of particles (later called photons) whose energy depended on their frequency, according to Planck's formula, $\mathrm{E} = \mathrm{h}\nu$ (or, in terms of wavelength using$\mathrm{c} = \nu\lambda, \mathrm{E} = \frac{\mathrm{hc}}{\lambda}$). Electrons were ejected when hit by photons having sufficient energy (a frequency greater than the threshold). The greater the frequency, the greater the kinetic energy imparted to the escaping electrons by the collisions. Einstein also argued that the light intensity did not depend on the amplitude of the incoming wave, but instead corresponded to the number of photons striking the surface within a given time period. This explains why the number of ejected electrons increased with increasing brightness, since the greater the number of incoming photons, the greater the likelihood that they would collide with some of the electrons.

With Einstein's findings, the nature of light took on a new air of mystery. Although many light phenomena could be explained either in terms of waves or particles, certain phenomena, such as the interference patterns obtained when light passed through a double slit, were completely contrary to a particle view of light, while other phenomena, such as the photoelectric effect, were completely contrary to a wave view of light. Somehow, at a deep fundamental level still not fully understood, light is both wavelike and particle-like. This is known as **wave-particle duality.**

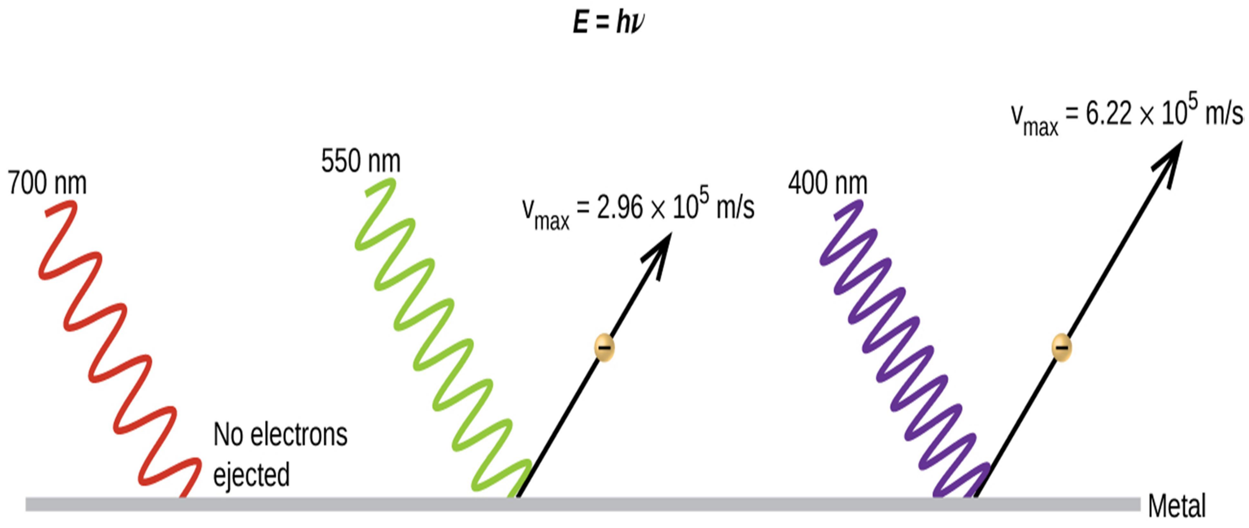


Figure 5.3: Photons with low frequencies do not have enough energy to cause electrons to be ejected via the photoelectric effect. For any frequency of light above the threshold frequency, the kinetic energy of an ejected electron will increase linearly with the energy of the incoming photon.

Example 5.2

Calculating the Energy of Radiation

When we see light from a neon sign, we are observing radiation from excited neon atoms. If this radiation has a wavelength of 640 nm, what is the energy of the photon being emitted?

Solution

We use the part of Planck's equation that includes the wavelength, *λ*, and convert units of nanometers to meters so that the units of *λ* and *c* are the same.

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

$$E = \frac{(6.626 \times 10^{-34} J\cancel{s})(2.998 \times 10^{8} m\cancel{s}^{-1})}{(640\cancel{nm})\left(\frac{1\,m}{109\cancel{nm}}\right)} = E = 3.10 \times 10^{-19} J$$

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The microwaves in an oven are of a specific frequency that will heat the water molecules contained in food. (This is why most plastics and glass do not become hot in a microwave oven-they do not contain water molecules.) This frequency is about 3×10^9 Hz. What is the energy of one photon in these microwaves?

5.2. The Bohr Model

Following the work of Ernest Rutherford and his colleagues in the early twentieth century, the picture of atoms consisting of tiny dense nuclei surrounded by lighter and even tinier electrons continually moving about the nucleus was well established. This picture was called the planetary model, since it pictured the atom as a miniature "solar system" with the electrons orbiting the nucleus like planets orbiting the sun. The simplest atom is hydrogen, consisting of a single proton as the nucleus about which a single electron moves. The electrostatic force attracting the electron to the proton depends only on the distance between the two particles. This classical mechanics description of the atom is incomplete, however, since an electron moving in an elliptical orbit would be accelerating (by changing direction) and, according to classical electromagnetism, it should continuously emit electromagnetic radiation. This loss in orbital energy should result in the electron's orbit getting continually smaller until it spirals into the nucleus, implying that atoms are inherently unstable.

In 1913, Niels Bohr attempted to resolve the atomic paradox by ignoring classical electromagnetism's prediction that the orbiting electron in hydrogen would continuously emit light. Instead, he incorporated into the classical mechanics description of the atom Planck's ideas of quantization and Einstein's finding that light consists of photons whose energy is proportional to their frequency. Bohr assumed that the electron orbiting the nucleus would not normally emit any radiation (the stationary state hypothesis), but it would emit or absorb a photon if it moved to a different orbit. The energy absorbed or emitted would reflect differences in the orbital energies according to this equation:

$$|\Delta E| = | E_f - E_i | = h\nu = \frac{hc}{\lambda}$$

In this equation, h is Planck's constant and E_i and E_f are the initial and final orbital energies, respectively. The absolute value of the energy difference is used, since frequencies and wavelengths are always positive. Instead of allowing for continuous values of energy, Bohr assumed the energies of these electron orbitals were quantized:

$$E_n = -\frac{k}{n^2}, n = 1,2,3,\ldots$$

In this expression, k is a constant comprising fundamental constants such as the electron mass and charge and Planck's constant. Inserting the expression for the orbit energies into the equation for ΔE gives

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

or

$$\frac{1}{\lambda} = \frac{k}{hc}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Which is identical to the Rydberg equation in which $\infty = \frac{k}{hc}$. When Bohr calculated his theoretical value for the Rydberg constant, R_∞, and compared it with the experimentally accepted value, he got excellent agreement. Since the Rydberg constant was one of the most precisely measured constants at that time, this level of agreement was astonishing and meant that Bohr's model was taken seriously, despite the many assumptions that Bohr needed to derive it.

The lowest few energy levels are shown in Figure 5.4. One of the fundamental laws of physics is that matter is most stable with the lowest possible energy. Thus, the electron in a hydrogen atom usually moves in the $n = 1$ orbit, the orbit in which it has the lowest energy. When the electron is in this lowest energy orbit, the atom is said to be in its ground electronic state (or simply ground state). If the atom receives energy from an outside source, it is possible for the electron to move to an orbit with a higher n value and the atom is now in an excited electronic state (or simply an excited state) with a higher energy. When an electron transitions from an excited state (higher energy orbit) to a less excited state, or ground state, the difference in energy is emitted as a photon. Similarly, if a photon is absorbed by an atom, the energy of the photon moves an electron from a lower energy orbit up to a more excited one. We can relate the energy of electrons in atoms to what we learned previously about energy. The law of conservation of energy says that we can neither create nor destroy energy. Thus, if a certain amount of external energy is required to excite an electron from one energy level to another, that same amount of energy will be liberated when the electron returns to its initial state (Figure 5.5.).

Since Bohr's model involved only a single electron, it could also be applied to the single electron ions He^{+}, Li^{2+}, Be^{3+}, and so forth, which differ from hydrogen only in their nuclear charges, and so one-electron atoms and ions are collectively referred to as hydrogen-like atoms. The energy expression for hydrogen-like atoms is a generalization of the hydrogen atom energy, in which Z is the nuclear charge (+1 for hydrogen, +2 for He, +3 for Li, and so on) and k has a value of 2.179×10^{-18} J.

$$En = -\frac{kZ^2}{n^2}$$

The sizes of the circular orbits for hydrogen-like atoms are given in terms of their radii by the following expression, in which $\alpha 0$ a constant is called the Bohr radius, with a value of 5.292×10^{-11} m:

$$r = \frac{n^2}{Z} a_0$$

The equation also shows us that as the electron's energy increases (as n increases), the electron is found at greater distances from the nucleus. This is implied by the inverse dependence of electrostatic attraction on distance, since, as the electron moves away from the nucleus, the electrostatic attraction between it and the nucleus decreases and it is held less tightly in the atom. Note that as n gets larger and the orbits get larger, their energies get closer to zero, and so the limits $n \longrightarrow \infty$ and $r \longrightarrow \infty$ imply that $E = 0$ corresponds to the ionization limit where the electron is completely removed from the nucleus. Thus, for hydrogen in the ground state $n = 1$, the ionization energy would be:

$$\Delta E = E_{n \rightarrow \infty} - E_1 = 0 + k = k$$

With three extremely puzzling paradoxes now solved (blackbody radiation, the photoelectric effect, and the hydrogen atom), and all involving Planck's constant in a fundamental manner, it became clear to most physicists at that time that the classical theories that worked so well in the macroscopic world were fundamentally flawed and could not be extended down into the microscopic domain of atoms and molecules. Unfortunately, despite Bohr's remarkable achievement in deriving a theoretical expression for the Rydberg constant, he was unable to extend his theory to the next simplest atom, He, which only has two electrons. Bohr's model was severely flawed, since it was still based on the classical mechanics notion of precise orbits, a concept that was later found to be untenable in the microscopic domain, when a proper model of quantum mechanics was developed to supersede classical mechanics.

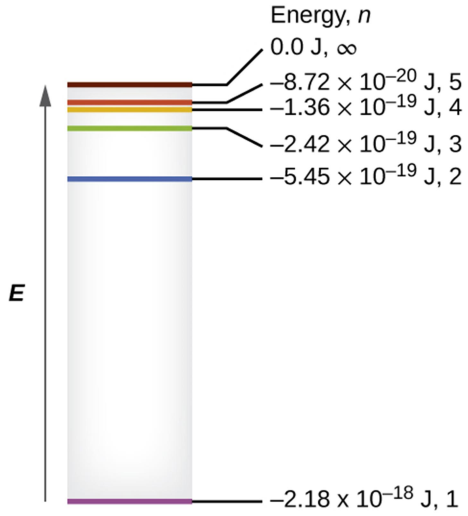


Figure 5.4: Quantum numbers and energy levels in a hydrogen atom. The more negative the calculated value, the lower the energy.

✍ **Check Your Learning**

The electron in figure 5.5 is promoted even further to an orbit with $n = 6$. What is its new energy?

Example 5.3

Calculating the Energy of an Electron in a Bohr Orbit

Early researchers were very excited when they were able to predict the energy of an electron at a particular distance from the nucleus in a hydrogen atom. If a spark promotes the electron in a hydrogen atom into an orbit with $n = 3$, what is the calculated energy, in joules, of the electron?

Solution

The energy of the electron is given by this equation:

$$E = -\frac{kZ^2}{n^2}$$

The atomic number, Z, of hydrogen is 1; $k = 2.179 \times 10^{-18}$ J; and the electron is characterized by an n value of 3. Thus,

$$E = -\frac{(2.179 \times 10^{-18} J) \times (1)^2}{(3)^2} = -2.421 \times 10^{-19} J$$

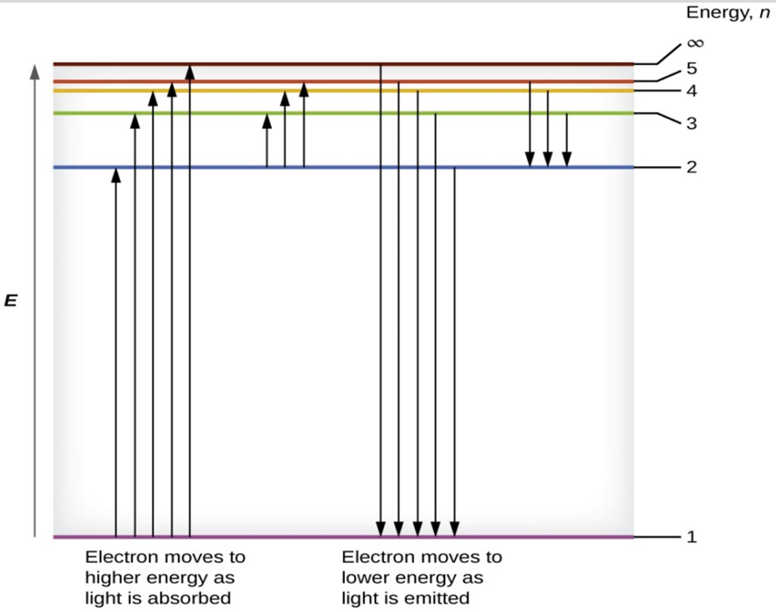


Figure 5.5: The horizontal lines show the relative energy of orbits in the Bohr model of the hydrogen atom, and the vertical arrows depict the energy of photons absorbed (left) or emitted (right) as electrons move between these orbits.

Example 5.4

Calculating the Energy and Wavelength of Electron Transitions in a one electron (Bohr) System

What is the energy (in joules) and the wavelength (in meters) of the line in the spectrum of hydrogen that represents the movement of an electron from Bohr orbit with $n = 4$ to the orbit with $n = 6$? In what part of the electromagnetic spectrum do we find this radiation?

Solution

In this case, the electron starts out with $n = 4$, so $n_1 = 4$. It comes to rest in the $n = 6$ orbit, so $n_2 = 6$. The difference in energy between the two states is given by this expression:

$$\Delta E = E1 - E2 = 2.179 \times 10^{-18} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\Delta E = 2.179 \times 10^{-18} \left(\frac{1}{4^{2}} - \frac{1}{6^{2}} \right) J$$

$$\Delta E = 2.179 \times 10^{-18} \left(\frac{1}{16} - \frac{1}{36} \right) J$$

$$\Delta E = 7.566 \times 10^{-2}\ J$$

This energy difference is positive, indicating a photon enters the system (is absorbed) to excite the electron from the *n* = 4 orbit up to the *n* = 6 orbit. The wavelength of a photon with this energy is found by the expression $E = \frac{hc}{\lambda}$. Rearrangement gives:

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

$$= \frac{(6.626x10^{-34} JS)x2.998x10^{8} m/s}{7.566x10^{-20} J} = 2.626x10^{-6} m$$

From the illustration of the electromagnetic spectrum in Electromagnetic Energy, we can see that this wavelength is found in the infrared portion of the electromagnetic spectrum.

✍**Check Your Learning**

What is the energy in joules and the wavelength in meters of the photon produced when an electron falls from the *n* = 5 to the *n* = 3 level in a He^{+} ion (*Z* = 2 for He^{+})?

Bohr's model of the hydrogen atom provides insight into the behavior of matter at the microscopic level, but it is does not account for electron–electron interactions in atoms with more than one electron. It does introduce several important features of all models used to describe the distribution of electrons in an atom. These features include the following:

- The energies of electrons (energy levels) in an atom are quantized, described by quantum numbers: integer numbers having only specific allowed value and used to characterize the arrangement of electrons in an atom.
- An electron's energy increases with increasing distance from the nucleus.
- The discrete energies (lines) in the spectra of the elements result from quantized electronic energies.

Of these features, the most important is the postulate of quantized energy levels for an electron in an atom. As a consequence, the model laid the foundation for the quantum mechanical model of the atom. Bohr won a Nobel Prize in Physics for his contributions to our understanding of the structure of atoms and how that is related to line spectra emissions.

5.3. Development of Quantum Theory

5.3.1. The Quantum–Mechanical Model of an Atom

Shortly after de Broglie published his ideas that the electron in a hydrogen atom could be better thought of as being a circular standing wave instead of a particle moving in quantized circular orbits, Erwin Schrödinger extended de Broglie's work by deriving what is today known as the Schrödinger equation. When Schrödinger applied his equation to hydrogen-like atoms, he was able to reproduce Bohr's expression for the energy and, thus, the Rydberg formula governing hydrogen spectra. Schrödinger described electrons as three-dimensional stationary waves, or wave functions, represented by the Greek letter psi, ψ. A few years later, Max Born proposed an interpretation of the wave function ψ that is still accepted today: Electrons are still particles, and so the waves represented by ψ are not physical waves but, instead, are complex probability amplitudes. The square of the magnitude of a wave function $|\psi|^2$ describes the probability of the quantum particle being present near a certain location in space. This means that wave functions can be used to determine the distribution of the electron's density with respect to the nucleus in an atom. In the most general form, the Schrödinger equation can be written as:

$$\widehat{H}\psi = E\psi$$

$\widehat{H}$ is the Hamiltonian operator, a set of mathematical operations representing the total energy of the quantum particle (such as an electron in an atom), ψ is the wave function of this particle that can be used to find the special distribution of the probability of finding the particle, and E is the actual value of the total energy of the particle.

Schrödinger's work, as well as that of Heisenberg and many other scientists following in their footsteps, is generally referred to as quantum mechanics.

5.3.2. 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 $n = 1, 2, 3, \ldots$. Generally speaking, the energy of an electron in an atom is greater for greater values of n. This number, n, is referred to as the principal quantum number. The principal quantum number defines the location of the energy level. It is essentially the same concept as the n in the Bohr atom description. Another name for the principal quantum number is the shell number. The shells of an atom can be thought of concentric circles radiating out from the nucleus. The electrons that belong to a specific shell are most likely to be found within the corresponding circular area. The further we precede from the nucleus, the higher the shell number, and so the higher the energy level (Figure 5.6). The positively charged protons in the nucleus stabilize the electronic orbitals by electrostatic attraction between the positive charges of the protons and the negative charges of the electrons. So the further away the electron is from the nucleus, the greater the energy it has.

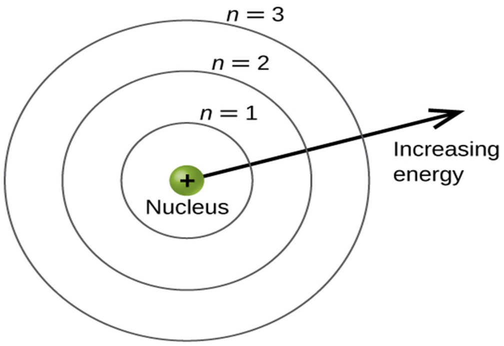


Figure 5.6: Different shells are numbered by principal quantum numbers.

This quantum mechanical model for where electrons reside in an atom can be used to look at electronic transitions, the events when an electron moves from one energy level to another. If the transition is to a higher energy level, energy is absorbed, and the energy change has a positive value. To obtain the amount of energy necessary for the transition to a higher energy level, a photon is absorbed by the atom. A transition to a lower energy level involves a release of energy, and the energy change is negative. This process is accompanied by emission of a photon by the atom. The following equation summarizes these relationships and is based on the hydrogen atom:

$$\boldsymbol{\Delta E = Efinal - Einitial = -2.18 \times 10^{-1} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) J}$$

The values n_f and n_i are the final and initial energy states of the electron. Example 5.4 in the previous section of the chapter demonstrates calculations of such energy changes.

The principal quantum number is one of three quantum numbers used to characterize an orbital. An atomic orbital is a general region in an atom within which an electron is most probable to reside. 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 secondary (angular momentum) quantum number. It is an integer that may take the values, $l = 0, 1, 2, \ldots, n - 1$. This means that an orbital with $n = 1$ can have only one value of l, $l = 0$, whereas $n = 2$ permits $l = 0$ and $l = 1$, and so on. Whereas the principal quantum number, n, defines the general size and energy of the orbital, the secondary quantum number l specifies the shape of the orbital. Orbitals with the same value of l define a subshell.

Orbitals with $l = 0$ are called *s* orbitals and they make up the *s* subshells. The value $l = 1$ corresponds to the *p* orbitals. For a given n, *p* orbitals constitute a *p* subshell (e.g., 3*p* if $n = 3$). The orbitals with $l = 2$ are called the *d* orbitals, followed by the *f-,g-, and h*-orbitals for $l = 3$, 4, and 5.

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 wave function 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.

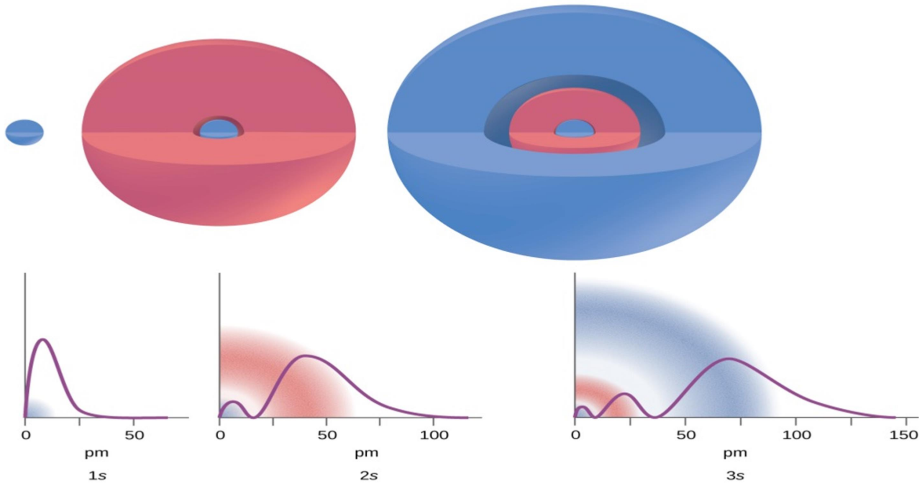


Figure 5.7: The graphs show the probability (y-axis) of finding an electron for the 1s, 2s, 3s orbitals as a function of distance from the nucleus.

Consider the examples in Figure 5.7. 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.

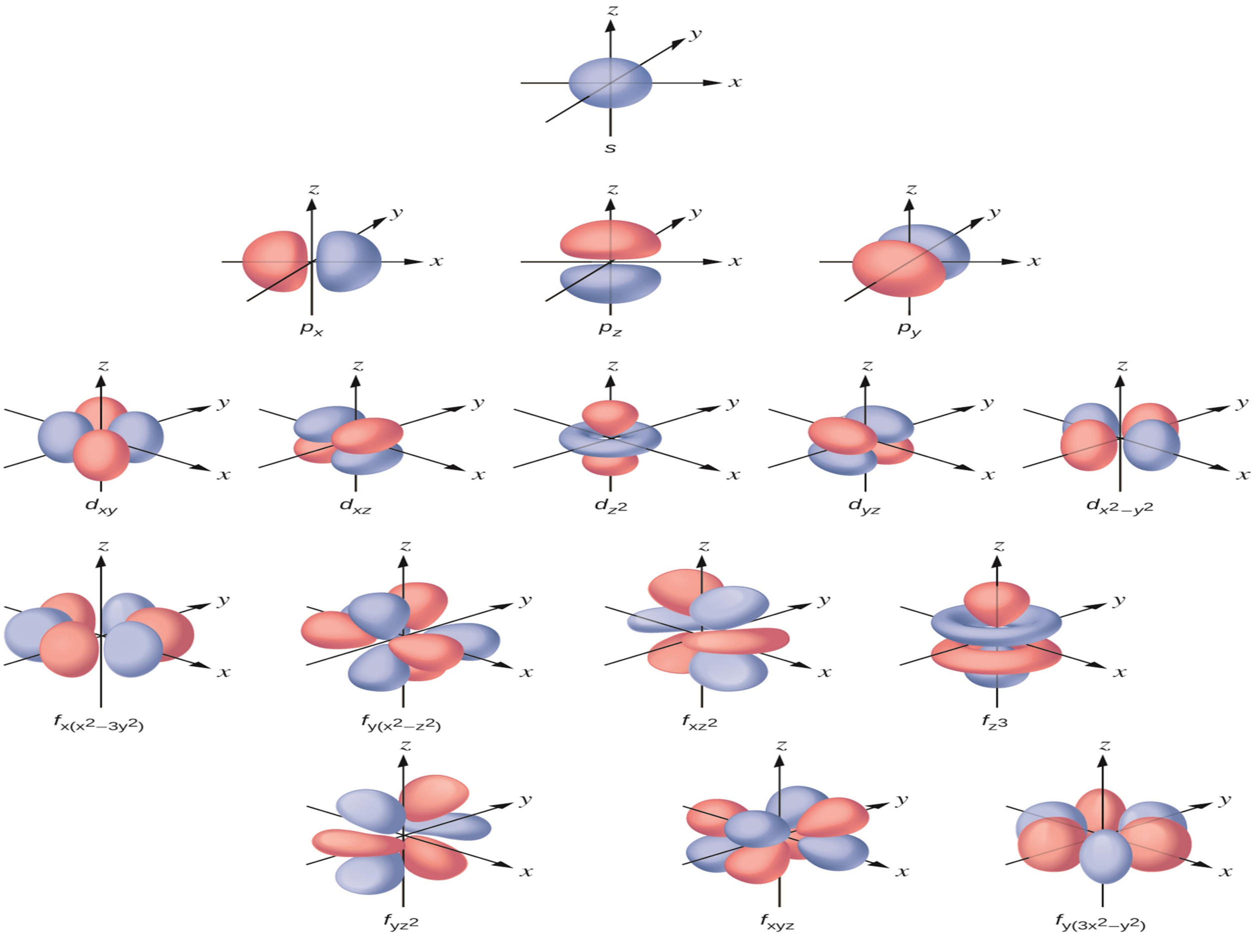


Figure 5.8: Shapes of s, p, d, and f orbitals.

The magnetic quantum number, m_l, specifies the relative spatial orientation of a particular orbital. Generally speaking, m_l can be equal to $-l$, $-(l-1)$, …, 0, …, $(l-1)$, l. The total number of possible orbitals with the same value of l (that is, in the same subshell) is $2l+1$. Thus, there is one *s*-orbital in an *s* subshell ($l = 0$), there are three *p*-orbitals in a *p* subshell ($l = 1$), five *d*-orbitals in a *d* subshell ($l = 2$), seven *f*-orbitals in an *f* subshell ($l = 3$), and so forth. The principal quantum number defines the general value of the electronic energy. The angular momentum quantum number determines the shape of the orbital. And the magnetic quantum number specifies orientation of the orbital in space, as can be seen in Figure 5.8.

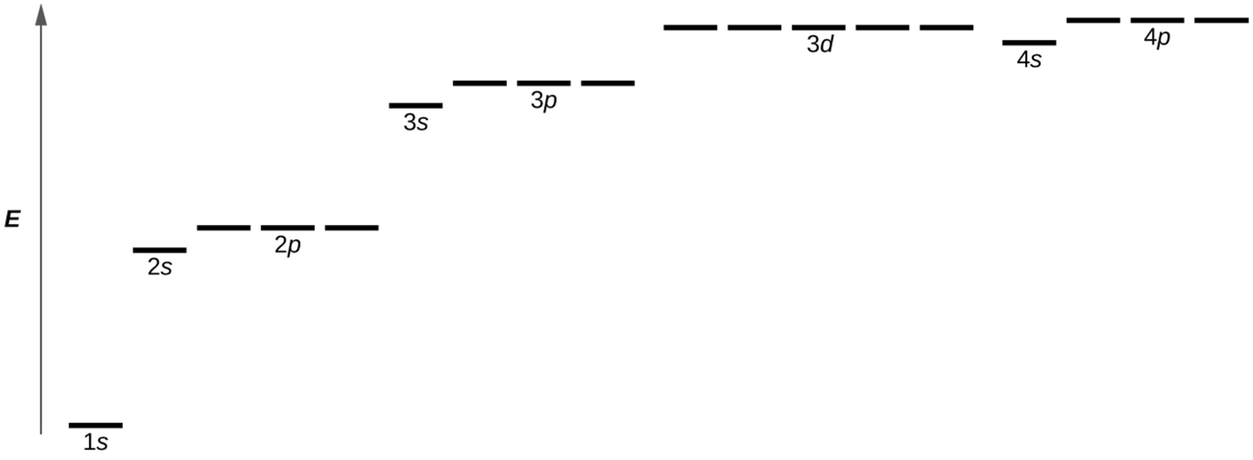


Figure 5.9: The chart shows the energies of electron orbitals in a multi-electron atom.

Figure 5.9 illustrates the energy levels for various orbitals. The number before the orbital name (such as 2*s*, 3*p*, and so forth) stands for the principal quantum number, *n*. The letter in the orbital name defines the subshell with a specific angular momentum quantum number *l* = 0 for *s* orbitals, 1 for *p* orbitals, 2 for *d* orbitals. Finally, there are more than one possible orbitals for $l \geq 1$, each corresponding to a specific value of m_l. In the case of a hydrogen atom or a one-electron ion (such as He^+, Li^{2+}, and so on), energies of all the orbitals with the same *n* are the same. This is called degeneracy, and the energy levels for the same principal quantum number, *n*, are called degenerate orbitals. However, in atoms with more than one electron, this degeneracy is eliminated by the electron–electron interactions, and orbitals that belong to different subshells have different energies, as shown on Figure 5.9. Orbitals within the same subshell 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, or as a loop with an electric current, even though this rotation or current cannot be observed in terms of 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$ms = +1/2$. The other is called the β state, with the z component of the spin being negative and$ms = -1/2$. 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 $ms = -1/2$ and $ms = +1/2$ are different if an external magnetic field is applied.

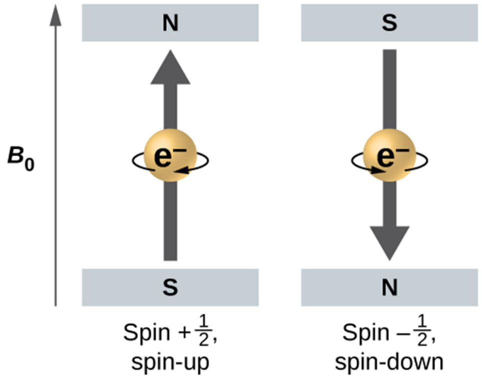


Figure 5.10: Electrons with spin values ±12 in an external magnetic field

An electron acts like a tiny magnet. Its moment is directed up (in the positive direction of the z axis) for the $+1/2$ spin quantum number and down (in the negative z direction) for the spin quantum number of $-1/2$. A magnet has a lower energy if its magnetic moment is aligned with the external magnetic field (the left electron on Figure 5.10) and a higher energy for the magnetic moment being opposite to the applied field. This is why an electron with $ms = +1/2$ has a slightly lower energy in an external field in the positive z direction, and an electron with ms

$-1/2$ 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.

5.3.3. The Pauli Exclusion Principle

An electron in an atom is completely described by four quantum numbers: n, l, m_l, andm_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 two electrons can share the same orbital (the same set of the quantum numbers n, l, and ml) only if their spin quantum numbers m_s have different values. Since the spin quantum number can only have two values ($\pm 1/2$), 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 5.1.

Table 5.1: Quantum Numbers, Their Properties, and Significance

Name	Symbol	Allowed values	Physical meaning
Principal Quantum Number	n	1, 2, 3, 4, ….	shell, the general region for the value of energy for an electron on the orbital
Angular Momentum or Azimuthal Quantum Number	l	$0 \leq l \leq n - 1$	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	12,−12	direction of the intrinsic quantum “spinning” of the electron

Example 5.5

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.

✍ Check Your Learning

Identify the subshell in which electrons with the following quantum numbers are found: (a) $n = 3$, $l = 1$; (b) $n = 5$, $l = 3$; (c) $n = 2$, $l = 0$

Example 5.6

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:

1orbital labeled5*s*
3orbitals labeled5*p*
5orbitals labeled5*d*
7orbitals labeled5*f*
+9orbitals labeled5*g*
25orbitals total

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 $2 \times n^2$.

✍Check Your Learning

If a shell contains a maximum of 32 electrons, what is the principal quantum number, *n*?

Example 5.7

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 $2l + 1$ (there is one *s* orbital, three *p* orbitals, five *d* orbitals, seven *f* orbitals, and so forth).
- The number of radial nodes is equal to $n - l - 1$.

Orbital	*n*	*L*	m_l degeneracy	Radial nodes (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

Check Your Learning

How many orbitals have $l = 2$ and $n = 3$?

5.4.1. Orbital Energies and Atomic Structure

The energy of atomic orbitals increases as the principal quantum number, n, increases. In any atom with two or more electrons, the repulsion between the electrons makes energies of subshells with different values of l differ so that the energy of the orbitals increases within a shell in the order $s<p<d<f$. Figure 5.11 depicts how these two trends in increasing energy relate. The 1*s* orbital at the bottom of the diagram is the orbital with electrons of lowest energy. The energy increases as we move up to the 2*s* and then 2*p*, 3*s*, and 3*p* orbitals, showing that the increasing n value has more influence on energy than the increasing l value for small atoms. However, this pattern does not hold for larger atoms. The 3*d* orbital is higher in energy than the 4*s* orbital. Such overlaps continue to occur frequently as we move up the chart.

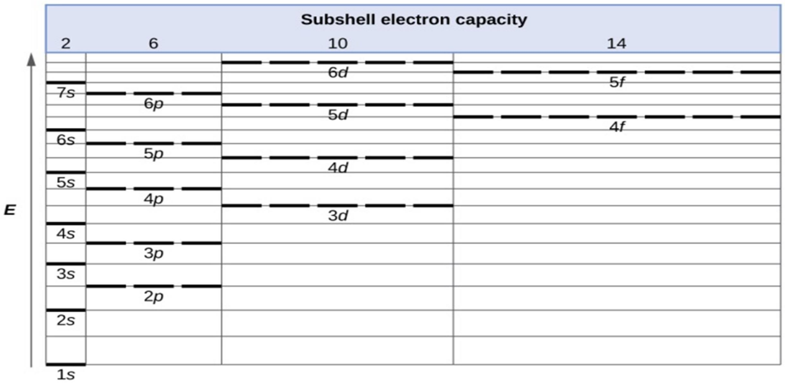


Figure 5.11: Generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale).

Electrons in successive atoms on the periodic table tend to fill low-energy orbitals first. Thus, many students find it confusing that, for example, the 5*p* orbitals fill immediately after the 4*d*, and immediately before the 6*s*. The filling order is based on observed experimental results, and has been confirmed by theoretical calculations. As the principal quantum number, n, increases, the size of the orbital increases and the electrons spend more time farther from the nucleus. Thus, the attraction to the nucleus is weaker and the energy associated with the orbital is higher (less stabilized). But this is not the only effect we have to take into account. Within each shell, as the value of *l* increases, the electrons are less penetrating (meaning there is less electron density found close to the nucleus), in the order *s*>*p*>*d*>*f*. Electrons that are closer to the nucleus slightly repel electrons that are farther out, offsetting the more dominant electron–nucleus attractions slightly (recall that all electrons have −1 charges, but nuclei have +*Z* charges). This phenomenon is called shielding and will be discussed in more detail in the next section. Electrons in orbitals that experience more shielding are less stabilized and thus higher in energy. For small orbitals (1*s* through 3*p*), the increase in energy due to *n* is more significant than the increase due to *l*; however, for larger orbitals the two trends are comparable and cannot be simply predicted. We will discuss methods for remembering the observed order.

The arrangement of electrons in the orbitals of an atom is called the electron configuration of the atom. We describe an electron configuration with a symbol that contains three pieces of information (Figure 5.12):

1. The number of the principal quantum shell, *n*,
2. The letter that designates the orbital type (the subshell, *l*), and
3. A superscript number that designates the number of electrons in that particular subshell.

For example, the notation $2p^4$ (read "two–p–four") indicates four electrons in a *p* subshell ($l = 1$) with a principal quantum number (*n*) of 2. The notation $3d^8$ (read "three–d–eight") indicates eight electrons in the *d* subshell (i.e., $l = 2$) of the principal shell for which $n = 3$.

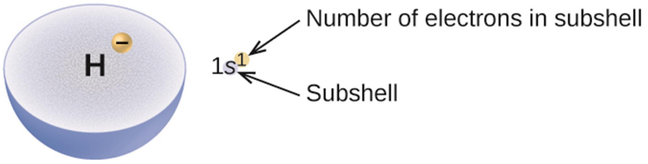


Figure 5.12: The diagram of an electron configuration specifies the subshell (n and l value, with letter symbol) and superscript number of electrons.

5.4.2. The Aufbau Principle

To determine the electron configuration for any particular atom, we can "build" the structures in the order of atomic numbers. Beginning with hydrogen, and continuing across the periods of the periodic table, we add one proton at a time to the nucleus and one electron to the proper subshell until we have described the electron configurations of all the elements. This procedure is called the Aufbau principle, from the German word *Aufbau* ("to build up"). Each added electron occupies the subshell of lowest energy available (in the order shown in Figure 5.11), subject to the limitations imposed by the allowed quantum numbers according to the Pauli Exclusion Principle. Electrons enter higher-energy subshells only after lower-energy subshells have been filled to capacity. Figure 5.13 illustrates the traditional way to remember the filling order for atomic orbitals. Since the arrangement of the periodic table is based on the electron configurations, Figure 5.14 provides an alternative method for determining the electron configuration. The filling order simply begins at hydrogen and includes each subshell as you proceed in increasing *Z* order. For example, after filling the 3*p* block up to Ar, we see the orbital will be 4s (K, Ca), followed by the 3*d* orbitals.

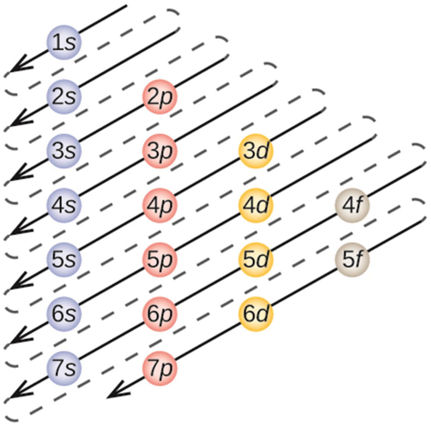


Figure 5.13: This diagram depicts the energy order for atomic orbitals and is useful for deriving ground-state electron configurations.

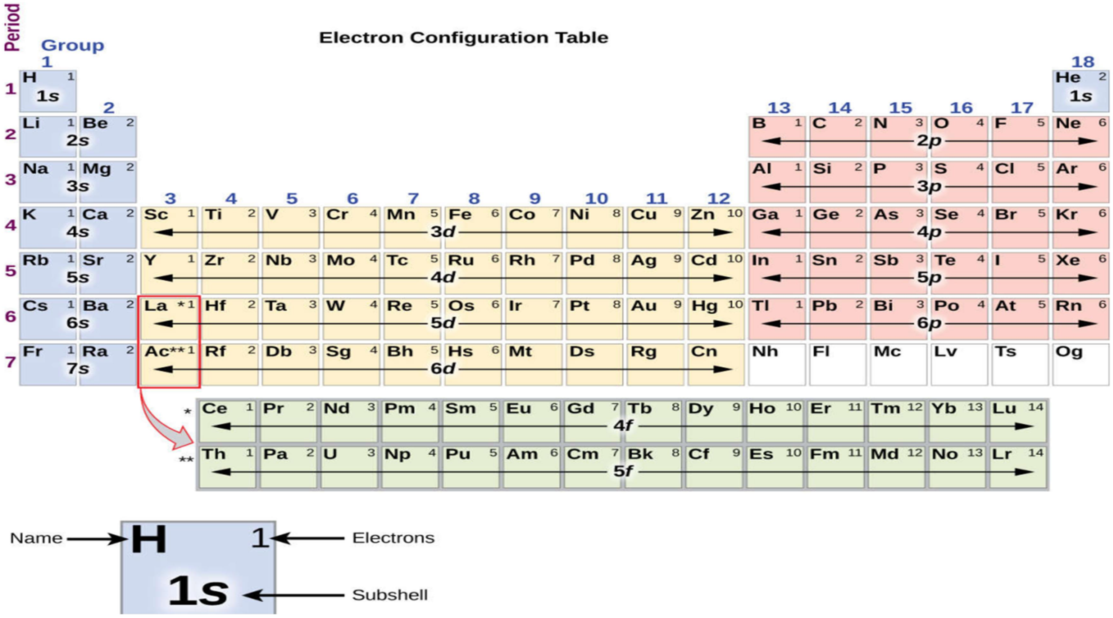
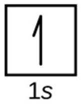


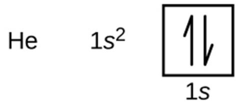
Figure 5.14: This periodic table shows the electron configuration for each subshell. By "building up" from hydrogen, this table can be used to determine the electron configuration for any atom on the periodic table.

We will now construct the ground-state electron configuration and orbital diagram for a selection of atoms in the first and second periods of the periodic table. Orbital diagrams are pictorial representations of the electron configuration, showing the individual orbitals and the pairing arrangement of electrons. We start with a single hydrogen atom (atomic number 1), which consists of one proton and one electron. Referring to Figure 5.13 or Figure 5.14, we would expect to find the electron in the 1*s* orbital. By convention, the $m_s = +1/2$ value is usually filled first. The electron configuration and the orbital diagram are:

H $1s^1$

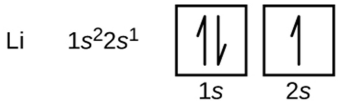


Following hydrogen is the noble gas helium, which has an atomic number of 2. The helium atom contains two protons and two electrons. The first electron has the same four quantum numbers as the hydrogen atom electron ($n = 1$, $l = 0$, $m_l = 0$, $m_s = +1/2$). The second electron also goes into the 1*s* orbital and fills that orbital. The second electron has the same *n*, *l*, and m_l quantum numbers, but must have the opposite spin quantum number, $m_s = -1/2$. This is in accord with the Pauli Exclusion Principle: No two electrons in the same atom can have the same set of four quantum numbers. For orbital diagrams, this means two arrows go in each box (representing two electrons in each orbital) and the arrows must point in opposite directions (representing paired spins). The electron configuration and orbital diagram of helium are:

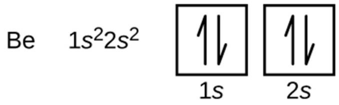


The $n = 1$ shell is completely filled in a helium atom.

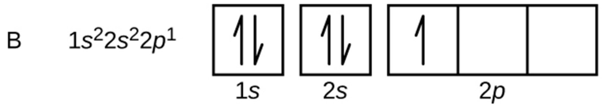
The next atom is the alkali metal lithium with an atomic number of 3. The first two electrons in lithium fill the 1*s* orbital and have the same sets of four quantum numbers as the two electrons in helium. The remaining electron must occupy the orbital of next lowest energy, the 2*s* orbital .Thus, the electron configuration and orbital diagram of lithium are:



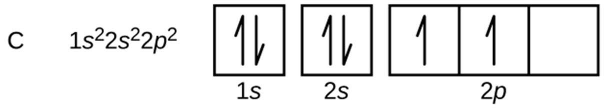
An atom of the alkaline earth metal beryllium, with an atomic number of 4, contains four protons in the nucleus and four electrons surrounding the nucleus. The fourth electron fills the remaining space in the 2*s* orbital.



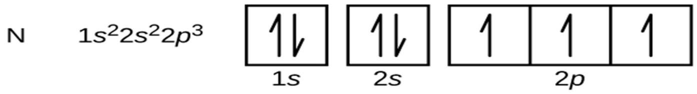
An atom of boron (atomic number 5) contains five electrons. The $n = 1$ shell is filled with two electrons and three electrons will occupy the $n = 2$ shell. Because any *s* subshell can contain only two electrons, the fifth electron must occupy the next energy level, which will be a 2*p* orbital. There are three degenerate 2*p* orbitals ($m_l = -1, 0, +1$) and the electron can occupy any one of these *p* orbitals. When drawing orbital diagrams, we include empty boxes to depict any empty orbitals in the same subshell that we are filling.

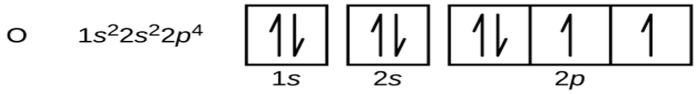


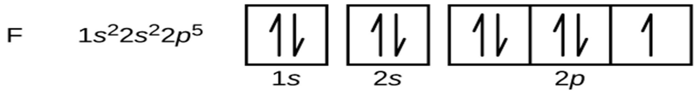
Carbon (atomic number 6) has six electrons. Four of them fill the 1*s* and 2*s* orbitals. The remaining two electrons occupy the 2*p* subshell. We now have a choice of filling one of the 2*p* orbitals and pairing the electrons or of leaving the electrons unpaired in two different, but degenerate, *p* orbitals. The orbitals are filled as described by Hund's rule: the lowest-energy configuration for an atom with electrons within a set of degenerate orbitals is that having the maximum number of unpaired electrons. Thus, the two electrons in the carbon 2*p* orbitals have identical *n*, *l*, and m_s quantum numbers and differ in their m_l quantum number (in accord with the Pauli exclusion principle). The electron configuration and orbital diagram for carbon are:

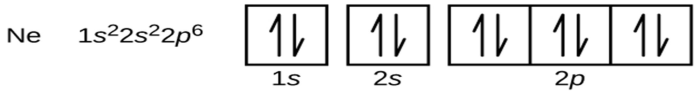


Nitrogen (atomic number 7) fills the 1*s* and 2*s* subshells and has one electron in each of the three 2*p* orbitals, in accordance with Hund's rule. These three electrons have unpaired spins. Oxygen (atomic number 8) has a pair of electrons in any one of the 2*p* orbitals (the electrons have opposite spins) and a single electron in each of the other two. Fluorine (atomic number 9) has only one 2*p* orbital containing an unpaired electron. All of the electrons in the noble gas neon (atomic number 10) are paired, and all of the orbitals in the *n* = 1 and the *n* = 2 shells are filled. The electron configurations and orbital diagrams of these four elements are:









The alkali metal sodium (atomic number 11) has one more electron than the neon atom. This electron must go into the lowest-energy subshell available, the 3*s* orbital, giving a $1s^22s^22p^63s^1$ configuration. The electrons occupying the outermost shell orbital(s) (highest value of *n*) are called valence electrons, and those occupying the inner shell orbitals are called core electrons (Figure 5.15). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1s^22s^22p^6$) and our abbreviated or condensed configuration is [Ne]$3s^1$.

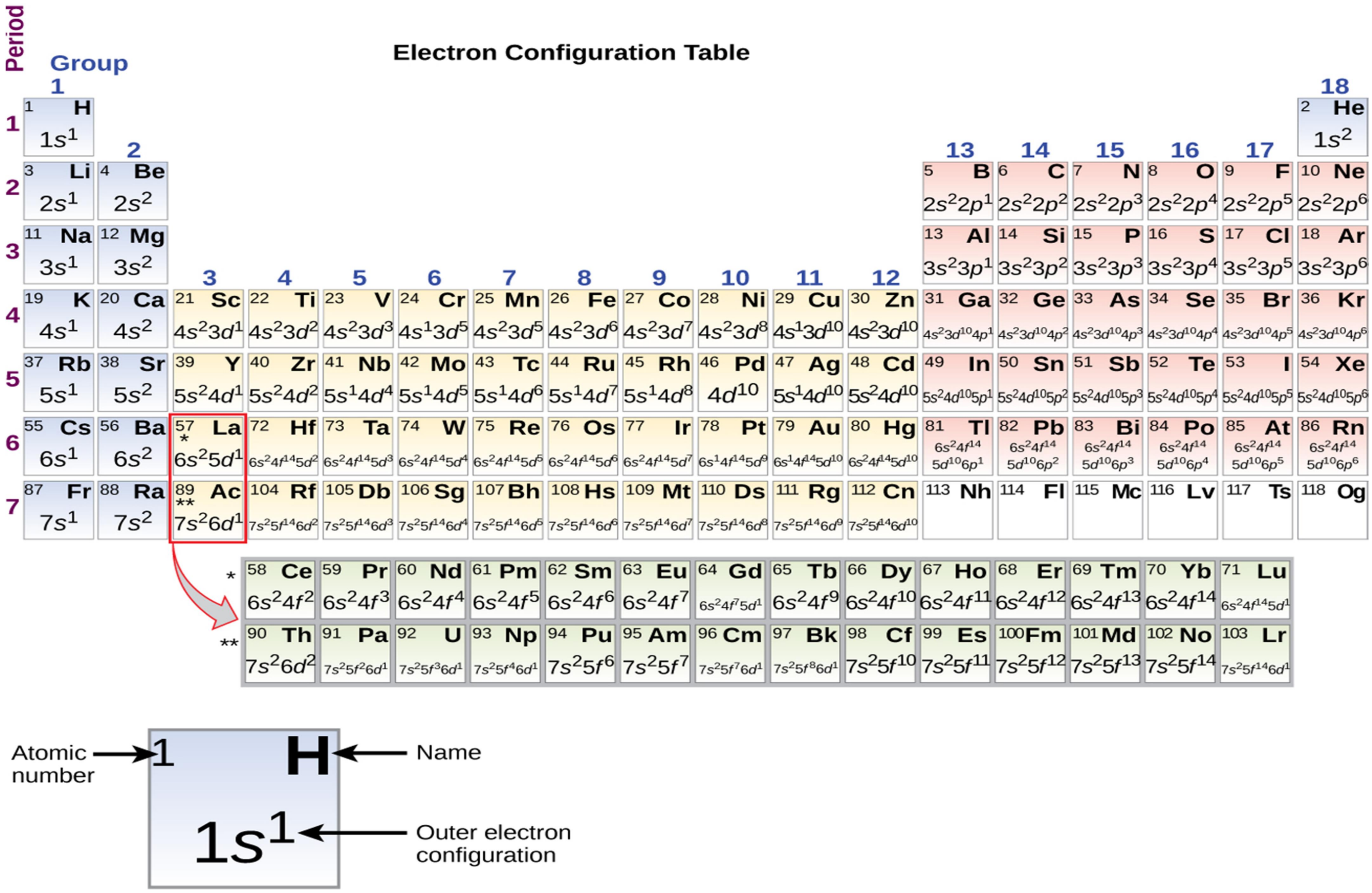
Figure 5.15: A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

Similarly, the abbreviated configuration of lithium can be represented as $[He]2s^1$, where [He] represents the configuration of the helium atom, which is identical to that of the filled inner shell of lithium. Writing the configurations in this way emphasizes the similarity of the configurations of lithium and sodium. Both atoms, which are in the alkali metal family, have only one electron in a valence *s* subshell outside a filled set of inner shells.

$$\text{Li: }[\text{He}]2\text{s}^1$$
$$\text{Na: }[\text{Ne}]3\text{s}^1$$

The alkaline earth metal magnesium (atomic number 12), with its 12 electrons in a $[Ne]3s^2$ configuration, is analogous to its family member beryllium, $[He]2s^2$. Both atoms have a filled *s* subshell outside their filled inner shells. Aluminum (atomic number 13), with 13 electrons and the electron configuration $[Ne]3s^23p^1$, is analogous to its family member boron, $[He]2s^22p^1$.

The electron configurations of silicon (14 electrons), phosphorus (15 electrons), sulfur (16 electrons), chlorine (17 electrons), and argon (18 electrons) are analogous in the electron configurations of their outer shells to their corresponding family members carbon, nitrogen, oxygen, fluorine, and neon, respectively, except that the principal quantum number of the outer shell of the heavier elements has increased by one to $n = 3$. Figure 5.16 shows the lowest energy, or ground-state, electron configuration for these elements as well as that for atoms of each of the known elements.



Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H $1s^1$																	2 He $1s^2$
2	3 Li $2s^1$	4 Be $2s^2$											5 B $2s^22p^1$	6 C $2s^22p^2$	7 N $2s^22p^3$	8 O $2s^22p^4$	9 F $2s^22p^5$	10 Ne $2s^22p^6$
3	11 Na $3s^1$	12 Mg $3s^2$											13 Al $3s^23p^1$	14 Si $3s^23p^2$	15 P $3s^23p^3$	16 S $3s^23p^4$	17 Cl $3s^23p^5$	18 Ar $3s^23p^6$
4	19 K $4s^1$	20 Ca $4s^2$	21 Sc $4s^23d^1$	22 Ti $4s^23d^2$	23 V $4s^23d^3$	24 Cr $4s^13d^5$	25 Mn $4s^23d^5$	26 Fe $4s^23d^6$	27 Co $4s^23d^7$	28 Ni $4s^23d^8$	29 Cu $4s^13d^{10}$	30 Zn $4s^23d^{10}$	31 Ga $4s^23d^{10}4p^1$	32 Ge $4s^23d^{10}4p^2$	33 As $4s^23d^{10}4p^3$	34 Se $4s^23d^{10}4p^4$	35 Br $4s^23d^{10}4p^5$	36 Kr $4s^23d^{10}4p^6$
5	37 Rb $5s^1$	38 Sr $5s^2$	39 Y $5s^24d^1$	40 Zr $5s^24d^2$	41 Nb $5s^14d^4$	42 Mo $5s^14d^5$	43 Tc $5s^14d^6$	44 Ru $5s^14d^7$	45 Rh $5s^14d^8$	46 Pd $4d^{10}$	47 Ag $5s^14d^{10}$	48 Cd $5s^24d^{10}$	49 In $5s^24d^{10}5p^1$	50 Sn $5s^24d^{10}5p^2$	51 Sb $5s^24d^{10}5p^3$	52 Te $5s^24d^{10}5p^4$	53 I $5s^24d^{10}5p^5$	54 Xe $5s^24d^{10}5p^6$
6	55 Cs $6s^1$	56 Ba $6s^2$	57 * La $6s^25d^1$	72 Hf $6s^24f^{14}5d^2$	73 Ta $6s^24f^{14}5d^3$	74 W $6s^24f^{14}5d^4$	75 Re $6s^24f^{14}5d^5$	76 Os $6s^24f^{14}5d^6$	77 Ir $6s^24f^{14}5d^7$	78 Pt $6s^14f^{14}5d^9$	79 Au $6s^14f^{14}5d^{10}$	80 Hg $6s^24f^{14}5d^{10}$	81 Tl $6s^24f^{14}$ $5d^{10}6p^1$	82 Pb $6s^24f^{14}$ $5d^{10}6p^2$	83 Bi $6s^24f^{14}$ $5d^{10}6p^3$	84 Po $6s^24f^{14}$ $5d^{10}6p^4$	85 At $6s^24f^{14}$ $5d^{10}6p^5$	86 Rn $6s^24f^{14}$ $5d^{10}6p^6$
7	87 Fr $7s^1$	88 Ra $7s^2$	89 ** Ac $7s^26d^1$	104 Rf $7s^25f^{14}6d^2$	105 Db $7s^25f^{14}6d^3$	106 Sg $7s^25f^{14}6d^4$	107 Bh $7s^25f^{14}6d^5$	108 Hs $7s^25f^{14}6d^6$	109 Mt $7s^25f^{14}6d^7$	110 Ds $7s^25f^{14}6d^8$	111 Rg $7s^25f^{14}6d^9$	112 Cn $7s^25f^{14}6d^{10}$	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

*	58 Ce $6s^24f^2$	59 Pr $6s^24f^3$	60 Nd $6s^24f^4$	61 Pm $6s^24f^5$	62 Sm $6s^24f^6$	63 Eu $6s^24f^7$	64 Gd $6s^24f^75d^1$	65 Tb $6s^24f^9$	66 Dy $6s^24f^{10}$	67 Ho $6s^24f^{11}$	68 Er $6s^24f^{12}$	69 Tm $6s^24f^{13}$	70 Yb $6s^24f^{14}$	71 Lu $6s^24f^{14}5d^1$
**	90 Th $7s^26d^2$	91 Pa $7s^25f^26d^1$	92 U $7s^25f^36d^1$	93 Np $7s^25f^46d^1$	94 Pu $7s^25f^6$	95 Am $7s^25f^7$	96 Cm $7s^25f^76d^1$	97 Bk $7s^25f^86d^1$	98 Cf $7s^25f^{10}$	99 Es $7s^25f^{11}$	100 Fm $7s^25f^{12}$	101 Md $7s^25f^{13}$	102 No $7s^25f^{14}$	103 Lr $7s^25f^{14}6d^1$

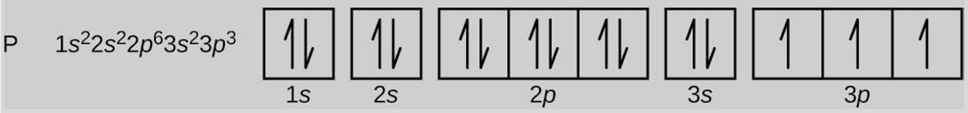
Figure 5.16: This version of the periodic table shows the outer-shell electron configuration of each element. Note that down each group, the configuration is often similar.

When we come to the next element in the periodic table, the alkali metal potassium (atomic number 19), we might expect that we would begin to add electrons to the 3*d* subshell. However, all available chemical and physical evidence indicates that potassium is like lithium and sodium, and that the next electron is not added to the 3*d* level but is, instead, added to the 4*s* level (Figure 5.16). As discussed previously, the 3*d* orbital with no radial nodes is higher in energy because it is less penetrating and more shielded from the nucleus than the 4*s*, which has three radial nodes. Thus, potassium has an electron configuration of $[Ar]4s^1$. Hence, potassium corresponds to Li and Na in its valence shell configuration. The next electron is added to complete the 4*s* subshell and calcium has an electron configuration of $[Ar]4s^2$. This gives calcium an outer-shell electron configuration corresponding to that of beryllium and magnesium.

Beginning with the transition metal scandium (atomic number 21), additional electrons are added successively to the 3*d* subshell. This subshell is filled to its capacity with 10 electrons (remember that for $l = 2$ [*d* orbitals], there are $2l + 1 = 5$ values of m_l, meaning that there are five *d* orbitals that have a combined capacity of 10 electrons). The 4*p* subshell fills next. Note that for three series of elements, scandium (Sc) through copper (Cu), yttrium (Y) through silver (Ag), and lutetium (Lu) through gold (Au), a total of 10 *d* electrons are successively added to the $(n - 1)$ shell next to the *n* shell to bring that $(n - 1)$ shell from 8 to 18 electrons. For two series, lanthanum (La) through lutetium (Lu) and actinium (Ac) through lawrencium (Lr), 14 *f* electrons ($l = 3$, $2l + 1 = 7$ m_l values; thus, seven orbitals with a combined capacity of 14 electrons) are successively added to the $(n - 2)$ shell to bring that shell from 18 electrons to a total of 32 electrons.

Example 5.8

Quantum Numbers and Electron Configurations What is the electron configuration and orbital diagram for a phosphorus atom? What are the four quantum numbers for the last electron added? Solution The atomic number of phosphorus is 15. Thus, a phosphorus atom contains 15 electrons. The order of filling of the energy levels is 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, . . . The 15 electrons of the phosphorus atom will fill up to the 3*p* orbital, which will contain three electrons:



The last electron added is a 3*p* electron. Therefore, $n = 3$ and, for a *p*-type orbital, $l = 1$. The m_l value could be –1, 0, or +1. The three *p* orbitals are degenerate, so any of these m_l values is correct. For unpaired electrons, convention assigns the value of $+1/2$ for the spin quantum number; thus, $m_s = +1/2$.

Check Your Learning

Identify the atoms from the electron configurations given:

(a) $[\mathrm{Ar}]4s^23d^5$

(b) $[\mathrm{Kr}]5s^24d^{10}5p^6$

The periodic table can be a powerful tool in predicting the electron configuration of an element. However, we do find exceptions to the order of filling of orbitals that are shown in Figure 5.13 or Figure 5.14. For instance, the electron configurations (shown in Figure 5.15) of the transition metals chromium (Cr; atomic number 24) and copper (Cu; atomic number 29), among others, are not those we would expect. In general, such exceptions involve subshells with very similar energy, and small effects can lead to changes in the order of filling.

In the case of Cr and Cu, we find that half-filled and completely filled subshells apparently represent conditions of preferred stability. This stability is such that an electron shifts from the 4*s* into the 3*d* orbital to gain the extra stability of a half-filled 3*d* subshell (in Cr) or a filled 3*d* subshell (in Cu). Other exceptions also occur. For example, niobium (Nb, atomic number 41) is predicted to have the electron configuration $[\text{Kr}]5s^2 4d^3$. Experimentally, we observe that its ground-state electron configuration is actually $[\text{Kr}]5s^1 4d^4$. We can rationalize this observation by saying that the electron–electron repulsions experienced by pairing the electrons in the 5*s* orbital are larger than the gap in energy between the 5*s* and 4*d* orbitals. There is no simple method to predict the exceptions for atoms where the magnitude of the repulsions between electrons is greater than the small differences in energy between subshells.

5.4.3. Electron Configurations and the Periodic Table

As described earlier, the periodic table arranges atoms based on increasing atomic number so that elements with the same chemical properties recur periodically. When their electron configurations are added to the table (Figure 5.16), we also see a periodic recurrence of similar electron configurations in the outer shells of these elements. Because they are in the outer shells of an atom, valence electrons play the most important role in chemical reactions. The outer electrons have the highest energy of the electrons in an atom and are more easily lost or shared than the core electrons. Valence electrons are also the determining factor in some physical properties of the elements.

Elements in any one group (or column) have the same number of valence electrons; the alkali metals lithium and sodium each have only one valence electron, the alkaline earth metals beryllium and magnesium each have two, and the halogens fluorine and chlorine each have seven valence electrons. The similarity in chemical properties among elements of the same group occurs because they have the same number of valence electrons. It is the loss, gain, or sharing of valence electrons that defines how elements react.

It is important to remember that the periodic table was developed on the basis of the chemical behavior of the elements, well before any idea of their atomic structure was available. Now we can understand why the periodic table has the arrangement it has—the arrangement puts elements whose atoms have the same number of valence electrons in the same group. This arrangement is emphasized in Figure 5.16, which shows in periodic-table form the electron configuration of the last subshell to be filled by the Aufbau principle. The colored sections of Figure 5.16 show the three categories of elements classified by the orbitals being filled: main group, transition, and inner transition elements. These classifications determine which orbitals are counted in the valence shell or highest energy level orbitals of an atom.

1. **Main group elements** (sometimes called **representative elements**) are those in which the last electron added enters an *s* or a *p* orbital in the outermost shell, shown in blue and red in Figure 5.16. This category includes all the nonmetallic elements, as well as many metals and the metalloids. The valence electrons for main group elements are those with the highest *n* level. For example, gallium (Ga, atomic number 31) has the electron configuration $[\mathrm{Ar}]\underline{4s^2}3d^{10}\underline{4p^1}$, which contains three valence electrons (underlined). The completely filled *d* orbitals count as core, not valence, electrons.
2. **Transition elements or transition metals**. These are metallic elements in which the last electron added enters a *d* orbital. The valence electrons (those added after the last noble gas configuration) in these elements include the *ns* and (*n* – 1) *d* electrons. The official IUPAC definition of transition elements specifies those with partially filled *d* orbitals. Thus, the elements with completely filled orbitals (Zn, Cd, Hg, as well as Cu, Ag, and Au in Figure 5.16) are not technically transition elements. However, the term is frequently used to refer to the entire *d* block (colored yellow in Figure 5.16), and we will adopt this usage in this textbook.
3. **Inner transition elements** are metallic elements in which the last electron added occupies an *f* orbital. They are shown in green in Figure 5.16. The valence shells of the inner transition elements consist of the (*n* – 2)*f,* the (*n* – 1)*d*, and the *ns* subshells. There are two inner transition series:
    a. The lanthanide series: lanthanide (La) through lutetium (Lu)
    b. The actinide series: actinide (Ac) through lawrencium (Lr)

Lanthanum and actinium, because of their similarities to the other members of the series, are included and used to name the series, even though they are transition metals with no *f* electrons.

5.4.4. Electron Configurations of Ions

Ions are formed when atoms gain or lose electrons. A cation (positively charged ion) forms when one or more electrons are removed from a parent atom. For main group elements, the electrons that were added last are the first electrons removed. For transition metals and inner transition metals, however, electrons in the *s* orbital are easier to remove than the *d* or *f* electrons, and so the highest *ns* electrons are lost, and then the $(n – 1)d$ or $(n – 2)f$ electrons are removed. An anion (negatively charged ion) forms when one or more electrons are added to a parent atom. The added electrons fill in the order predicted by the Aufbau principle.

Example 5.9

Predicting Electron Configurations of Ions

What is the electron configuration of:

a) Na^+ b) P^{3-} c) Al^{2+} d) Fe^{2+} e)Sm^{3+}

Solution

First, write out the electron configuration for each parent atom. We have chosen to show the full, unabbreviated configurations to provide more practice for students who want it, but listing the core-abbreviated electron configurations is also acceptable.

Next, determine whether an electron is gained or lost. Remember electrons are negatively charged, so ions with a positive charge have *lost* an electron. For main group elements, the last orbital gains or loses the electron. For transition metals, the last *s* orbital loses an electron before the *d* orbitals.

a) Na: $1s^22s^22p^63s^1$. Sodium cation loses one electron, so Na^+: $1s^22s^22p^63s^1$ = Na^+: $1s^22s^22p^6$.
b) P: $1s^22s^22p^63s^23p^3$. Phosphorus trianion gains three electrons, so P^{3-}: $1s^22s^22p^63s^23p^6$.
c) Al: $1s^22s^22p^63s^23p^1$. Aluminum dication loses two electrons Al^{2+}: $1s^22s^22p^63s^23p^1$ = Al^{2+}: $1s^22s^22p^63s^1$.
d) Fe: $1s^22s^22p^63s^23p^64s^23d^6$. Iron(II) loses two electrons and, since it is a transition metal, they are removed from the 4*s* orbital Fe^{2+}: $1s^22s^22p^63s^23p^64s^23d^6 = 1s^22s^22p^63s^23p^63d^6$.
e) Sm: $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^6$. Samarium trication loses three electrons. The first two will be lost from the 6*s* orbital, and the final one is removed from the 4*f* orbital. Sm^{3+}: $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^6$ = $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^64f^5$.

5.5. Periodic Variation in Element Properties

5.5.1. Variation in Covalent Radius

The quantum mechanical picture makes it difficult to establish a definite size of an atom. However, there are several practical ways to define the radius of atoms and, thus, to determine their relative sizes that give roughly similar values. We will use the covalent radius (Figure 5.17), which is defined as one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond (this measurement is possible because atoms within molecules still retain much of their atomic identity). We know that as we scan down a group, the principal quantum number, *n*, increases by one for each element. Thus, the electrons are being added to a region of space that is increasingly distant from the nucleus. Consequently, the size of the atom (and its covalent radius) must increase as we increase the distance of the outermost electrons from the nucleus. This trend is illustrated for the covalent radii of the halogens in Table 5.2 and Figure 5.17. The trends for the entire periodic table can be seen in Figure 5.17.

Table 5.2: Covalent Radii of the Halogen Group Elements

Atom	Covalent radius (pm)	Nuclear charge
F	64	+9
Cl	99	+17
Br	114	+35
I	133	+53
At	148	+85

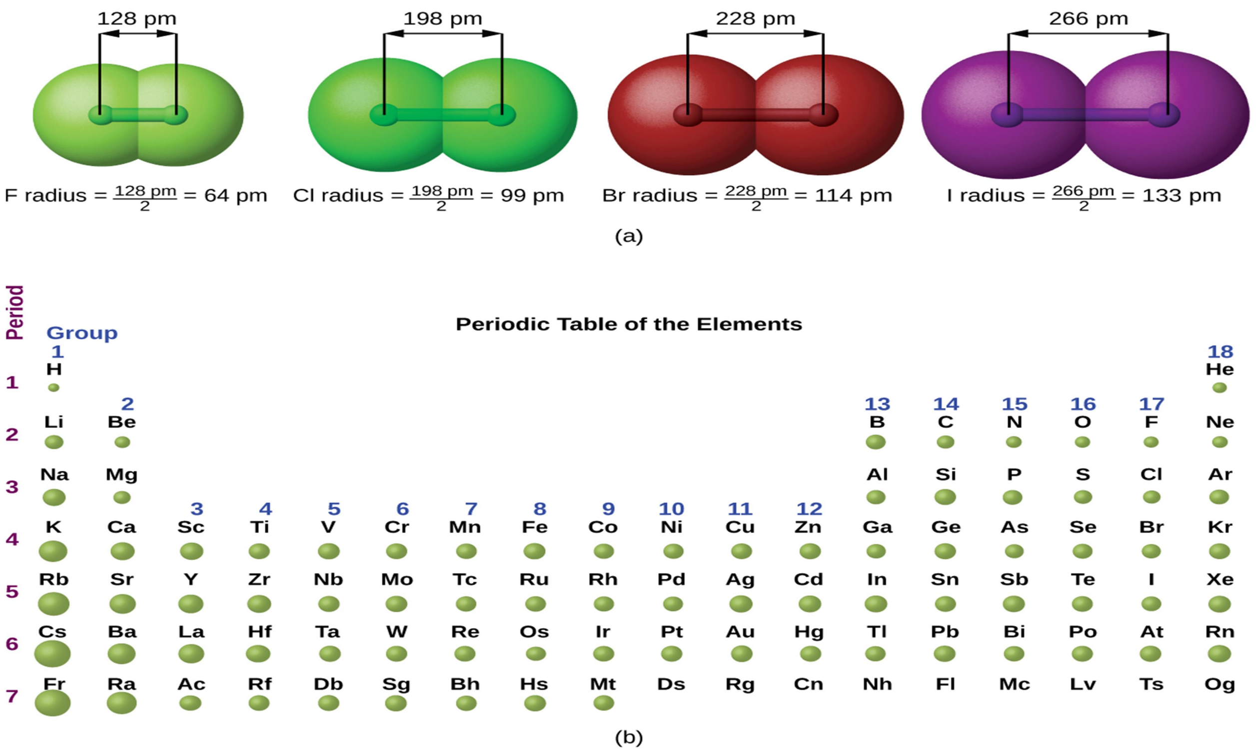


Figure 5.17: (a) The radius of an atom is defined as one-half the distance between the nuclei in a molecule consisting of two identical atoms joined by a covalent bond. The atomic radius for the halogens increases down the group as n increases. (b) Covalent radii of the elements are shown to scale. The general trend is that radii increase down a group and decrease across a period.

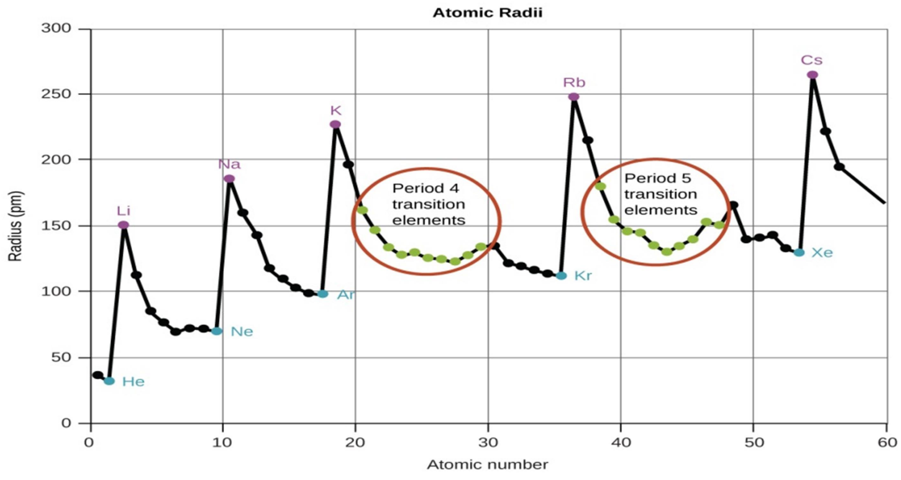


Figure 5.18: Within each period, the trend in atomic radius decreases as Z increases; for example, from K to Kr. Within each group (e.g., the alkali metals shown in purple), the trend is that atomic radius increases as Z increases.

As shown in Figure 5.18, as we move across a period from left to right, we generally find that each element has a smaller covalent radius than the element preceding it. This might seem counterintuitive because it implies that atoms with more electrons have a smaller atomic radius. This can be explained with the concept of effective nuclear charge, Z_{eff}. This is the pull exerted on a specific electron by the nucleus, taking into account any electron–electron repulsions. For hydrogen, there is only one electron and so the nuclear charge (Z) and the effective nuclear charge (Z_{eff}) are equal. For all other atoms, the inner electrons partially *shield* the outer electrons from the pull of the nucleus, and thus:

$$\boldsymbol{Z_{eff} = Z - shielding}$$

Shielding is determined by the probability of another electron being between the electron of interest and the nucleus, as well as by the electron–electron repulsions the electron of interest encounters. Core electrons are adept at shielding, while electrons in the same valence shell do not block the nuclear attraction experienced by each other as efficiently. Thus, each time we move from one element to the next across a period, Z increases by one, but the shielding increases only slightly. Thus, Z_{eff} increases as we move from left to right across a period. The stronger pull (higher effective nuclear charge) experienced by electrons on the right side of the periodic table draws them closer to the nucleus, making the covalent radii smaller.

Thus, as we would expect, the outermost or valence electrons are easiest to remove because they have the highest energies, are shielded more, and are farthest from the nucleus. As a general rule, when the representative elements form cations, they do so by the loss of the *ns* or *np* electrons that were added last in the Aufbau process. The transition elements, on the other hand, lose the *ns* electrons before they begin to lose the $(n - 1)d$ electrons, even though the *ns* electrons are added first, according to the Aufbau principle.

Example 5.10

Sorting Atomic Radii

Predict the order of increasing covalent radius for Ge, Fl, Br, Kr.

Solution

Radius increases as we move down a group, so Ge < Fl (Note: Fl is the symbol for flerovium, element 114, NOT fluorine). Radius decreases as we move across a period, so Kr < Br < Ge. Putting the trends together, we obtain Kr < Br < Ge < Fl.

5.5.2. Variation in Ionic Radii

Ionic radius is the measure used to describe the size of an ion. A cation always has fewer electrons and the same number of protons as the parent atom; it is smaller than the atom from which it is derived (Figure 5.19). For example, the covalent radius of an aluminum atom ($1s^22s^22p^63s^23p^1$) is 118 pm, whereas the ionic radius of an Al^{3+} ($1s^22s^22p^6$) is 68 pm. As electrons are removed from the outer valence shell, the remaining core electrons occupying smaller shells experience a greater effective nuclear charge Z_{eff} (as discussed) and are drawn even closer to the nucleus.

Figure 5.19: The radius for a cation is smaller than the parent atom (Al), due to the lost electrons; the radius for an anion is larger than the parent (S), due to the gained electrons.

Cations with larger charges are smaller than cations with smaller charges (e.g., V^{2+} has an ionic radius of 79 pm, while that of V^{3+} is 64 pm). Proceeding down the groups of the periodic table, we find that cations of successive elements with the same charge generally have larger radii, corresponding to an increase in the principal quantum number, n.

An anion (negative ion) is formed by the addition of one or more electrons to the valence shell of an atom. This results in a greater repulsion among the electrons and a decrease in Z_{eff} per electron. Both effects (the increased number of electrons and the decreased Z_{eff}) cause the radius of an anion to be larger than that of the parent atom (Figure 5.19). For example, a sulfur atom ($[Ne]3s^23p^4$) has a covalent radius of 104 pm, whereas the ionic radius of the sulfide anion ($[Ne]3s^23p^6$) is 170 pm. For consecutive elements proceeding down any group, anions have larger principal quantum numbers and, thus, larger radii.

Atoms and ions that have the same electron configuration are said to be isoelectronic. Examples of isoelectronic species are N^{3-}, O^{2-}, F^-, Ne, Na^+, Mg^{2+}, and Al^{3+} ($1s^22s^22p^6$). Another isoelectronic series is P^{3-}, S^{2-}, Cl^-, Ar, K^+, Ca^{2+}, and Sc^{3+} ($[Ne]3s^23p^6$). For atoms or ions that are isoelectronic, the number of protons determines the size. The greater the nuclear charge, the smaller the radius in a series of isoelectronic ions and atoms.

5.5.3. Variation in Ionization Energies

The amount of energy required to remove the most loosely bound electron from a gaseous atom in its ground state is called its first ionization energy (IE_1). The first ionization energy for an element, X, is the energy required to form a cation with +1 charge:

$$\boldsymbol{X(g) \longrightarrow X + (g) + e^- \quad IE1}$$

The energy required to remove the second most loosely bound electron is called the second ionization energy (IE_2).

$$\boldsymbol{X + (g) \longrightarrow X_2 + (g) + e^- \quad IE_2}$$

The energy required to remove the third electron is the third ionization energy, and so on. Energy is always required to remove electrons from atoms or ions, so ionization processes are endothermic and IE values are always positive. For larger atoms, the most loosely bound electron is located farther from the nucleus and so is easier to remove. Thus, as size (atomic radius) increases, the ionization energy should decrease. Relating this logic to what we have just learned about radii, we would expect first ionization energies to decrease down a group and to increase across a period.

Figure 5.20 graphs the relationship between the first ionization energy and the atomic number of several elements. The values of first ionization energy for the elements are given in Figure 5.21. Within a period, the IE_1 generally increases with increasing Z. Down a group, the IE_1 value generally decreases with increasing Z. There are some systematic deviations from this trend, however. Note that the ionization energy of boron (atomic number 5) is less than that of beryllium (atomic number 4) even though the nuclear charge of boron is greater by one proton. This can be explained because the energy of the subshells increases as l increases, due to penetration and shielding (as discussed previously in this chapter). Within any one shell, the *s* electrons are lower in energy than the *p* electrons. This means that an *s* electron is harder to remove from an atom than a *p* electron in the same shell. The electron removed during the ionization of beryllium ($[He]2s^2$) is an *s* electron, whereas the electron removed during the ionization of boron ($[He]2s^22p^1$) is a *p* electron; this results in a lower first ionization energy for boron, even though its nuclear charge is greater by one proton. Thus, we see a small deviation from the predicted trend occurring each time a new subshell begins.

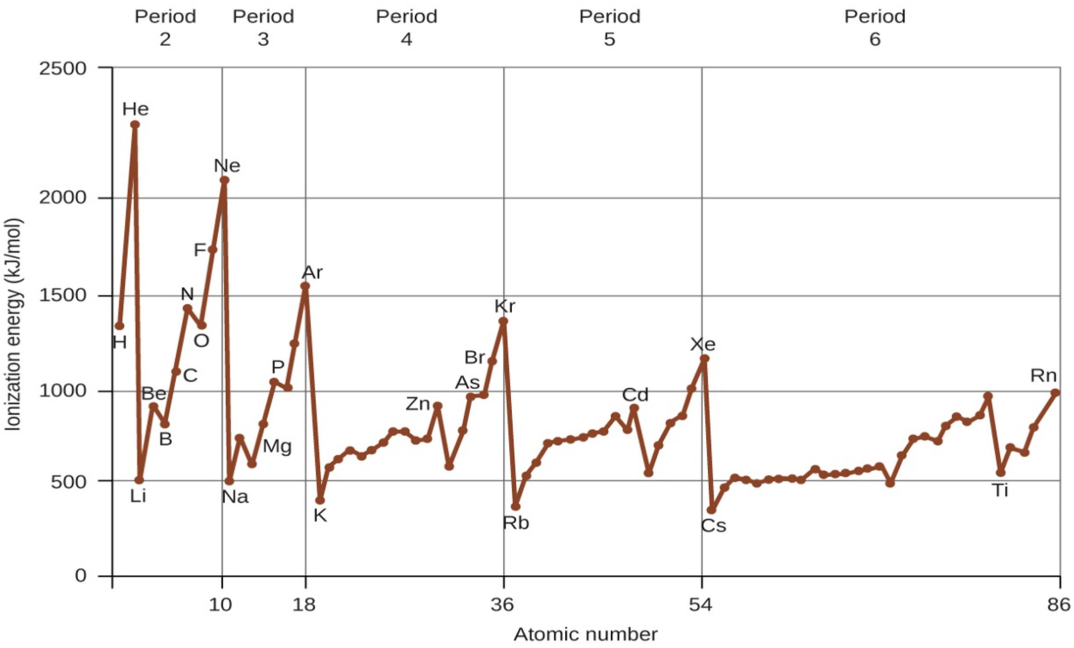
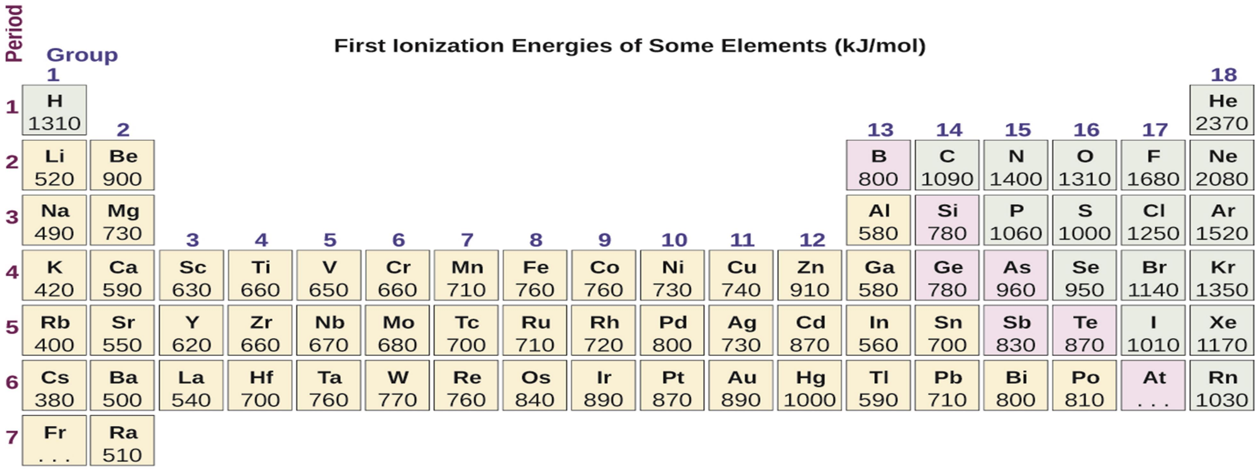


Figure 5.20: The first ionization energy of the elements in the first five periods is plotted against their atomic number.

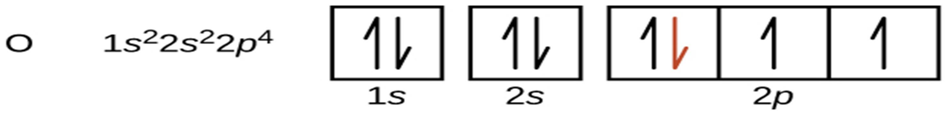


First Ionization Energies of Some Elements (kJ/mol)

Period / Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	**H** 1310																	**He** 2370
2	**Li** 520	**Be** 900											**B** 800	**C** 1090	**N** 1400	**O** 1310	**F** 1680	**Ne** 2080
3	**Na** 490	**Mg** 730											**Al** 580	**Si** 780	**P** 1060	**S** 1000	**Cl** 1250	**Ar** 1520
4	**K** 420	**Ca** 590	**Sc** 630	**Ti** 660	**V** 650	**Cr** 660	**Mn** 710	**Fe** 760	**Co** 760	**Ni** 730	**Cu** 740	**Zn** 910	**Ga** 580	**Ge** 780	**As** 960	**Se** 950	**Br** 1140	**Kr** 1350
5	**Rb** 400	**Sr** 550	**Y** 620	**Zr** 660	**Nb** 670	**Mo** 680	**Tc** 700	**Ru** 710	**Rh** 720	**Pd** 800	**Ag** 730	**Cd** 870	**In** 560	**Sn** 700	**Sb** 830	**Te** 870	**I** 1010	**Xe** 1170
6	**Cs** 380	**Ba** 500	**La** 540	**Hf** 700	**Ta** 760	**W** 770	**Re** 760	**Os** 840	**Ir** 890	**Pt** 870	**Au** 890	**Hg** 1000	**Tl** 590	**Pb** 710	**Bi** 800	**Po** 810	**At** . . .	**Rn** 1030
7	**Fr** . . .	**Ra** 510																

Figure 5.21: This version of the periodic table shows the first ionization energy (IE_1), in kJ/mol, of selected elements.

Another deviation occurs as orbitals become more than one-half filled. The first ionization energy for oxygen is slightly less than that for nitrogen, despite the trend in increasing IE_1 values across a period. Looking at the orbital diagram of oxygen, we can see that removing one electron will eliminate the electron–electron repulsion caused by pairing the electrons in the 2*p* orbital and will result in a half-filled orbital (which is energetically favorable). Analogous changes occur in succeeding periods (note the dip for sulfur after phosphorus in figure 5.21.



Removing an electron from a cation is more difficult than removing an electron from a neutral atom because of the greater electrostatic attraction to the cation. Likewise, removing an electron from a cation with a higher positive charge is more difficult than removing an electron from an ion with a lower charge. Thus, successive ionization energies for one element always increase. As seen in Table 5.3, there is a large increase in the ionization energies for each element. This jump corresponds to removal of the core electrons, which are harder to remove than the valence electrons. For example, Sc and Ga both have three valence electrons, so the rapid increase in ionization energy occurs after the third ionization.

Table 5.3: Successive Ionization Energies for Selected Elements (kJ/mol)

Element	**IE_1**	**IE_2**	**IE_3**	**IE_4**	**IE_5**	**IE_6**	**IE_7**
K	418.8	3051.8	4419.6	5876.9	7975.5	9590.6	11343
Ca	589.8	1145.4	4912.4	6490.6	8153.0	10495.7	12272.9
Sc	633.1	1235.0	2388.7	7090.6	8842.9	10679.0	13315.0
Ga	578.8	1979.4	2964.6	6180	8298.7	10873.9	13594.8
Ge	762.2	1537.5	3302.1	4410.6	9021.4	Not available	Not available
As	944.5	1793.6	2735.5	4836.8	6042.9	12311.5	Not available

Example 5.11

Ranking Ionization Energies

Predict the order of increasing energy for the following processes: IE_1 for Al, IE_1 for Tl, IE_2 for Na, IE_3 for Al.

Solution

Removing the $6p^1$ electron from Tl is easier than removing the $3p^1$ electron from Al because the higher *n* orbital is farther from the nucleus, so $IE_1(Tl) < IE_1(Al)$. Ionizing the third electron from Al($Al^{2+} \longrightarrow Al^{3+} + e^-$) requires more energy because the cation Al^{2+} exerts a stronger pull on the electron than the neutral Al atom, so $IE_1(Al) < IE_3(Al)$. The second ionization energy for sodium removes a core electron, which is a much higher energy process than removing valence electrons. Putting this all together, we obtain: $IE_1(Tl) < IE_1(Al) < IE_3(Al) < IE_2(Na)$.

5.5.4. Variation in Electron Affinities

The electron affinity (EA) is the energy change for the process of adding an electron to a gaseous atom to form an anion (negative ion).

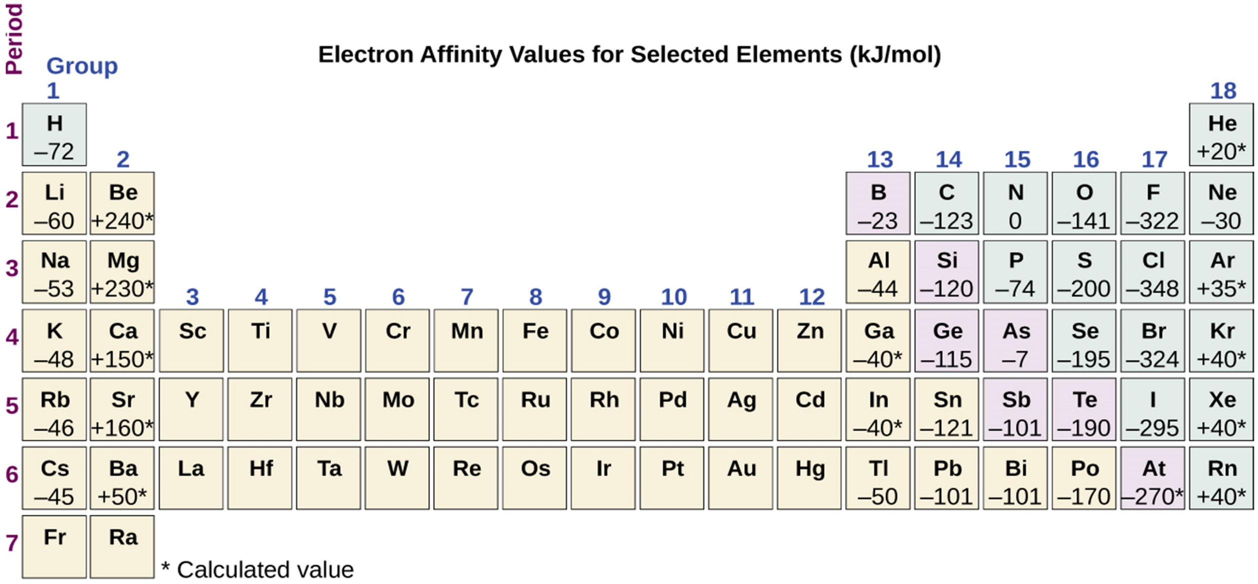
$$X(g) + e^- \longrightarrow X^-(g) \qquad EA_1$$

This process can be either endothermic or exothermic, depending on the element. The EA of some of the elements is given in Figure 5.22. You can see that many of these elements have negative values of EA, which means that energy is released when the gaseous atom accepts an electron. However, for some elements, energy is required for the atom to become negatively charged and the value of their EA is positive. Just as with ionization energy, subsequent EA values are associated with forming ions with more charge. The second EA is the energy associated with adding an electron to an anion to form a –2 ion, and so on.

As we might predict, it becomes easier to add an electron across a series of atoms as the effective nuclear charge of the atoms increases. We find, as we go from left to right across a period, EAs tend to become more negative. The exceptions found among the elements of group 2 (2A), group 15 (5A), and group 18 (8A) can be understood based on the electronic structure of these groups. The noble gases, group 18 (8A), have a completely filled shell and the incoming electron must be added to a higher *n* level, which is more difficult to do. Group 2 (2A) has a filled *ns* subshell, and so the next electron added goes into the higher energy *np*, so, again, the observed EA value is not as the trend would predict. Finally, group 15 (5A) has a half-filled *np* subshell and the next electron must be paired with an existing *np* electron. In all of these cases, the initial relative stability of the electron configuration disrupts the trend in EA.

We also might expect the atom at the top of each group to have the most negative EA; their first ionization potentials suggest that these atoms have the largest effective nuclear charges.

However, as we move down a group, we see that the *second* element in the group most often has the most negative EA. This can be attributed to the small size of the *n* = 2 shell and the resulting large electron – electron repulsions. For example, chlorine, with an EA value of –348 kJ/mol, has the highest value of any element in the periodic table. The E_A of fluorine is –322 kJ/mol. When we add an electron to a fluorine atom to form a fluoride anion (F^-), we add an electron to the *n* = 2 shell. The electron is attracted to the nucleus, but there is also significant repulsion from the other electrons already present in this small valence shell. The chlorine atom has the same electron configuration in the valence shell, but because the entering electron is going into the *n* = 3 shell, it occupies a considerably larger region of space and the electron–electron repulsions are reduced. The entering electron does not experience as much repulsion and the chlorine atom accepts an additional electron more readily, resulting in a more negative EA.


Electron Affinity Values for Selected Elements (kJ/mol)

Period	Group 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H –72																	He +20*
2	Li –60	Be +240*											B –23	C –123	N 0	O –141	F –322	Ne –30
3	Na –53	Mg +230*											Al –44	Si –120	P –74	S –200	Cl –348	Ar +35*
4	K –48	Ca +150*	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga –40*	Ge –115	As –7	Se –195	Br –324	Kr +40*
5	Rb –46	Sr +160*	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In –40*	Sn –121	Sb –101	Te –190	I –295	Xe +40*
6	Cs –45	Ba +50*	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl –50	Pb –101	Bi –101	Po –170	At –270*	Rn +40*
7	Fr	Ra																

* Calculated value

Figure 5:22: This version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements.

The properties discussed in this section (size of atoms and ions, effective nuclear charge, ionization energies, and electron affinities) are central to understanding chemical reactivity. For example, because fluorine has an energetically favorable EA and a large energy barrier to ionization (IE), it is much easier to form fluorine anions than cations. Metallic properties including conductivity and malleability (the ability to be formed into sheets) depend on having electrons that can be removed easily. Thus, metallic character increases as we move down a group and decreases across a period in the same trend observed for atomic size because it is easier to remove an electron that is farther away from the nucleus.

Review Exercise

1. The light produced by a red neon sign is due to the emission of light by excited neon atoms. Qualitatively describe the spectrum produced by passing light from a neon lamp through a prism.
2. An FM radio station found at 103.1 on the FM dial broadcasts at a frequency of 1.031×10^8 s^{-1} (103.1 MHz). What is the wavelength of these radio waves in meters?
3. A bright violet line occurs at 435.8 nm in the emission spectrum of mercury vapor. What amount of energy, in joules, must be released by an electron in a mercury atom to produce a photon of this light?
4. Light with a wavelength of 614.5 nm looks orange. What is the energy, in joules, per photon of this orange light? What is the energy in eV (1 eV = 1.602×10^{-19} J)?
5. Heated lithium atoms emit photons of light with an energy of 2.961×10^{-19} J. Calculate the frequency and wavelength of one of these photons. What is the total energy in 1 mole of these photons? What is the color of the emitted light?
6. When rubidium ions are heated to a high temperature, two lines are observed in its line spectrum at wavelengths (a) 7.9×10^{-7} m and (b) 4.2×10^{-7} m. What are the frequencies of the two lines? What color do we see when we heat a rubidium compound?
7. Photons of infrared radiation are responsible for much of the warmth we feel when holding our hands before a fire. These photons will also warm other objects. How many infrared photons with a wavelength of 1.5×10^{-6} m must be absorbed by the water to warm a cup of water (175 g) from 25.0 °C to 40 °C?
8. One of the radiographic devices used in a dentist's office emits an X-ray of wavelength 2.090×10^{-11} m. What is the energy, in joules, and frequency of this X-ray?
9. The eyes of certain reptiles pass a single visual signal to the brain when the visual receptors are struck by photons of a wavelength of 850 nm. If a total energy of 3.15×10^{-14} J is required to trip the signal, what is the minimum number of photons that must strike the receptor?

10. RGB color television and computer displays use cathode ray tubes that produce colors by mixing red, green, and blue light. If we look at the screen with a magnifying glass, we can see individual dots turn on and off as the colors change. Using a spectrum of visible light, determine the approximate wavelength of each of these colors. What is the frequency and energy of a photon of each of these colors?
11. What is the threshold frequency for sodium metal if a photon with frequency 6.66×10^{14} s^{-1} ejects an electron with 7.74×10^{-20} J kinetic energy? Will the photoelectric effect be observed if sodium is exposed to orange light?
12. Why is the electron in a Bohr hydrogen atom bound less tightly when it has a quantum number of 3 than when it has a quantum number of 1?
13. What does it mean to say that the energy of the electrons in an atom is quantized?
14. Using the Bohr model, determine the energy, in joules, necessary to ionize a ground-state hydrogen atom. Show your calculations.
15. The electron volt (eV) is a convenient unit of energy for expressing atomic-scale energies. It is the amount of energy that an electron gains when subjected to a potential of 1 volt; 1 eV = 1.602×10^{-19} J. Using the Bohr model, determine the energy, in electron volts, of the photon produced when an electron in a hydrogen atom moves from the orbit with $n = 5$ to the orbit with $n = 2$. Show your calculations.
16. Using the Bohr model, determine the lowest possible energy, in joules, for the electron in the Li^{2+} ion.
17. Using the Bohr model, determine the energy of an electron with $n = 6$ in a hydrogen atom.
18. What is the radius, in angstroms, of the orbital of an electron with $n = 8$ in a hydrogen atom?
19. Using the Bohr model, determine the energy in joules of the photon produced when an electron in a He^{+} ion moves from the orbit with $n = 5$ to the orbit with $n = 2$.
20. What are the allowed values for each of the four quantum numbers: n, l, m_l, and m_s?
21. Answer the following questions:
    a) Without using quantum numbers, describe the differences between the shells, subshells, and orbitals of an atom.
    b) How do the quantum numbers of the shells, subshells, and orbitals of an atom differ?
22. Identify the subshell in which electrons with the following quantum numbers are found:
    a) $n = 2, l = 1$ *b)* $n = 4, l = 2$ c) $n = 6, l = 0$

23. . Using complete subshell notation ($1s^2 2s^2 2p^6$, and so forth), predict the electron configurations of the following ions.

a) N^{3-}	c) S^{-}	e) Cr^{2+}
b) Ca^{2+}	d) Cs^{2+}	f) Gd^{3+}

24. In one area of Australia, the cattle did not thrive despite the presence of suitable forage. An investigation showed the cause to be the absence of sufficient cobalt in the soil. Cobalt forms cations in two oxidation states, Co^{2+} and Co^{3+}. Write the electron structure of the two cations.
25. Write a set of quantum numbers for each of the electrons with an *n* of 3 in a Sc atom.
26. Based on their positions in the periodic table, predict which has the smallest atomic radius: Mg, Sr, Si, Cl, I.
27. Based on their positions in the periodic table, predict which has the largest first ionization energy: Mg, Ba, B, O, Te. Li, Cs, N, F, I.
28. Atoms of which group in the periodic table have a valence shell electron configuration of ns^2np^3?
29. Atoms of which group in the periodic table have a valence shell electron configuration of ns^2?
30. List the following ions in order of increasing radius: Li^+, Mg^{2+}, Br^-, Te^{2-}.
31. Which atom and/or ion is (are) isoelectronic with Br^+: Se^{2+}, Se, As^-, Kr, Ga^{3+}, Cl^-?
32. The ionic radii of the ions S^{2-}, Cl^-, and K^+ are 184, 181, 138 pm respectively. Explain why these ions have different sizes even though they contain the same number of electrons.

CHAPTER SIX

Chemical Bonding and Molecular Geometry

Introduction

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

Learning objectives of the chapter: At the end of this chapter you will be able to

- Explain the formation of cations, anions, and ionic compounds
- Describe the formation of covalent bonds
- Define electronegativity and identify the polarity of covalent bonds
- Draw Lewis structures depicting the bonding in simple molecules
- Compute formal charges for atoms in any Lewis structure
- Identify the most reasonable Lewis structure for a given molecule using formal charges
- Explain the concept of resonance and draw Lewis structures representing resonance forms for a given molecule
- Compute lattice energies for ionic compounds using Born-Haber cycle
- Predict the structures of molecules using valence shell electron pair repulsion (VSEPR) theory
- Explain the concepts of polar covalent bonds and molecular polarity

6.1. Ionic Bonding

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

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

Neutral atoms and their associated ions have very different physical and chemical properties. Sodium *atoms* form sodium metal, a soft, silvery-white metal that burns vigorously in air and reacts explosively with water. Chlorine *atoms* form chlorine gas, Cl_2, a yellow-green gas that is extremely corrosive to most metals and very poisonous to animals and plants. The vigorous reaction between the elements sodium and chlorine forms the white, crystalline compound sodium chloride, common table salt, which contains sodium *cations* and chloride *anions* (Figure 6.1). The compound composed of these ions exhibits properties entirely different from the properties of the elements sodium and chlorine. Chlorine is poisonous, but sodium chloride is essential to life; sodium atoms react vigorously with water, but sodium chloride simply dissolves in water.


(a) (b) (c)

Figure 6.1: (a) Sodium is a soft metal that must be stored in mineral oil to prevent reaction with air or water. (b) Chlorine is a pale yellow-green gas. (c) When combined, they form white crystals of sodium chloride (table salt).

6.1.1. The Formation of Ionic Compounds

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

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

It is important to note, however, that the formula for an ionic compound does notrepresent the physical arrangement of its ions. It is incorrect to refer to a sodium chloride (NaCl) "molecule" because there is not a single ionic bond, per se, between any specific pair of sodium and chloride ions. The attractive forces between ions are isotropic-the same in all directions-meaning that any particular ion is equally attracted to all of the nearby ions of opposite charge. This results in the ions arranging themselves into a tightly bound, three-dimensional lattice structure. Sodium chloride, for example, consists of a regular arrangement of equal numbers of Na^+ cations and Cl^- anions (Figure 6.2).

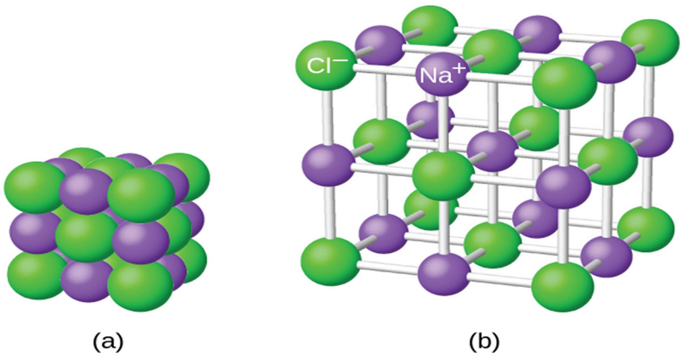


Figure 6.2: The atoms in sodium chloride (common table salt) are arranged to (a) maximize opposite charges interacting. The smaller spheres represent sodium ions, the larger ones represent chloride ions. In the expanded view (b), the geometry can be seen more clearly. Note that each ion is "bonded" to all of the surrounding ions—six in this case.

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

$$\mathbf{NaCl(s) \longrightarrow N\boldsymbol{a}^+(g) + Cl^-(g) \quad \Delta H = 769kJ}$$

6.1.2. Electronic Structures of Cations and Anions

When forming a cation, an atom of a main group element tends to lose all of its valence electrons, thus assuming the electronic structure of the noble gas that precedes it in the periodic table. For groups 1 (the alkali metals) and 2 (the alkaline earth metals), the group numbers are equal to the numbers of valence shell electrons and, consequently, to the charges of the cations formed from atoms of these elements when all valence shell electrons are removed. For example, calcium is a group 2 element whose neutral atoms have 20 electrons and a ground state electron configuration of $1s^22s^22p^63s^23p^64s^2$. When a Ca atom loses both of its valence electrons, the result is a cation with 18 electrons, a 2+ charge, and an electron configuration of $1s^22s^22p^63s^23p^6$. The Ca^{2+} ion is therefore isoelectronic with the noble gas Ar.

For groups 13–17, the group numbers exceed the number of valence electrons by 10 (accounting for the possibility of full *d* subshells in atoms of elements in the fourth and greater periods). Thus, the charge of a cation formed by the loss of all valence electrons is equal to the group number minus 10. For example, aluminum (in group 13) forms 3+ ions (Al^{3+}).

Exceptions to the expected behavior involve elements toward the bottom of the groups. In addition to the expected ions Tl^{3+}, Sn^{4+}, Pb^{4+}, and Bi^{5+}, a partial loss of these atoms' valence shell electrons can also lead to the formation of Tl^{+}, Sn^{2+}, Pb^{2+}, and Bi^{3+} ions. The formation of these 1+, 2+, and 3+ cations is ascribed to the inert pair effect, which reflects the relatively low energy of the valence *s*-electron pair for atoms of the heavy elements of groups 13, 14, and 15. Mercury (group 12) also exhibits an unexpected behavior: it forms a diatomic ion, Hg_2^{2+} (an ion formed from two mercury atoms, with an Hg-Hg bond), in addition to the expected monatomic ion Hg^{2+} (formed from only one mercury atom).

Transition and inner transition metal elements behave differently than main group elements. Most transition metal cations have 2+ or 3+ charges that result from the loss of their outermost *s* electron(s) first, sometimes followed by the loss of one or two *d* electrons from the next-to-outermost shell. For example, iron ($1s^22s^22p^63s^23p^63d^64s^2$) forms the ion Fe^{2+} ($1s^22s^22p^63s^23p^63d^6$) by the loss of the 4*s* electrons and the ion Fe^{3+} ($1s^22s^22p^63s^23p^63d^5$) by the loss of the 4*s* electrons and one of the 3*d* electrons. Although the *d* orbitals of the transition elements are-according to the Aufbau principle—the last to fill when building up electron configurations, the outermost *s* electrons are the first to be lost when these atoms ionize. When the inner transition metals form ions, they usually have a 3+ charge, resulting from the loss of their outermost *s* electrons and a *d* or *f* electron.

Example 6.1

Determining the Electronic Structures of Cations

There are at least 14 elements categorized as "essential trace elements" for the human body. They are called "essential" because they are required for healthy bodily functions, "trace" because they are required only in small amounts, and "elements" in spite of the fact that they are really ions. Two of these essential trace elements, chromium and zinc, are required as Cr^{3+} and Zn^{2+}. Write the electron configurations of these cations.

Solution

First, write the electron configuration for the neutral atoms:

Zn: $[Ar]3d^{10}4s^2$

Cr: $[Ar]3d^54s^1$

Next, remove electrons from the highest energy orbital. For the transition metals, electrons are removed from the *s* orbital first and then from the *d* orbital. For the *p*-block elements, electrons are removed from the *p* orbitals and then from the *s* orbital. Zinc is a member of group 12, so it should have a charge of 2+, and thus loses only the two electrons in its *s* orbital. Chromium is a transition element and should lose its *s* electrons and then its *d* electrons when forming a cation. Thus, we find the following electron configurations of the ions:

Zn^{2+}: $[Ar]3d^{10}$

Cr^{3+}: $[Ar]3d^{3}$

Most monatomic anions form when a neutral nonmetal atom gains enough electrons to completely fill its outer *s* and *p* orbitals, thereby reaching the electron configuration of the next noble gas. Thus, it is simple to determine the charge on such a negative ion: The charge is equal to the number of electrons that must be gained to fill the *s* and *p* orbitals of the parent atom. Oxygen, for example, has the electron configuration $1s^22s^22p^4$, whereas the oxygen anion has the electron configuration of the noble gas neon (Ne), $1s^22s^22p^6$. The two additional electrons required to fill the valence orbitals give the oxide ion the charge of 2– (O^{2-}).

Example 6.2

Determining the Electronic Structure of Anions

Selenium and iodine are two essential trace elements that form anions. Write the electron configurations of the anions.

Solution

Se^{2-}: $[Ar]3d^{10}4s^24p^6$ I^-: $[Kr]4d^{10}5s^25p^6$

6.2. Covalent Bonding

Ionic bonding results from the electrostatic attraction of oppositely charged ions that are typically produced by the transfer of electrons between metallic and nonmetallic atoms. A different type of bonding results from the mutual attraction of atoms for a “shared” pair of electrons. Such bonds are called covalent bonds. Covalent bonds are formed between two atoms when both have similar tendencies to attract electrons to themselves (i.e., when both atoms have identical or fairly similar ionization energies and electron affinities). For example, two hydrogen atoms bond covalently to form an H_2 molecule; each hydrogen atom in the H_2 molecule has two electrons stabilizing it, giving each atom the same number of valence electrons as the noble gas He.

Compounds that contain covalent bonds exhibit different physical properties than ionic compounds. Because the attraction between molecules, which are electrically neutral, is weaker than that between electrically charged ions, covalent compounds generally have much lower melting and boiling points than ionic compounds. In fact, many covalent compounds are liquids or gases at room temperature, and, in their solid states, they are typically much softer than ionic solids. Furthermore, whereas ionic compounds are good conductors of electricity when dissolved in water, most covalent compounds are insoluble in water; since they are electrically neutral, they are poor conductors of electricity in any state.

6.2.1. Formation of Covalent Bonds

Nonmetal atoms frequently form covalent bonds with other nonmetal atoms. For example, the hydrogen molecule, H_2, contains a covalent bond between its two hydrogen atoms. Figure 6.3 illustrates why this bond is formed. Starting on the far right, we have two separate hydrogen atoms with a particular potential energy, indicated by the red line. Along the x-axis is the distance between the two atoms. As the two atoms approach each other (moving left along the x-axis), their valence orbitals (1*s*) begin to overlap. The single electrons on each hydrogen atom then interact with both atomic nuclei, occupying the space around both atoms. The strong attraction of each shared electron to both nuclei stabilizes the system, and the potential energy decreases as the bond distance decreases. If the atoms continue to approach each other, the positive charges in the two nuclei begin to repel each other, and the potential energy increases. The bond length is determined by the distance at which the lowest potential energy is achieved.

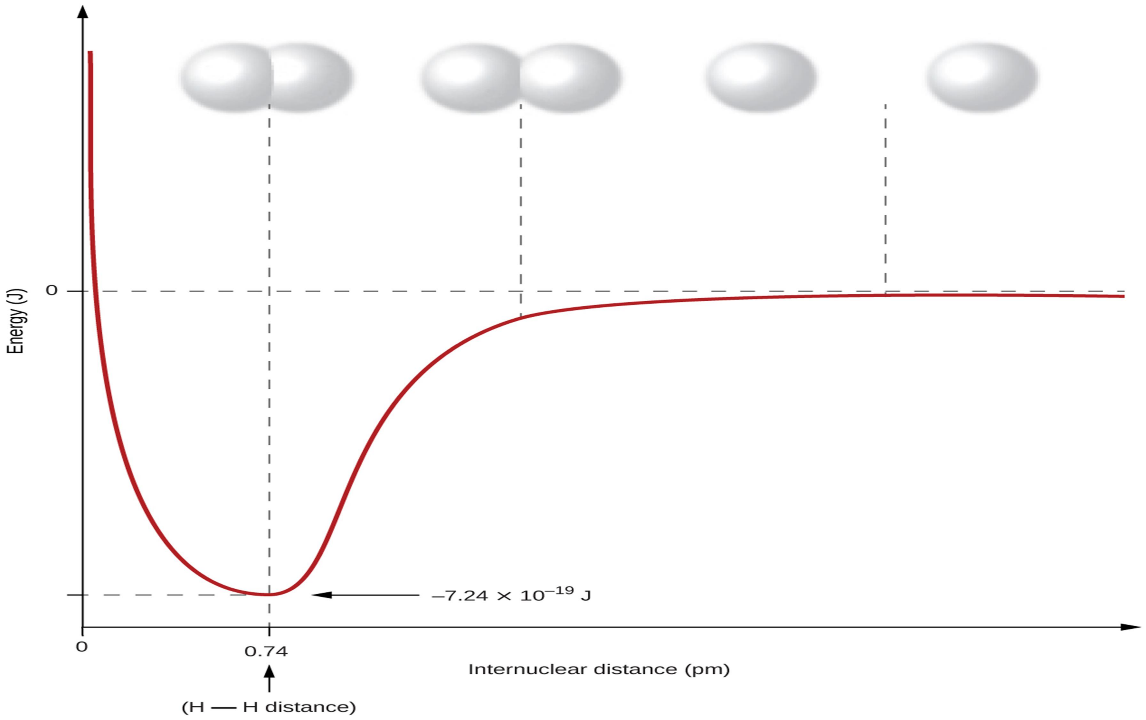


Figure 6.3: The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the inter-nuclear distance at which the lowest potential energy is achieved.

It is essential to remember that energy must be added to break chemical bonds (an endothermic process), whereas forming chemical bonds releases energy (an exothermic process). In the case of H_2, the covalent bond is very strong; a large amount of energy, 436 kJ, must be added to break the bonds in one mole of hydrogen molecules and cause the atoms to separate:

$$\boldsymbol{H_2(g) \longrightarrow 2H(g) \quad \Delta H = 436kJ}$$

Conversely, the same amount of energy is released when one mole of H_2 molecules forms from two moles of H atoms:

$$\boldsymbol{2H(g) \longrightarrow H_2(g)\Delta H = -436kJ}$$

6.2.2. Polarity of Covalent Bonds

If the atoms that form a covalent bond are identical, as in H_2, Cl_2, and other diatomic molecules, then the electrons in the bond must be shared equally. We refer to this as a pure covalent bond. Electrons shared in pure covalent bonds have an equal probability of being near each nucleus.

In the case of Cl_2, each atom starts off with seven valence electrons, and each Cl shares one electron with the other, forming one covalent bond:

$$Cl + Cl \longrightarrow Cl_2$$

The total number of electrons around each individual atom consists of six nonbonding electrons and two shared (i.e., bonding) electrons for eight total electrons, matching the number of valence electrons in the noble gas argon. Since the bonding atoms are identical, Cl_2 also features a pure covalent bond.

When the atoms linked by a covalent bond are different, the bonding electrons are shared, but no longer equally. Instead, the bonding electrons are more attracted to one atom than the other, giving rise to a shift of electron density toward that atom. This unequal distribution of electrons is known as a polar covalent bond, characterized by a partial positive charge on one atom and a partial negative charge on the other. The atom that attracts the electrons more strongly acquires the partial negative charge and vice versa. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Thus, in an HCl molecule, the chlorine atom carries a partial negative charge and the hydrogen atom has a partial positive charge. Figure 6.4 shows the distribution of electrons in the H–Cl bond. Note that the shaded area around Cl is much larger than it is around H. Compare this to Figure 6.2, which shows the even distribution of electrons in the H_2 nonpolar bond.

We sometimes designate the positive and negative atoms in a polar covalent bond using a lowercase Greek letter "delta," δ, with a plus sign or minus sign to indicate whether the atom has a partial positive charge (δ+) or a partial negative charge (δ–). This symbolism is shown for the H–Cl molecule in Figure 6.3.

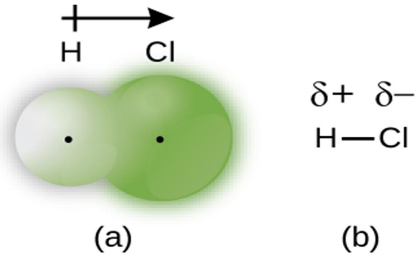


Figure 6.4: (a) The distribution of electron density in the HCl molecule is uneven. The electron density is greater around the chlorine nucleus. The small, black dots indicate the location of the hydrogen and chlorine nuclei in the molecule. (b) Symbols δ^{+} and δ^{-} indicate the polarity of the H–Cl bond.

6.3. Lewis structures

We also use Lewis symbols to indicate the formation of covalent bonds, which are shown in Lewis structures, drawings that describe the bonding in molecules and polyatomic ions. For example, when two chlorine atoms form a chlorine molecule, they share one pair of electrons:

The Lewis structure indicates that each Cl atom has three pairs of electrons that are not used in bonding (called lone pairs) and one shared pair of electrons (written between the atoms). A dash (or line) is sometimes used to indicate a shared pair of electrons:

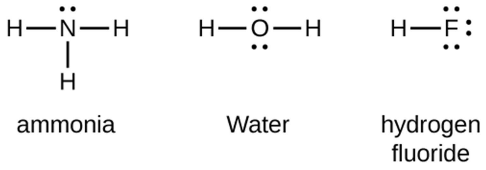
A single shared pair of electrons is called a single bond. Each Cl atom interacts with eight valence electrons: the six in the lone pairs and the two in the single bond.

The Octet Rule

The other halogen molecules (F_2, Br_2, I_2, and At_2) form bonds like those in the chlorine molecule: one single bond between atoms and three lone pairs of electrons per atom. This allows each halogen atom to have a noble gas electron configuration. The tendency of main group atoms to form enough bonds to obtain eight valence electrons is known as the octet rule.

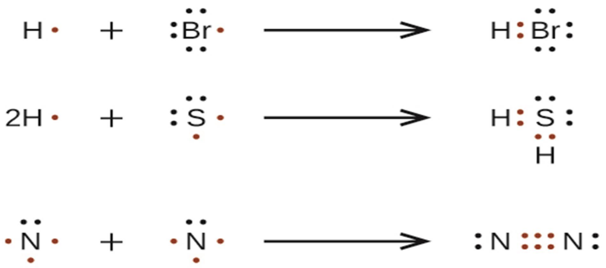
The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons); this is especially true of the nonmetals of the second period of the periodic table (C, N, O, and F). For example, each atom of a group 14 element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming four covalent bonds, as illustrated here for carbon in CCl_4 (carbon tetrachloride) and silicon in SiH_4 (silane). Because hydrogen only needs two electrons to fill its valence shell, it is an exception to the octet rule. The transition elements and inner transition elements also do not follow the octet rule:

Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in NH_3 (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:



6.3.1. Writing Lewis Structures with the Octet Rule

For very simple molecules and molecular ions, we can write the Lewis structures by merely pairing up the unpaired electrons on the constituent atoms. See these examples:



For more complicated molecules and molecular ions, it is helpful to follow the step-by-step procedure outlined here:

1. Determine the total number of valence (outer shell) electrons. For cations, subtract one electron for each positive charge. For anions, add one electron for each negative charge.
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom. (Generally, the least electronegative element should be placed in the center.) Connect each atom to the central atom with a single bond (one electron pair).
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.
4. Place all remaining electrons on the central atom.
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

Let us determine the Lewis structures of SiH_4, CHO_2^-, NO^+, and OF_2 as examples in following this procedure:

1. Determine the total number of valence (outer shell) electrons in the molecule or ion.

   For a molecule, we add the number of valence electrons on each atom in the molecule: SiH_4

Si: 4 valence electrons/atom×1 atom = 4
+H: 1 valence electron/atom×4atoms = 4
= 8 valence electrons

For a negative ion, such as CHO_2^-, we add the number of valence electrons on the atoms to the number of negative charges on the ion (one electron is gained for each single negative charge):

CHO_2^-
C: 4 valence electrons/atom×1 atom=4
H: 1 valence electron/atom×1 atom=1
O: 6 valence electrons/atom×2 atoms=12
+1 additional electron
=18 valence electrons

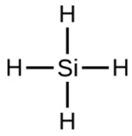
For a positive ion, such as NO^+, we add the number of valence electrons on the atoms in the ion and then subtract the number of positive charges on the ion (one electron is lost for each single positive charge) from the total number of valence electrons:

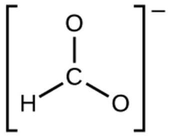
NO^+
N: 5 valence electrons/atom×1 atom=5
O: 6 valence electron/atom×1 atom=6
+ −1 electron (positive charge = -1
=10 valence electrons

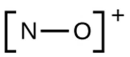
Since OF_2 is a neutral molecule, we simply add the number of valence electrons:

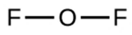
OF_2
O: 6 valence electrons/atom×1 atom=6
F: 7 valence electrons/atom×2 atoms = 14
= 20 valence electrons

2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. (Note that we denote ions with brackets around the structure, indicating the charge outside the brackets:)





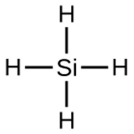


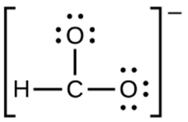


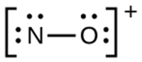
When several arrangements of atoms are possible, as for CHO_2^-, we must use experimental evidence to choose the correct one. In general, the less electronegative elements are more likely to be central atoms. In CHO_2^-, the less electronegative carbon atom occupies the central position with the oxygen and hydrogen atoms surrounding it. Other examples include P in $POCl_3$, S in SO_2, and Cl in ClO_4^-. An exception is that hydrogen is almost never a central atom. As the most electronegative element, fluorine also cannot be a central atom.

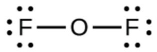
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.

There are no remaining electrons on SiH_4, so it is unchanged:



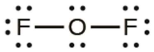






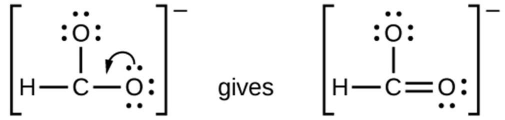
4. Place all remaining electrons on the central atom.

1. For SiH_4, CHO_{2-}, and NO^+, there are no remaining electrons; we already placed all of the electrons determined in Step 1.
2. For OF_2, we had 16 electrons remaining in Step 3, and we placed 12, leaving 4 to be placed on the central atom:

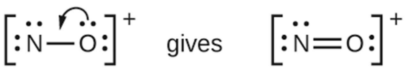


5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

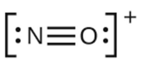
- SiH_4: Si already has an octet, so nothing needs to be done.
- CHO_2^-: We have distributed the valence electrons as lone pairs on the oxygen atoms, but the carbon atom lacks an octet:



NO^+: For this ion, we added eight valence electrons, but neither atom has an octet. We cannot add any more electrons since we have already used the total that we found in Step 1, so we must move electrons to form a multiple bond:



This still does not produce an octet, so we must move another pair, forming a triple bond:



In OF_2, each atom has an octet as drawn, so nothing changes

Example 6.3

Writing Lewis Structures

Write the Lewis structure of the following molecules?

- HCN, H_3CCH_3, HCCH, NH_3

Solution

Step 1: Calculate the number of valence electrons.

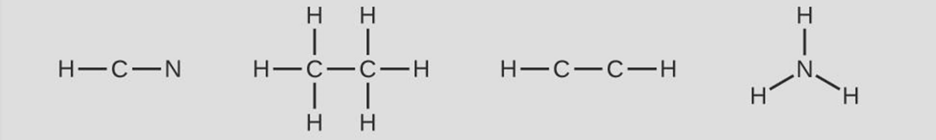
HCN: (1 × 1) + (4 × 1) + (5 × 1) = 10

H_3CCH_3: (1 × 3) + (2 × 4) + (1 × 3) = 14

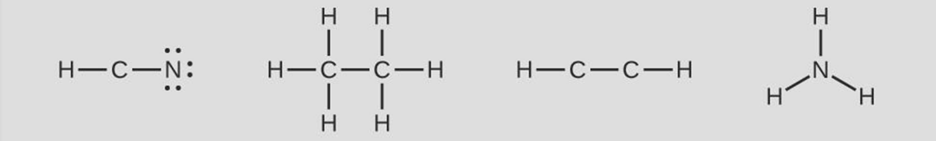
HCCH: (1 × 1) + (2 × 4) + (1 × 1) = 10

NH_3: (5 × 1) + (3 × 1) = 8

Step 2: Draw a skeleton and connect the atoms with single bonds. Remember that H is never a central atom:



Step 3: Where needed, distribute electrons to the terminal atoms:



HCN: six electrons placed on N

H_3CCH_3: no electrons remain

HCCH: no terminal atoms capable of accepting electrons

NH_3: no terminal atoms capable of accepting electrons

Step 4: Where needed, place remaining electrons on the central atom:

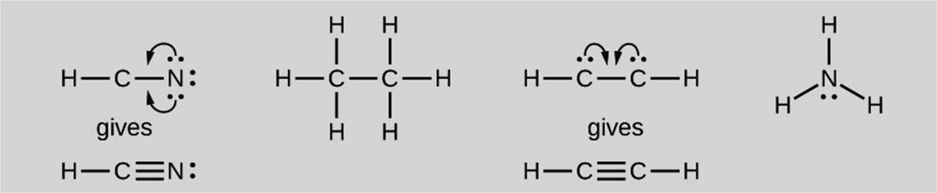
Step 5: Where needed, rearrange electrons to form multiple bonds in order to obtain an octet on each atom:

HCN: form two more C–N bonds

H_3CCH_3: all atoms have the correct number of electrons

HCCH: form a triple bond between the two carbon atoms

NH_3: all atoms have the correct number of electrons



6.3.2. Exceptions to the Octet Rule

Many covalent molecules have central atoms that do not have eight electrons in their Lewis structures. These molecules fall into three categories:

- Odd-electron molecules have an odd number of valence electrons, and therefore have an unpaired electron.
- Electron-deficient molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
- Hypervalent molecules have a central atom that has more electrons than needed for a noble gas configuration.

Odd-electron Molecules

We call molecules that contain an odd number of electrons free radicals. Nitric oxide, NO, is an example of an odd-electron molecule; it is produced in internal combustion engines when oxygen and nitrogen react at high temperatures.

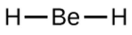
To draw the Lewis structure for an odd-electron molecule like NO, we follow the same five steps we would for other molecules, but with a few minor changes:

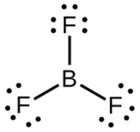
1. *Determine the total number of valence (outer shell) electrons*. The sum of the valence electrons is 5 (from N) + 6 (from O) = 11. The odd number immediately tells us that we have a free radical, so we know that not every atom can have eight electrons in its valence shell.
2. *Draw a skeleton structure of the molecule*. We can easily draw a skeleton with an N–O single bond N–O
3. *Distribute the remaining electrons as lone pairs on the terminal atoms*. In this case, there is no central atom, so we distribute the electrons around both atoms. We give eight electrons to the more electronegative atom in these situations; thus oxygen has the filled valence shell:

4. Place all remaining electrons on the central atom. Since there are no remaining electrons, this step does not apply.
5. Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever possible. We know that an odd-electron molecule cannot have an octet for every atom, but we want to get each atom as close to an octet as possible. In this case, nitrogen has only five electrons around it. To move closer to an octet for nitrogen, we take one of the lone pairs from oxygen and use it to form a NO double bond. (We cannot take another lone pair of electrons on oxygen and form a triple bond because nitrogen would then have nine electrons.)

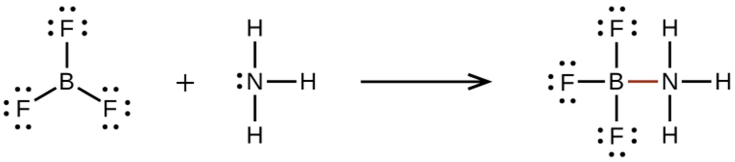
Electron-deficient Molecules

We will also encounter a few molecules that contain central atoms that do not have a filled valence shell. Generally, these are molecules with central atoms from groups 2 and 13, outer atoms that are hydrogen, or other atoms that do not form multiple bonds. For example, in the Lewis structures of beryllium dihydride, BeH_2, and boron trifluoride, BF_3, the beryllium and boron atoms each have only four and six electrons, respectively. It is possible to draw a structure with a double bond between a boron atom and a fluorine atom in BF_3, satisfying the octet rule, but experimental evidence indicates the bond lengths are closer to that expected for B–F single bonds. This suggests the best Lewis structure has three B–F single bonds and an electron deficient boron. The reactivity of the compound is also consistent with an electron deficient boron. However, the B–F bonds are slightly shorter than what is actually expected for B–F single bonds, indicating that some double bond character is found in the actual molecule.





An atom like the boron atom in BF_3, which does not have eight electrons, is very reactive. It readily combines with a molecule containing an atom with a lone pair of electrons. For example, NH_3 reacts with BF_3 because the lone pair on nitrogen can be shared with the boron atom:



Example 6.4

Writing Lewis Structures:

Octet Rule Violations Xenon is a noble gas, but it forms a number of stable compounds. We examined XeF_4 earlier. What are the Lewis structures of XeF_2 and XeF_6?

Solution

We can draw the Lewis structure of any covalent molecule by following the six steps discussed earlier. In this case, we can condense the last few steps, since not all of them apply.

Step 1: *Calculate the number of valence electrons:*

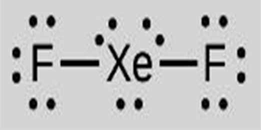
XeF_2: 8 + (2 × 7) = 22

XeF_6: 8 + (6 × 7) = 50

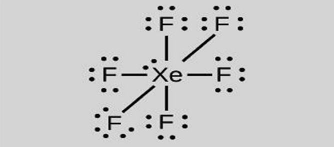
Step 2: *Draw a skeleton joining the atoms by single bonds.* Xenon will be the central atom because fluorine cannot be a central atom:

Step 3: *Distribute the remaining electrons.*

XeF_2: We place three lone pairs of electrons around each F atom, accounting for 12 electrons and giving each F atom 8 electrons. Thus, six electrons (three lone pairs) remain. These lone pairs must be placed on the Xe atom. This is acceptable because Xe atoms have empty valence shell *d* orbitals and can accommodate more than eight electrons. The Lewis structure of XeF_2 shows two bonding pairs and three lone pairs of electrons around the Xe atom



XeF_6: We place three lone pairs of electrons around each F atom, accounting for 36 electrons. Two electrons remain, and this lone pair is placed on the Xe atom:



6.4. Formal Charges and Resonances

In the previous section, we discussed how to write Lewis structures for molecules and polyatomic ions. As we have seen, however, in some cases, there is seemingly more than one valid structure for a molecule. We can use the concept of formal charges to help us predict the most appropriate Lewis structure when more than one is reasonable.

6.4.1. Calculating Formal Charge

The **formal charge** of an atom in a molecule is the *hypothetical* charge the atom would have if we could redistribute the electrons in the bonds evenly between the atoms. Another way of saying this is that formal charge results when we take the number of valence electrons of a neutral atom, subtract the nonbonding electrons, and then subtract the number of bonds connected to that atom in the Lewis structure.

Thus, we calculate formal charge as follows:

$$\textbf{Formal charge} = \#\,\textbf{valence shell electrons (fre ato} \quad - \#\,\textbf{non} - \textbf{bondin electrons} - \frac{1}{2}\#\,\textbf{bonding electrons}$$

We can double-check formal charge calculations by determining the sum of the formal charges for the whole structure. The sum of the formal charges of all atoms in a molecule must be zero; the sum of the formal charges in an ion should equal the charge of the ion.

We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

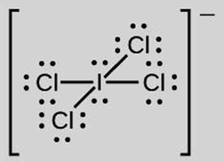
Example 6.5

Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen ion ICl_4^-.

Solution

Step 1: We divide the bonding electron pairs equally for all I–Cl bonds:



Step 2: *We assign lone pairs of electrons to their atoms*. Each Cl atom now has seven electrons Assigned to it, and the I atom has eight.

Step 3: *Subtract this number from the number of valence electrons for the neutral atom:*

I: 7 – 8 = –1

Cl: 7 – 7 = 0

The sum of the formal charges of all the atoms equals –1, which is identical to the charge of the ion (–1).

✍**Check Your Learning**

Calculate the formal charge for each atom in the carbon monoxide molecule:

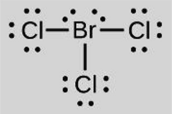
Example 6.6

Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen molecule $BrCl_3$.

Solution

Step 1: *Assign one of the electrons in each Br–Cl bond to the Br atom and one to the Cl atom in that bond:*



Step 2: *Assign the lone pairs to their atom.* Now each Cl atom has seven electrons and the Br atom has seven electrons.

Step 3: *Subtract this number from the number of valence electrons for the neutral atom.* This gives the formal charge:

Br: 7 – 7 = 0 Cl: 7 – 7 = 0

All atoms in $BrCl_3$ have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.

✍**Check Your Learning**

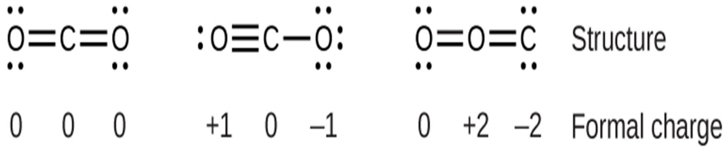
Determine the formal charge for each atom in NCl_3.

6.4.2. Predicting molecular structure using formal charge

The arrangement of atoms in a molecule or ion is called its molecular structure. In many cases, following the steps for writing Lewis structures may lead to more than one possible molecular structure-different multiple bond and lone-pair electron placements or different arrangements of atoms, for instance. A few guidelines involving formal charge can be helpful in deciding which of the possible structures is most likely for a particular molecule or ion:

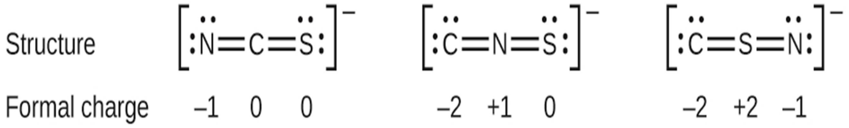
1. A molecular structure in which all formal charges are zero is preferable to one in which some formal charges are not zero.
2. If the Lewis structure must have nonzero formal charges, the arrangement with the smallest nonzero formal charges is preferable.
3. Lewis structures are preferable when adjacent formal charges are zero or of the opposite sign.
4. When we must choose among several Lewis structures with similar distributions of formal charges, the structure with the negative formal charges on the more electronegative atoms is preferable.

To see how these guidelines apply, let us consider some possible structures for carbon dioxide, CO_2. We know from our previous discussion that the less electronegative atom typically occupies the central position, but formal charges allow us to understand *why* this occurs. We can draw three possibilities for the structure: carbon in the center and double bonds, carbon in the center with a single and triple bond, and oxygen in the center with double bonds:



Comparing the three formal charges, we can definitively identify the structure on the left as preferable because it has only formal charges of zero (Guideline 1).

As another example, the thiocyanate ion, an ion formed from a carbon atom, a nitrogen atom, and a sulfur atom, could have three different molecular structures: NCS^-, CNS^-, or CSN^-. The formal charges present in each of these molecular structures can help us pick the most likely arrangement of atoms. Possible Lewis structures and the formal charges for each of the three possible structures for the thiocyanate ion are shown here:



Note that the sum of the formal charges in each case is equal to the charge of the ion (–1). However, the first arrangement of atoms is preferred because it has the lowest number of atoms with nonzero formal charges (Guideline 2). Also, it places the least electronegative atom in the center, and the negative charge on the more electronegative element (Guideline 4).

Example 6.7

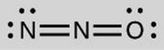
Using Formal Charge to Determine Molecular Structure

Nitrous oxide, N_2O, commonly known as laughing gas, is used as an anesthetic in minor surgeries, such as the routine extraction of wisdom teeth. Which is the likely structure for nitrous oxide?

Solution

Determining formal charge yields the following:

The structure with a terminal oxygen atom best satisfies the criteria for the most stable distribution of formal charge:



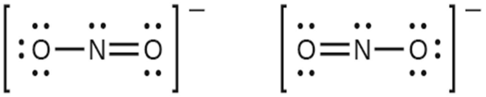
The number of atoms with formal charges are minimized (Guideline 2), and there is no formal charge larger than one (Guideline 2). This is again consistent with the preference for having the less electronegative atom in the central position.

Check Your Learning

Which is the most likely molecular structure for the nitrite (NO_2^-) ion?

6.4.3. Resonance

The more likely structure for the nitrite anion may actually be drawn in two different ways, distinguished by the locations of the N-O and N=O bonds:

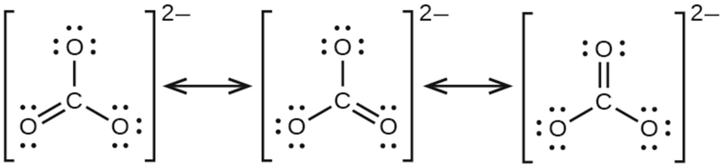


If nitrite ions do indeed contain a single and a double bond, we would expect for the two bond lengths to be different. A double bond between two atoms is shorter (and stronger) than a single bond between the same two atoms. Experiments show, however, that both N–O bonds in NO_2^- have the same strength and length, and are identical in all other properties.

It is not possible to write a single Lewis structure for NO_2^- in which nitrogen has an octet and both bonds are equivalent. Instead, we use the concept of resonance: if two or more Lewis structures with the same arrangement of atoms can be written for a molecule or ion, the actual distribution of electrons is an *average* of that shown by the various Lewis structures. The actual distribution of electrons in each of the nitrogen-oxygen bonds in NO_2^- is the average of a double bond and a single bond. We call the individual Lewis structures resonance forms. The actual electronic structure of the molecule (the average of the resonance forms) is called a resonance hybrid of the individual resonance forms. A double-headed arrow between Lewis structures indicates that they are resonance forms.

We should remember that a molecule described as a resonance hybrid *never* possesses an electronic structure described by either resonance form. It does not fluctuate between resonance forms; rather, the actual electronic structure is *always* the average of that shown by all resonance forms.

The carbonate anion, CO_3^{2-}, provides a second example of resonance:



One oxygen atom must have a double bond to carbon to complete the octet on the central atom. All oxygen atoms, however, are equivalent, and the double bond could form from any one of the three atoms. This gives rise to three resonance forms of the carbonate ion. Because we can write three identical resonance structures, we know that the actual arrangement of electrons in the carbonate ion is the average of the three structures. Again, experiments show that all three C–O bonds are exactly the same.

6.5. Strengths of ionic and covalent bonds

A bond's strength describes how strongly each atom is joined to another atom, and therefore how much energy is required to break the bond between the two atoms. In this section, you will learn about the bond strength of covalent bonds, and then compare that to the strength of ionic bonds, which is related to the lattice energy of a compound.

6.5.1. Ionic bond strength and lattice energy

An ionic compound is stable because of the electrostatic attraction between its positive and negative ions. The lattice energy of a compound is a measure of the strength of this attraction. The lattice energy ($\Delta\mathrm{H}_{lattice}$) of an ionic compound is defined as the energy required to separate one mole of the solid into its component gaseous ions. For the ionic solid MX, the lattice energy is the enthalpy change of the process:

$$\boldsymbol{MX(s) \longrightarrow Mn + (g) + Xn - (g) \quad \Delta H_{lattice}}$$

Note that we are using the convention where the ionic solid is separated into ions, so our lattice energies will be *endothermic* (positive values). Some texts use the equivalent but opposite convention, defining lattice energy as the energy released when separate ions combine to form a lattice and giving negative (exothermic) values. Thus, if you are looking up lattice energies in another reference, be certain to check which definition is being used. In both cases, a larger magnitude for lattice energy indicates a more stable ionic compound. For sodium chloride, $\Delta\mathrm{H}_{lattice}$= +769 kJ. Thus, it requires 769 kJ to separate one mole of solid NaCl into gaseous Na^+ and Cl^- ions. When one mole each of gaseous Na^+ and Cl^- ions form solid NaCl, 769 kJ of heat is released.

The lattice energy$\Delta\mathrm{H}_{lattice}$ of an ionic crystal can be expressed by the following equation (derived from Coulomb's law, governing the forces between electric charges):

$$\boldsymbol{\Delta Hlattice = \frac{C(Z^+)}{Z^-} R_0}$$

In which C is a constant that depends on the type of crystal structure; Z^+ and Z^- are the charges on the ions; and R_o is the interionic distance (the sum of the radii of the positive and negative ions). Thus, the lattice energy of an ionic crystal increases rapidly as the charges of the ions increase and the sizes of the ions decrease. When all other parameters are kept constant, doubling the charge of both the cation and anion quadruples the lattice energy. For example, the lattice energy of LiF (Z^+ and $Z^- = 1$) is 1023 kJ/mol, whereas that of MgO (Z^+ and $Z^- = 2$) is 3900 kJ/mol (R_o is nearly the same-about 200 pm for both compounds).

Different interatomic distances produce different lattice energies. For example, we can compare the lattice energy of MgF_2 (2957 kJ/mol) to that of MgI_2 (2327 kJ/mol) to observe the effect on lattice energy of the smaller ionic size of F^- as compared to I^-.

Example 6.8

Lattice Energy Comparisons

The precious gem ruby is aluminum oxide, Al_2O_3, containing traces of Al^{3+}. The compound Al_2Se_3 is used in the fabrication of some semiconductor devices. Which has the larger lattice energy, Al_2O_3 or Al_2Se_3?

Solution

In these two ionic compounds, the charges Z^+ and Z^- are the same, so the difference in lattice energy will depend upon R_o. The O^{2-} ion is smaller than the Se^{2-} ion. Thus, Al_2O_3 would have a shorter interionic distance than Al_2Se_3, and Al_2O_3 would have the larger lattice energy.

✍**Check Your Learning**

Zinc oxide, ZnO, is a very effective sunscreen. How would the lattice energy of ZnO compare to that of NaCl?

The Born-Haber Cycle

It is not possible to measure lattice energies directly. However, the lattice energy can be calculated using the equation given in the previous section or by using a thermochemical cycle. The Born-Haber cycle is an application of Hess's law that breaks down the formation of an ionic solid into a series of individual steps:

- ΔH_f^0, the standard enthalpy of formation of the compound
- IE, the ionization energy of the metal
- EA, the electron affinity of the nonmetal
- ΔH_s^0, the enthalpy of sublimation of the metal
- *D*, the bond dissociation energy of the nonmetal
- $\Delta \mathrm{H}_{\mathrm{lattice}}$, the lattice energy of the compound

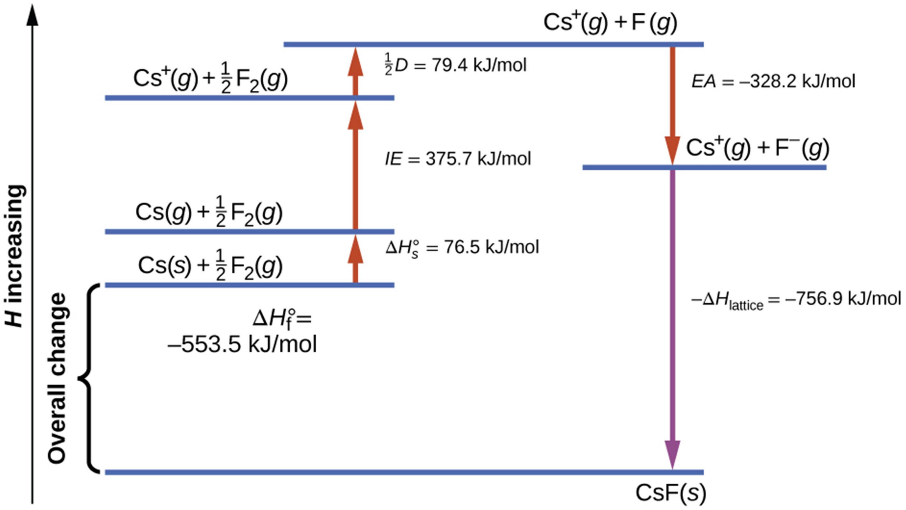


Figure 6.5: The Born-Haber cycle shows the relative energies of each step involved in the formation of solid cesium fluoride from the necessary elements in their reference states.

We begin with the elements in their most common states, Cs(*s*) and F_2(*g*). The ΔH°_s represents the conversion of solid cesium into a gas, and then the ionization energy converts the gaseous cesium atoms into cations. In the next step, we account for the energy required to break the F–F bond to produce fluorine atoms. Converting one mole of fluorine atoms into fluoride ions is an exothermic process, so this step gives off energy (the electron affinity) and is shown as decreasing along the *y*-axis. We now have one mole of Cs cations and one mole of F anions. These ions combine to produce solid cesium fluoride. The enthalpy change in this step is the negative of the lattice energy, so it is also an exothermic quantity. The total energy involved in this conversion is equal to the experimentally determined enthalpy of formation, $\Delta H^\circ_\mathrm{f}$, of the compound from its elements. In this case, the overall change is exothermic.

Hess's law can also be used to show the relationship between the enthalpies of the individual steps and the enthalpy of formation. Table 6.1 shows this for fluoride, CsF.

Table 6.1: show the relationship between the enthalpies of the individual steps and the enthalpy of formation of CsF.

Enthalpy of sublimation of Cs(*s*)	$Cs(s) \longrightarrow Cs(g)$	$\Delta H = \Delta H^\circ s = 76.5 kJ/mol$
One-half of the bond energy of F_2	$12F_2(g) \longrightarrow F(g)$	$\Delta H = 12D = 79.4 kJ/mol$
Ionization energy of Cs(*g*)	$Cs(g) \longrightarrow Cs+(g) + e-$	$\Delta H = IE = 375.7 kJ/mol$
Negative of the electron affinity of F	$F(g) + e- \longrightarrow F^{-}(g)$	$\Delta H = -EA = -328.2 kJ/mol$
Negative of the lattice energy of CsF(*s*)	$Cs+(g) + F^{-}(g) \longrightarrow CsF(s)$	$\Delta H = -\Delta H lattice = ?$
Enthalpy of formation of CsF(*s*), add steps 1–5	$\Delta H = \Delta H^\circ f = \Delta H^\circ s + \frac{1}{2} D + IE + (-EA) + (-\Delta H_{\text{lattice}})$ $Cs(s) + 1/2 F2(g) \longrightarrow CsF(s)$	$\Delta H = -553.5 kJ/mol$
Enthalpy of sublimation of Cs(*s*)	$Cs(s) \longrightarrow Cs(g)$	$\Delta H = \Delta H^\circ s = 76.5 kJ/mol$

Thus, the lattice energy can be calculated from other values. For cesium fluoride, using this data, the lattice energy is:

$$\Delta H_{\ lattice} = (553.5 + 76.5 + 79.4 + 375.7 + 328.2) kJ/mol = 1413.3 kJ/mol$$

The Born-Haber cycle may also be used to calculate any one of the other quantities in the equation for lattice energy, provided that the remainder is known. For example, if the relevant enthalpy of sublimation $\Delta H^\circ s$, ionization energy (IE), bond dissociation enthalpy (D), lattice energy$\Delta H_{lattice}$, and standard enthalpy of formation $\Delta H^\circ f$ are known, the Born-Haber cycle can be used to determine the electron affinity of an atom.

Lattice energies calculated for ionic compounds are typically much higher than bond dissociation energies measured for covalent bonds. Whereas lattice energies typically fall in the range of 600–4000 kJ/mol (some even higher), covalent bond dissociation energies are typically between 150–400 kJ/mol for single bonds. Keep in mind, however, that these are not directly comparable values. For ionic compounds, lattice energies are associated with many interactions, as cations and anions pack together in an extended lattice. For covalent bonds, the bond dissociation energy is associated with the interaction of just two atoms.

6.5.2. Bond strength of covalent bond

Stable molecules exist because covalent bonds hold the atoms together. We measure the strength of a covalent bond by the energy required to break it, that is, the energy necessary to separate the bonded atoms. Separating any pair of bonded atoms requires energy (see Figure 6.1). The stronger a bond, the greater the energy required to break it.

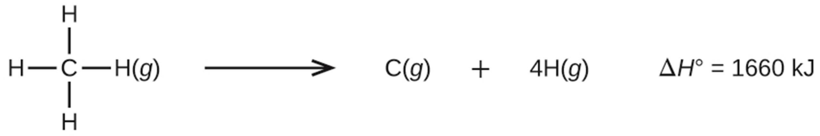
The energy required to break a specific covalent bond in one mole of gaseous molecules is called the bond energy or the bond dissociation energy. The bond energy for a diatomic molecule, $D_{X–Y}$, is defined as the standard enthalpy change for the endothermic reaction:

$$\boldsymbol{XY(g) \longrightarrow X(g) + Y(g) \qquad DX - Y = \qquad {}^{\circ}}$$

For example, the bond energy of the pure covalent H–H bond, $D_{H–H}$, is 436 kJ per mole of H–H bonds broken:

$$\boldsymbol{H_2(g) \longrightarrow 2H(g) \qquad DH - H = \qquad {}^{\circ} = 436kJ}$$

Molecules with three or more atoms have two or more bonds. The sum of all bond energies in such a molecule is equal to the standard enthalpy change for the endothermic reaction that breaks all the bonds in the molecule. For example, the sum of the four C–H bond energies in CH_4, 1660 kJ, is equal to the standard enthalpy change of the reaction:



$$CH_4(g) \longrightarrow C(g) + 4H(g) \qquad \Delta H^{\circ} = 1660\ \text{kJ}$$

The average C–H bond energy, $D_{C–H}$, is 1660/4 = 415 kJ/mol because there are four moles of C–H bonds broken per mole of the reaction. Although the four C–H bonds are equivalent in the original molecule, they do not each require the same energy to break; once the first bond is broken (which requires 439 kJ/mol), the remaining bonds are easier to break. The 415 kJ/mol value is the average, not the exact value required to break any one bond.

The strength of a bond between two atoms increases as the number of electron pairs in the bond increases. Generally, as the bond strength increases, the bond length decreases. Thus, we find that triple bonds are stronger and shorter than double bonds between the same two atoms; likewise, double bonds are stronger and shorter than single bonds between the same two atoms. Average bond energies for some common bonds appear in Table 6.2, and a comparison of bond lengths and bond strengths for some common bonds appears in Table 6.3. When one atom bonds to various atoms in a group, the bond strength typically decreases as we move down the group. For example, C–F is 439 kJ/mol, C–Cl is 330 kJ/mol, and C–Br is 275 kJ/mol.

Table 6.2: Bond Energies (kJ/mol)

Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy
H–H	436	C–S	260	F–Cl	255
H–C	415	C–Cl	330	F–Br	235
H–N	390	C–Br	275	Si–Si	230
H–O	464	C–I	240	Si–P	215
H–F	569	N–N	160	Si–S	225
H–Si	395	N=N	418	Si–Cl	359
H–P	320	N≡N	946	Si–Br	290
H–S	340	N–O	200	Si–I	215
H–Cl	432	N–F	270	P–P	215
H–Br	370	N–P	210	P–S	230
H–I	295	N–Cl	200	P–Cl	330
C–C	345	N–Br	245	P–Br	270
C=C	611	O–O	140	P–I	215
C≡C	837	O=O	498	S–S	215
C–N	290	O–F	160	S–Cl	250
C=N	615	O–Si	370	S–Br	215
C≡N	891	O–P	350	Cl–Cl	243
C–O	350	O–Cl	205	Cl–Br	220
C=O	741	O–I	200	Cl–I	210
C≡O	1080	F–F	160	Br–Br	190
C–F	439	F–Si	540	Br–I	180
C–Si	360	F–P	489	I–I	150
C–P	265	F–S	285		

Table 6.3: Average Bond Lengths and Bond Energies for Some Common Bonds

Bond	Bond Length (Å)	Bond Energy (kJ/mol)
C–C	1.54	345
C=C	1.34	611
C≡C	1.20	837
C–N	1.43	290
C=N	1.38	615
C≡N	1.16	891
C–O	1.43	350
C=O	1.23	741
C≡O	1.13	1080

We can use bond energies to calculate approximate enthalpy changes for reactions where enthalpies of formation are not available. Calculations of this type will also tell us whether a reaction is exothermic or endothermic. An exothermic reaction (Δ*H* negative, heat produced) results when the bonds in the products are stronger than the bonds in the reactants. An endothermic reaction (Δ*H* positive, heat absorbed) results when the bonds in the products are weaker than those in the reactants.

The enthalpy change, Δ*H*, for a chemical reaction is approximately equal to the sum of the energy required to break all bonds in the reactants (energy "in", positive sign) plus the energy released when all bonds are formed in the products (energy "out," negative sign). This can be expressed mathematically in the following way:

$$\boldsymbol{\Delta H = \Sigma D_{bonds\ broken} - \Sigma D_{bonds\ formed}}$$

In this expression, the symbol Σ means "the sum of" and D represents the bond energy in kilojoules per mole, which is always a positive number. The bond energy is obtained from a table (like Table 6.3) and will depend on whether the particular bond is a single, double, or triple bond. Thus, in calculating enthalpies in this manner, it is important that we consider the bonding in all reactants and products. Because D values are typically averages for one type of bond in many different molecules, this calculation provides a rough estimate, not an exact value, for the enthalpy of reaction.

Consider the following reaction:

$$\mathbf{H_2}(g) + Cl_2(g) \longrightarrow 2HCl(g \;\; or$$

$$H\text{–}\,H(g) \; + Cl\text{–}\,Cl(g) \longrightarrow 2H\text{–}\,Cl(g$$

To form two moles of HCl, one mole of H–H bonds and one mole of Cl–Cl bonds must be broken. The energy required to break these bonds is the sum of the bond energy of the H–H bond (436 kJ/mol) and the Cl–Cl bond (243 kJ/mol). During the reaction, two moles of H–Cl bonds are formed (bond energy = 432 kJ/mol), releasing 2 × 432 kJ; or 864 kJ. Because the bonds in the products are stronger than those in the reactants, the reaction releases more energy than it consumes:

$$\mathbf{\Delta H = \Sigma D_{bonds\ broken} - \Sigma D_{\ bonds\ formed}}$$

$$\mathbf{\Delta H = \; [DH - H + DCl - Cl] \; - 2DH -}$$

$$\Delta\mathrm{H} \; = \; [436 + 243] - 2(432) \; = -185\mathrm{kJ}$$

This excess energy is released as heat, so the reaction is exothermic.

Example 6.9

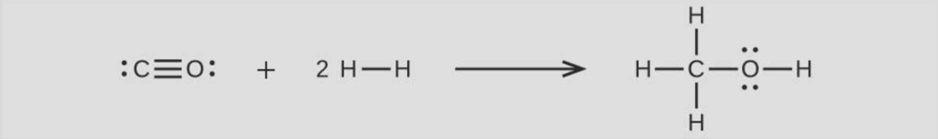
Using Bond Energies to Calculate Approximate Enthalpy Changes

Methanol, CH_3OH, may be an excellent alternative fuel. The high-temperature reaction of steam and carbon produces a mixture of the gases carbon monoxide, CO, and hydrogen, H_2, from which methanol can be produced. Using the bond energies in Table 6.3, calculate the approximate enthalpy change, Δ*H*, for the reaction here:

$$CO(g) \quad 2H2(g) \longrightarrow CH3OH(g)$$

Solution

First, we need to write the Lewis structures of the reactants and the products:



From this, we see that Δ*H* for this reaction involves the energy required to break a C–O triple bond and two H–H single bonds, as well as the energy produced by the formation of three C–H single bonds, a C–O single bond, and an O–H single bond. We can express this as follows:

$$\Delta H \quad \Sigma D\ bonds\ broken - \Sigma D\ bonds\ formed$$

$$[DC \equiv O + 2(DH - H)] - [3(DC - H) + DC - O + DO - H]$$

Using the bond energy values in Table 6.3, we obtain:

$$\Delta H = [1080 + 2(436)] - [3(415) + 350 + 464] = -107 kJ$$

We can compare this value to the value calculated based on ΔH°_f data from Appendix G:

$$\Delta H = [\Delta H \circ fCH3OH(g)] - [\Delta H \circ fCO(g \quad 2 \times \Delta H \circ fH2]$$

$$= [-201.0] - [-110.52 + 2 \times 0]$$

$$= -90.5 kJ$$

Note that there is a fairly significant gap between the values calculated using the two different methods. This occurs because D values are the *average* of different bond strengths; therefore, they often give only rough agreement with other data.

Check Your Learning

Ethyl alcohol, CH_3CH_2OH, was one of the first organic chemicals deliberately synthesized by humans. It has many uses in industry, and it is the alcohol contained in alcoholic beverages. It can be obtained by the fermentation of sugar or synthesized by the hydration of ethylene in the following reaction:

Using the bond energies in Table 6.3, calculate an approximate enthalpy change, Δ*H*, for this reaction.

Thus far, we have used two-dimensional Lewis structures to represent molecules. However, molecular structure is actually three-dimensional, and it is important to be able to describe molecular bonds in terms of their distances, angles, and relative arrangements in space (Figure 6.6). A bond angle is the angle between any two bonds that include a common atom, usually measured in degrees. A bond distance (or bond length) is the distance between the nuclei of two bonded atoms along the straight line joining the nuclei. Bond distances are measured in Ångstroms (1 Å = 10^{-10} m) or picometers (1 pm = 10^{-12} m, 100 pm = 1 Å).

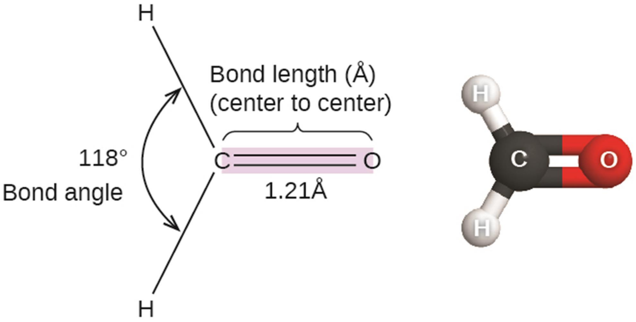


Figure 6.6: Bond distances (lengths) and angles are shown for the formaldehyde molecule, H_2CO.

6.6. Molecular structure and polarity

6.6.1. 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 6.7) 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 6.7).

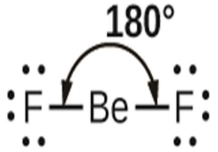


Figure 6.7: The BeF_2 molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the $\boldsymbol{Be}$ atom.

Figure 6.8 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

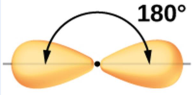
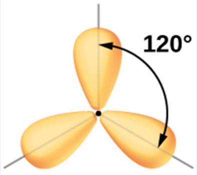
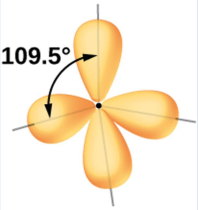
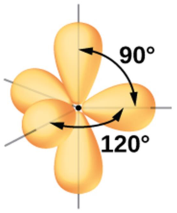
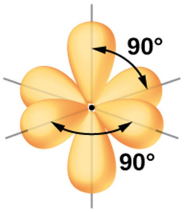
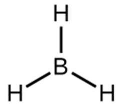
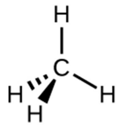
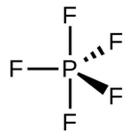
Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions 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 6.8: The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).

Electron-pair Geometry versus Molecular Structure

It is important to note that electron-pair geometry around a central atom is *not* the same thing as its molecular structure. The electron-pair geometries shown in Figure 6.7 describe all regions where electrons are located, bonds as well as lone pairs. Molecular structure describes the location of the *atoms*, not the electrons.

We differentiate between these two situations by naming the geometry that includes *all* electron pairs the electron-pair geometry. The structure that includes only the placement of the atoms in the molecule is called the molecular structure. The electron-pair geometries will be the same as the molecular structures when there are no lone electron pairs around the central atom, but they will be different when there are lone pairs present on the central atom.

For example, the methane molecule, CH_4, which is the major component of natural gas, has four bonding pairs of electrons around the central carbon atom; the electron-pair geometry is tetrahedral, as is the molecular structure (Figure 6.9). On the other hand, the ammonia molecule, NH_3, also has four electron pairs associated with the nitrogen atom, and thus has a tetrahedral electron-pair geometry. One of these regions, however, is a lone pair, which is not included in the molecular structure, and this lone pair influences the shape of the molecule (Figure 6.10).

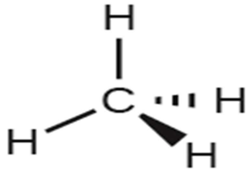


Figure 6.9: The molecular structure of the methane molecule, CH_4, is shown with a tetrahedral arrangement of the hydrogen atoms. VSEPR structures like this one are often drawn using the wedge and dash notation, in which solid lines represent bonds in the plane of the page, solid wedges represent bonds coming up out of the plane, and dashed lines represent bonds going down into the plane.

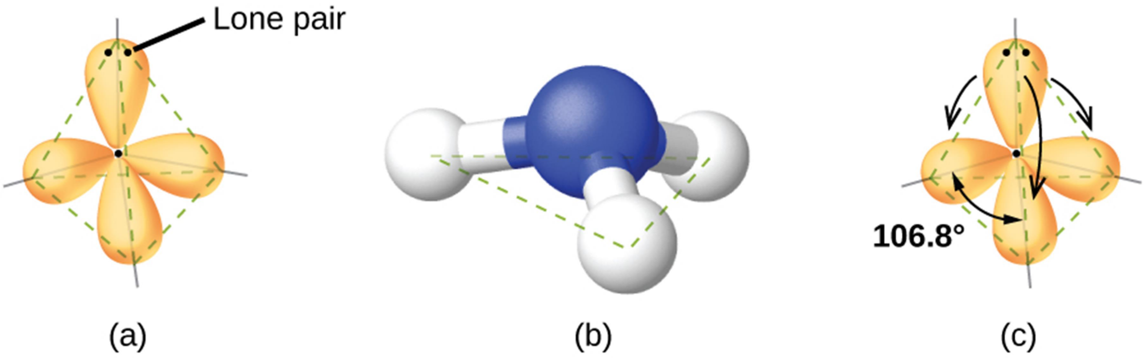


Figure 6.10: (a) The electron-pair geometry for the ammonia molecule is tetrahedral with one lone pair and three single bonds. (b) The trigonal pyramidal molecular structure is determined from the electron-pair geometry. (c) The actual bond angles deviate slightly from the idealized angles because the lone pair takes up a larger region of space than do the single bonds, causing the HNH angle to be slightly smaller than 109.5°.

As seen in Figure 6.10, small distortions from the ideal angles in Figure 6.8 can result from differences in repulsion between various regions of electron density. VSEPR theory predicts these distortions by establishing an order of repulsions and an order of the amount of space occupied by different kinds of electron pairs. The order of electron-pair repulsions from greatest to least repulsion is:

Lone pair-lone pair>lone pair-bonding pair>bonding pair-bonding pair

This order of repulsions determines the amount of space occupied by different regions of electrons. A lone pair of electrons occupies a larger region of space than the electrons in a triple bond; in turn, electrons in a triple bond occupy more space than those in a double bond, and so on. The order of sizes from largest to smallest is:

Lone pair>triple bond>double bond>single bond

Consider formaldehyde, H_2CO, which is used as a preservative for biological and anatomical specimens (Figure 6.6). This molecule has regions of high electron density that consist of two single bonds and one double bond. The basic geometry is trigonal planar with 120° bond angles, but we see that the double bond causes slightly larger angles (121°), and the angle between the single bonds is slightly smaller (118°).

In the ammonia molecule, the three hydrogen atoms attached to the central nitrogen are not arranged in a flat, trigonal planar molecular structure, but rather in a three-dimensional trigonal pyramid (Figure 6.10) with the nitrogen atom at the apex and the three hydrogen atoms forming the base. The ideal bond angles in a trigonal pyramid are based on the tetrahedral electron pair geometry. Again, there are slight deviations from the ideal because lone pairs occupy larger regions of space than do bonding electrons. The H–N–H bond angles in NH_3 are slightly smaller than the 109.5° angle in a regular tetrahedron (Figure 6.8) because the lone pair-bonding pair repulsion is greater than the bonding pair-bonding pair repulsion (Figure 6.10). Figure 6.11 illustrates the ideal molecular structures, which are predicted based on the electron-pair geometries for various combinations of lone pairs and bonding pairs.

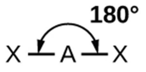
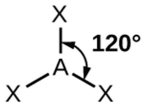
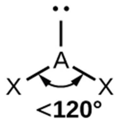
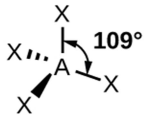
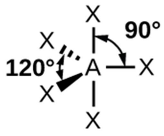
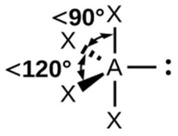
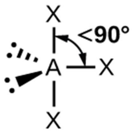
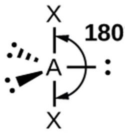
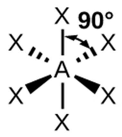
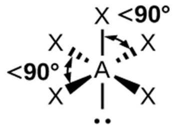
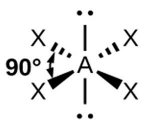
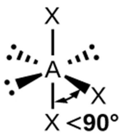
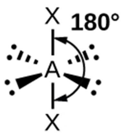
Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal planar	 Bent or angular			
4	 Tetrahedral	 Trigonal pyramid	 Bent or angular		
5	 Trigonal bipyramid	 Sawhorse or seesaw	 T-shape	 Linear	
6	 Octahedral	 Square pyramid	 Square planar	 T-shape	 Linear

Figure 6.11: The molecular structures are identical to the electron-pair geometries when there are no lone pairs present (first column). For a particular number of electron pairs (row), the molecular structures for one or more lone pairs are determined based on modifications of the corresponding electron-pair geometry.

According to VSEPR theory, the terminal atom locations (Xs in Figure 6.11) are equivalent within the linear, trigonal planar, and tetrahedral electron-pair geometries (the first three rows of the table). It does not matter which X is replaced with a lone pair because the molecules can be rotated to convert positions. For trigonal bipyramidal electron-pair geometries, however, there are two distinct X positions, as shown in Figure 6.12: an axial position (if we hold a model of a trigonal bipyramid by the two axial positions, we have an axis around which we can rotate the model) and an equatorial position (three positions form an equator around the middle of the molecule). As shown in Figure 6.11, the axial position is surrounded by bond angles of 90°, whereas the equatorial position has more space available because of the 120° bond angles. In a trigonal bipyramidal electron-pair geometry, lone pairs always occupy equatorial positions because these more spacious positions can more easily accommodate the larger lone pairs.

Theoretically, we can come up with three possible arrangements for the three bonds and two lone pairs for the ClF_3 molecule (Figure 6.12). The stable structure is the one that puts the lone pairs in equatorial locations, giving a T-shaped molecular structure.

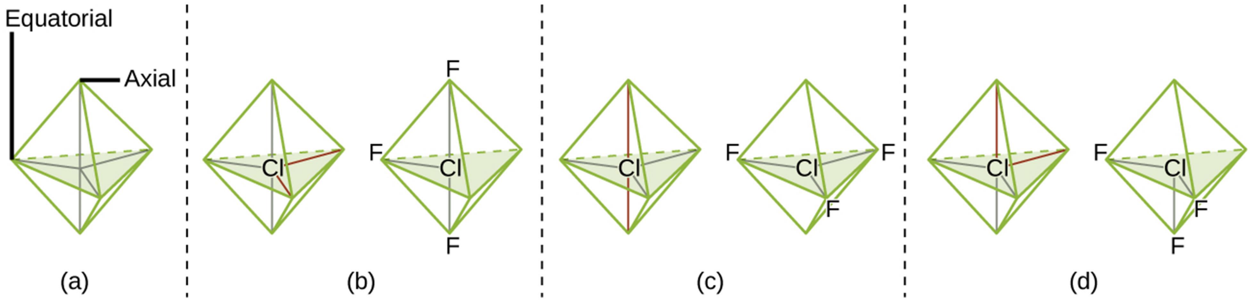


Figure 6.12: (a) In a trigonal bipyramid, the two axial positions are located directly across from one another, whereas the three equatorial positions are located in a triangular arrangement. (b–d) The two lone pairs (red lines) in ClF_3 have several possible arrangements, but the T-shaped molecular structure (b) is the one actually observed, consistent with the larger lone pairs both occupying equatorial positions.

When a central atom has two lone electron pairs and four bonding regions, we have an octahedral electron-pair geometry. The two lone pairs are on opposite sides of the octahedron (180° apart), giving a square planar molecular structure that minimizes lone pair-lone pair repulsions (Figure 6.11).

Predicting Electron Pair Geometry and Molecular Structure

The following procedure uses VSEPR theory to determine the electron pair geometries and the molecular structures:

1. Write the Lewis structure of the molecule or polyatomic ion.
2. Count the number of regions of electron density (lone pairs and bonds) around the central atom. A single, double, or triple bond counts as one region of electron density.
3. Identify the electron-pair geometry based on the number of regions of electron density: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral (Figure 6.10, first column).

4. Use the number of lone pairs to determine the molecular structure (Figure 6.10). If more than one arrangement of lone pairs and chemical bonds is possible, choose the one that will minimize repulsions, remembering that lone pairs occupy more space than multiple bonds, which occupy more space than single bonds. In trigonal bipyramidal arrangements, repulsion is minimized when every lone pair is in an equatorial position. In an octahedral arrangement with two lone pairs, repulsion is minimized when the lone pairs are on opposite sides of the central atom.

The following examples illustrate the use of VSEPR theory to predict the molecular structure of molecules or ions that have no lone pairs of electrons. In this case, the molecular structure is identical to the electron pair geometry.

Example 6.10

Predicting Electron-pair Geometry and Molecular Structure: CO_2 and BCl_3

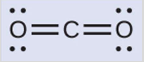
Predict the electron-pair geometry and molecular structure for each of the following:

(a) carbon dioxide, CO_2, a molecule produced by the combustion of fossil fuels

(b) boron trichloride, BCl_3, an important industrial chemical

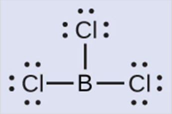
Solution

(a) We write the Lewis structure of CO_2 as:



This shows us two regions of high electron density around the carbon atom-each double bond counts as one region, and there are no lone pairs on the carbon atom. Using VSEPR theory, we predict that the two regions of electron density arrange themselves on opposite sides of the central atom with a bond angle of 180°. The electron-pair geometry and molecular structure are identical, and CO_2 molecules are linear.

(b) We write the Lewis structure of BCl_3 as:



The electron-pair geometry and molecular structure of BCl_3 are both trigonal planar. Note that the VSEPR geometry indicates the correct bond angles (120°), unlike the Lewis structure shown above.

6.6.2. Molecular structure and dipole moment

As discussed previously, polar covalent bonds connect two atoms with differing electronegativities, leaving one atom with a partial positive charge (δ^+) and the other atom with a partial negative charge (δ^-), as the electrons are pulled toward the more electronegative atom. This separation of charge gives rise to a bond dipole moment. The magnitude of a bond dipole moment is represented by the Greek letter mu (μ) and is given by the formula shown here, where Q is the magnitude of the partial charges (determined by the electronegativity difference) and r is the distance between the charges:

$$\mu = Qr$$

This bond moment can be represented as a vector, a quantity having both direction and magnitude (Figure 6.13). Dipole vectors are shown as arrows pointing along the bond from the less electronegative atom toward the more electronegative atom. A small plus sign is drawn on the less electronegative end to indicate the partially positive end of the bond. The length of the arrow is proportional to the magnitude of the electronegativity difference between the two atoms.

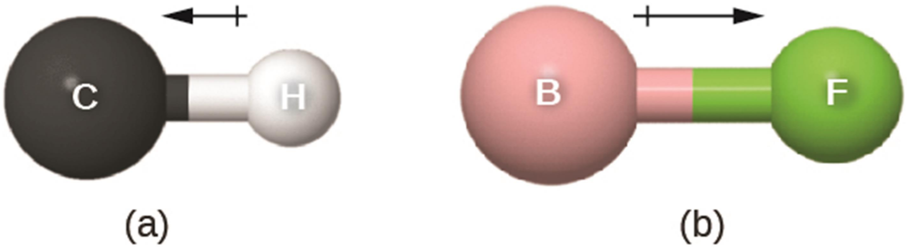


Figure 6.13: (a) There is a small difference in electronegativity between C and H, represented as a short vector. (b) The electronegativity difference between B and F is much larger, so the vector representing the bond moment is much longer.

A whole molecule may also have a separation of charge, depending on its molecular structure and the polarity of each of its bonds. If such a charge separation exists, the molecule is said to be a polar molecule (or dipole); otherwise the molecule is said to be nonpolar. The dipole moment measures the extent of net charge separation in the molecule as a whole. We determine the dipole moment by adding the bond moments in three-dimensional space, taking into account the molecular structure.

For diatomic molecules, there is only one bond, so its bond dipole moment determines the molecular polarity. Homonuclear diatomic molecules such as Br_2 and N_2 have no difference in electronegativity, so their dipole moment is zero. For heteronuclear molecules such as CO, there is a small dipole moment. For HF, there is a larger dipole moment because there is a larger difference in electronegativity.

When a molecule contains more than one bond, the geometry must be taken into account. If the bonds in a molecule are arranged such that their bond moments cancel (vector sum equals zero), then the molecule is nonpolar. This is the situation in CO_2 (Figure 6.14). Each of the bonds is polar, but the molecule as a whole is nonpolar. From the Lewis structure, and using VSEPR theory, we determine that the CO_2 molecule is linear with polar C=O bonds on opposite sides of the carbon atom. The bond moments cancel because they are pointed in opposite directions. In the case of the water molecule (Figure 6.14), the Lewis structure again shows that there are two bonds to a central atom, and the electronegativity difference again shows that each of these bonds has a nonzero bond moment. In this case, however, the molecular structure is bent because of the lone pairs on O, and the two bond moments do not cancel. Therefore, water does have a net dipole moment and is a polar molecule (dipole).

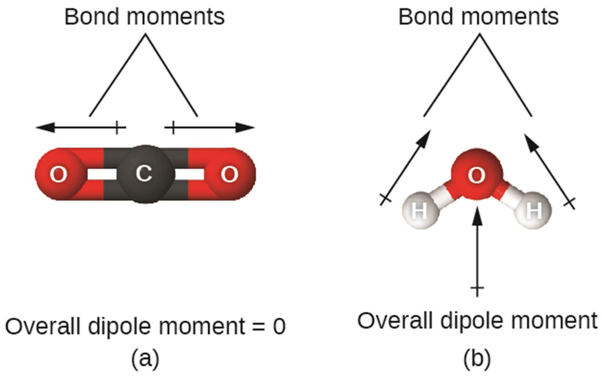
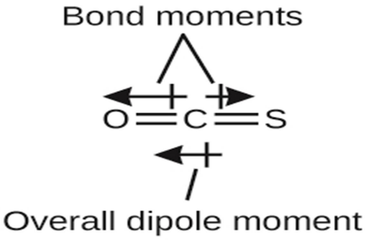


Figure 6.14: The overall dipole moment of a molecule depends on the individual bond dipole moments and how they are arranged. (a) Each CO bond has a bond dipole moment, but they point in opposite directions so that the net CO_2 molecule is nonpolar. (b) In contrast, water is polar because the OH bond moments do not cancel out.

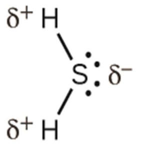
The OCS molecule has a structure similar to CO_2, but a sulfur atom has replaced one of the oxygen atoms. To determine if this molecule is polar, we draw the molecular structure. VSEPR theory predicts a linear molecule:

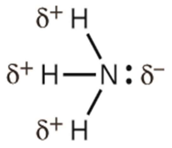


The C-O bond is considerably polar. Although C and S have very similar electronegativity values, S is slightly more electronegative than C, and so the C-S bond is just slightly polar. Because oxygen is more electronegative than sulfur, the oxygen end of the molecule is the negative end.

Chloromethane, CH_3Cl, is a tetrahedral molecule with three slightly polar C-H bonds and a more polar C-Cl bond. The relative electronegativities of the bonded atoms is H < C < Cl, and so the bond moments all point toward the Cl end of the molecule and sum to yield a considerable dipole moment (the molecules are relatively polar).

For molecules of high symmetry such as BF_3 (trigonal planar), CH_4 (tetrahedral), PF_5 (trigonal bipymidal), and SF_6 (octahedral), all the bonds are of identical polarity (same bond moment) and they are oriented in geometries that yield nonpolar molecules (dipole moment is zero). Molecules of less geometric symmetry, however, may be polar even when all bond moments are identical. For these molecules, the directions of the equal bond moments are such that they sum to give a nonzero dipole moment and a polar molecule. Examples of such molecules include hydrogen sulfide, H_2S (nonlinear), and ammonia, NH_3 (trigonal pyramidal).





To summarize, to be polar, a molecule must:

1. Contain at least one polar covalent bond.
2. Have a molecular structure such that the sum of the vectors of each bond dipole moment does not cancel.

Properties of Polar Molecules

Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate (Figure 6.15). We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted. Also, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.

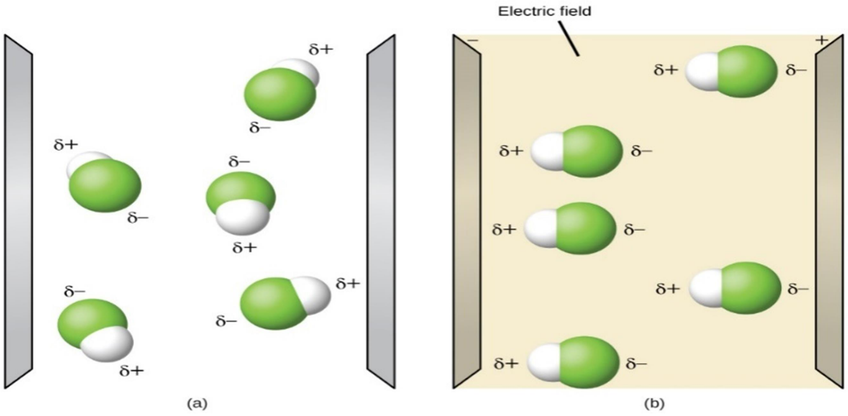


Figure 6.15: (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction.

Review Exercise

1. Does a cation gain protons to form a positive charge or does it lose electrons?
2. Write the electron configuration for each of the following ions:
   (a) As^{3-} (b) I^- (c) Be^{2+} (d) Cd^{2+} (e) O^{2-} (f) Ga^{3+} (g) Li^+ (h) N^{3-} (i) Sn^{2+} (j) Co^{2+} (k) Fe^{2+}
3. From the labels of several commercial products, prepare a list of six ionic compounds in the products. For each compound, write the formula. (You may need to look up some formulas in a suitable reference.
4. Predict which of the following compounds are ionic and which are covalent, based on the location of their constituent atoms in the periodic table:
   a. Cl_2CO
   b. MnO
   c. NCl_3
   d. $CoBr_2$
   e. K_2S
   f. CO

g. CaF_2 i. CaO k. CO_2

h. HI j. IBr

5. Explain the difference between a nonpolar covalent bond, a polar covalent bond, and an ionic bond.
6. From its position in the periodic table, determine which atom in each pair is more electronegative:

a. Br or Cl d. P or S g. N or K

b. N or O e. Si or N

c. S or O f. Ba or P

7. From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:

(a) C, F, H, N, O (c) F, H, O, P, S (e) Ba, H, N, O, As

(b) Br, Cl, F, H, I (d) Al, H, Na, O, P

8. Which is the most polar bond?

(a) C–C (c) N–H (e) Se–H

(b) C–H (d) O–H

9. Identify the more polar bond in each of the following pairs of bonds:

(a) HF or HCl (d) PCl or SCl (g) CN or NN

(b) NO or CO (e) CH or NH

(c) SH or OH (f) SO or PO

10. Which of the following molecules or ions contain polar bonds?

(a) O_3 (d) $NO3^-$ (g) BH_4^-

(b) S_8 (e) CO_2

(c) $O2^{2-}$ (f) H_2S

11. Write the Lewis symbols for each of the following ions:

(a) As^{3-} (d) O^{2-} (g) N^{3-}

(b) I^- (e) Ga^{3+}

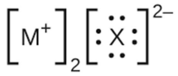
(c) Be^{2+} (f) Li^+

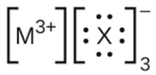
12. Write the Lewis symbols of the ions in each of the following ionic compounds and the Lewis symbols of the atom from which they are formed:

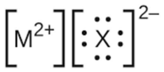
(a) MgS (c) $GaCl_3$ (e) Li_3N

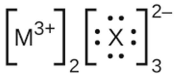
(b) Al_2O_3 (d) K_2O (f) KF

13. In the Lewis structures listed here, M and X represent various elements in the third period of the periodic table. Write the formula of each compound using the chemical symbols of each element:

(a) 

(b) 

(c) 

(d) 

14. Write Lewis structures for the following:

(a) H_2
(b) HBr
(c) PCl_3
(d) SF_2
(e) H_2CCH_2
(f) HNNH
(g) H_2CNH
(h) NO^-
(i) N_2
(j) CO
(k) CN^-

15. Methanol, H_3COH, is used as the fuel in some race cars. Ethanol, C_2H_5OH, is used extensively as motor fuel in Brazil. Both methanol and ethanol produce CO_2 and H_2O when they burn. Write the chemical equations for these combustion reactions using Lewis structures instead of chemical formulas.

16. A compound with a molar mass of about 28 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.

17. Two arrangements of atoms are possible for a compound with a molar mass of about 45 g/mol that contains 52.2% C, 13.1% H, and 34.7% O by mass. Write the Lewis structures for the two molecules.

18. Determine the formal charge of each element in the following:

(a) HCl
(b) CF_4
(c) PCl_3
(d) PF_5

19. Calculate the formal charge of each element in the following compounds and ions:

(a) F_2CO
(b) NO^-
(c) BF_4^-
(d) $SnCl_3^-$
(e) H_2CCH_2
(f) ClF_3
(g) SeF_6
(h) PO_4^{3-}

20. Draw all possible resonance structures for each of these compounds. Determine the formal charge on each atom in each of the resonance structures:

(a) O_3
(b) SO_2
(c) NO_2^-
(d) NO_3^-

21. Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in nitrosyl chloride: ClNO or ClON and hypochlorous acid: HOCl or OClH?
22. Draw the structure of hydroxylamine, H_3NO, and assign formal charges; look up the structure. Is the actual structure consistent with the formal charges?
23. Explain why the HOH molecule is bent, whereas the HBeH molecule is linear.
24. Explain the difference between electron-pair geometry and molecular structure.
25. Why is the H–N–H angle in NH_3 smaller than the H–C–H bond angle in CH_4? Why is the H–N–H angle in NH4+ identical to the H–C–H bond angle in CH_4?
26. Explain how a molecule that contains polar bonds can be nonpolar.
27. Predict the electron pair geometry and the molecular structure of each of the following molecules or ions:
    (a) SF_6
    (b) PCl_5
    (c) BeH_2
    (d) CH3+
28. Identify the electron pair geometry and the molecular structure of each of the following molecules or ions:
    (a) IF_6^+
    (b) CF_4
    (c) BF_3
    (d) SiF_5^-
    (e) $BeCl_2$
29. Which of the following molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?
    (a) ClF_5
    (b) ClO2−
    (c) TeCl42−
    (d) PCl_3
    (e) SeF_4
    (f) PH2−
    (g) XeF_2
30. Which of these molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?
    (a) H_3O^+
    (b) PCl4−
    (c) SnCl3−
    (d) BrCl4−
    (e) ICl_3
    (f) XeF_4
    (g) SF_2
31. Which of the following molecules have dipole moments?
    (a) CS_2
    (b) SeS_2
    (c) CCl_2F_2
    (d) PCl_3 (P is the central atom)
    (e) ClNO (N is the central atom)

32. Draw the Lewis structures and predict the shape of each compound or ion:

(a) CO_2 (c) SO_3

(b) NO_2^- (d) SO_3^{2-}

33. What is the molecular structure of the stable form of FNO_2? (N is the central atom.)

34. A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen. What is its molecular structure?

CHAPTER SEVEN

Equilibrium Concepts and Acid-base Equilibrium

Introduction

Imagine a beach populated with sunbathers and swimmers. As those basking in the sun get too hot, they enter the surf to swim and cool off. As the swimmers tire, they return to the beach to rest. If the rate at which sunbathers enter the surf were to equal the rate at which swimmers return to the sand, then the numbers (though not the identities) of sunbathers and swimmers would remain constant. This scenario illustrates a dynamic phenomenon known as ***equilibrium***, in which opposing processes occur at equal rates. Chemical and physical processes are subject to this phenomenon; these processes are at equilibrium when the forward and reverse reaction rates are equal. Equilibrium systems are pervasive in nature; the various reactions involving carbon dioxide dissolved in blood are examples. This chapter provides a thorough introduction to the essential aspects of chemical equilibria.

Learning Objectives of the Chapter: At the end of this chapter you will be able to

- Explain the dynamic nature of a chemical equilibrium
- Predict the response of a stressed equilibrium using Le Châtelier's principle
- Calculate equilibrium concentrations and equilibrium constants
- Identify acids, bases based on the three acid-base concepts
- Express hydronium and hydroxide ion concentrations on the pH and pOH scales
- Calculate the pH and pOH of a given solution
- Determine the relative strengths of acids and bases
- Describe the composition and function of acid-base buffer
- Calculate the pH of the buffer before and after the addition of added acid or base

The convention for writing chemical equations involves placing reactant formulas on the left side of a reaction arrow and product formulas on the right side. By this convention, and the definitions of "reactant" and "product," a chemical equation represents the reaction in question as proceeding from left to right. **Reversible reactions**, however, may proceed in both forward (left to right) and reverse (right to left) directions. When the rates of the forward and reverse reactions are equal, the concentrations of the reactant and product species remain constant over time and the system is at equilibrium. The relative concentrations of reactants and products in **equilibrium** systems vary greatly; some systems contain mostly products at equilibrium, some contain mostly reactants, and some contain appreciable amounts of both.

Figure 7.1 illustrates fundamental equilibrium concepts using the reversible decomposition of colorless dinitrogen tetroxide to yield brown nitrogen dioxide, an elementary reaction described by the equation:

$$\boldsymbol{N_2O_4(g) \rightleftharpoons 2NO_2(g)}$$

Note that a special double arrow is used to emphasize the reversible nature of the reaction.

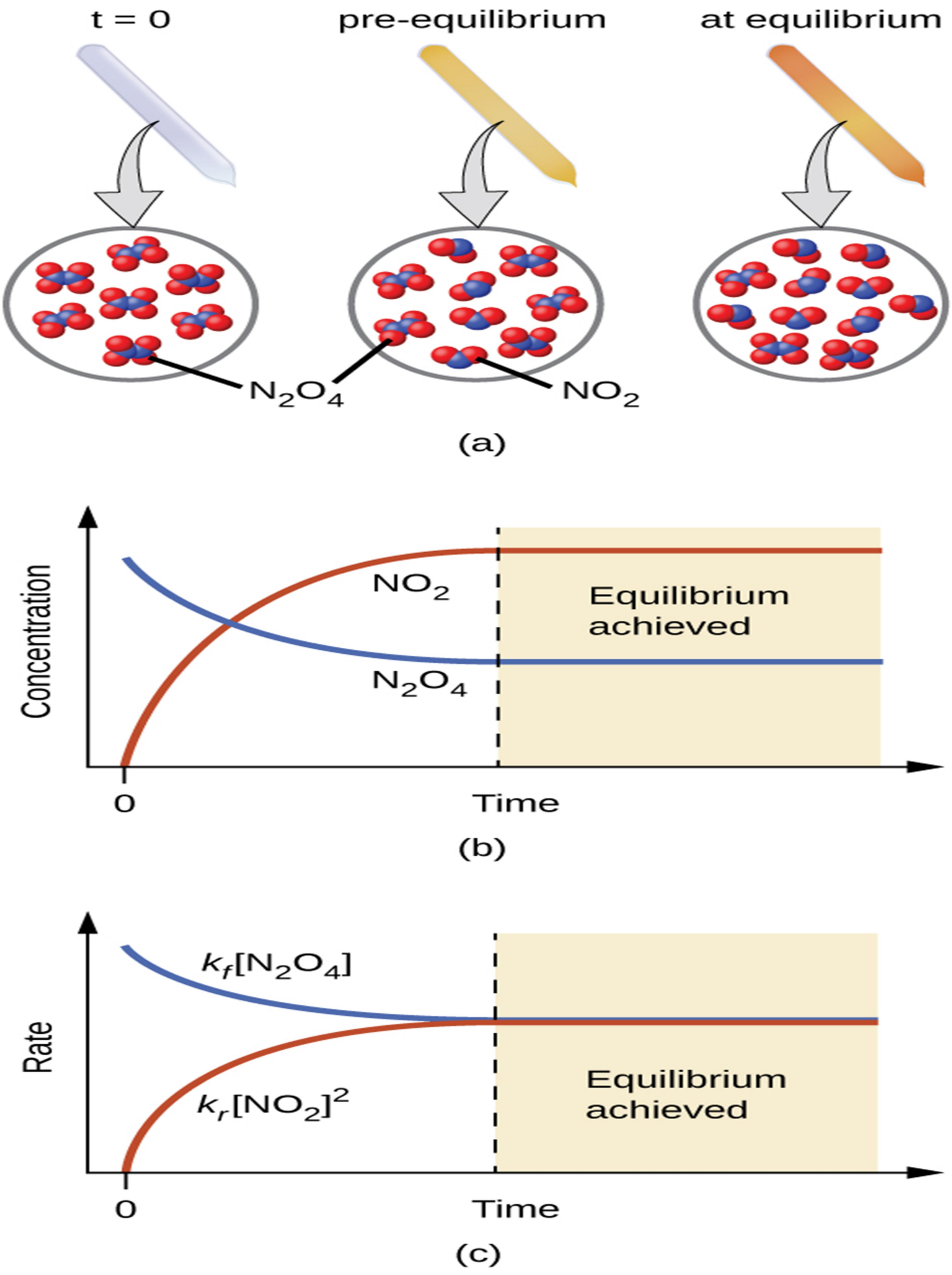

t = 0
pre-equilibrium
at equilibrium
N_2O_4
NO_2
(a)
Concentration
NO_2
N_2O_4
Equilibrium achieved
0
Time
(b)
Rate
$k_f[N_2O_4]$
$k_r[NO_2]^2$
Equilibrium achieved
0
Time
(c)

Figure 7.1: (a) A sealed tube containing colorless N_2O_4 darkens as it decomposes to yield brown NO_2. (b) Changes in concentration over time as the decomposition reaction achieves equilibrium. (c) At equilibrium, the forward and reverse reaction rates are equal.

For this elementary process, rate laws for the forward and reverse reactions may be derived directly from the reaction stoichiometry:

$$\mathbf{rate}_f = \boldsymbol{k_f}[\boldsymbol{N_2O_4}]$$

$$\mathbf{rate}_r = \boldsymbol{k_r}[\boldsymbol{NO_2}]^2$$

As the reaction begins (t = 0), the concentration of the N_2O_4 reactant is finite and that of the NO_2 product is zero, so the forward reaction proceeds at a finite rate while the reverse reaction rate is zero. As time passes, N_2O_4 is consumed and its concentration falls, while NO_2 is produced and its concentration increases (Figure 7.1b). The decreasing concentration of the reactant slows the forward reaction rate, and the increasing product concentration speeds the reverse reaction rate (Figure 7.1c). This process continues until the forward and reverse reaction rates become equal, at which time the reaction has reached equilibrium, as characterized by constant concentrations of its reactants and products (shaded areas of Figure 7.1b and Figure 7.1c). It's important to emphasize that chemical equilibria are dynamic; a reaction at equilibrium has not "stopped," but is proceeding in the forward and reverse directions at the same rate. This dynamic nature is essential to understanding equilibrium behavior as discussed in this and subsequent chapters of the text.

Physical changes, such as phase transitions, are also reversible and may establish equilibria. This concept was introduced in another chapter of this text through discussion of the vapor pressure of a condensed phase (liquid or solid). As one example, consider the vaporization of bromine:

$$\boldsymbol{Br_2(l)} \rightleftharpoons \boldsymbol{Br_2(g)}$$

When liquid bromine is added to an otherwise empty container and the container is sealed, the forward process depicted above (vaporization) will commence and continue at a roughly constant rate as long as the exposed surface area of the liquid and its temperature remain constant. As increasing amounts of gaseous bromine are produced, the rate of the reverse process (condensation) will increase until it equals the rate of vaporization and equilibrium is established.

7.1. Chemical Equilibrium

The status of a reversible reaction is conveniently assessed by evaluating its **reaction quotient (*Q*).** For a reversible reaction described by

$$mA + nB + \rightleftharpoons xC + yD$$

The reaction quotient is derived directly from the stoichiometry of the balanced equation as

$$Qc = \frac{[C]^x[D]^y}{[A]^m[B]^n}$$

Where, the subscript *c* denotes the use of molar concentrations in the expression. If the reactants and products are gaseous, a reaction quotient may be similarly derived using partial pressures:

$$Qp = \frac{P_C^x P_D^y}{P_A^m P_B^n}$$

Note that the reaction quotient equations above are a simplification of more rigorous expressions that use *relative* values for concentrations and pressures rather than *absolute* values. These relative concentration and pressure values are dimensionless (they have no units); consequently, so are the reaction quotients. For purposes of this introductory text, it will suffice to use the simplified equations and to disregard units when computing *Q*. In most cases, this will introduce only modest errors in calculations involving reaction quotients.

Example 7.1

Writing Reaction Quotient Expressions

Write the concentration-based reaction quotient expression for each of the following reactions:

a) $3O_2(g) \rightleftharpoons 2O_3(g)$
b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
c) $4NH_3(g) + 7O_2(g) \rightleftharpoons 4NO_2(g) + 6H_2O(g)$

Solution

(a) $Qc = \frac{[O_3]^2}{[O_2]^3}$

(b) $Qc = \frac{[NH_3]^2}{[N_2][H_2]^3}$

(c) $Q_C = \frac{[NO_2]^4[H_2O]^6}{[NH_3]^4[O_2]^7}$

✍Check Your Learning

Write the concentration-based reaction quotient expression for each of the following reactions:

(a) $2SO_2(g)+O_2(g)\rightleftharpoons 2SO_3(g)$

(b) $C_4H_8(g)\rightleftharpoons 2C_2H_4(g)$

(c) $2C_4H_{10}(g)+13O_2(g)\rightleftharpoons 8CO_2(g)+10H_2O(g)$

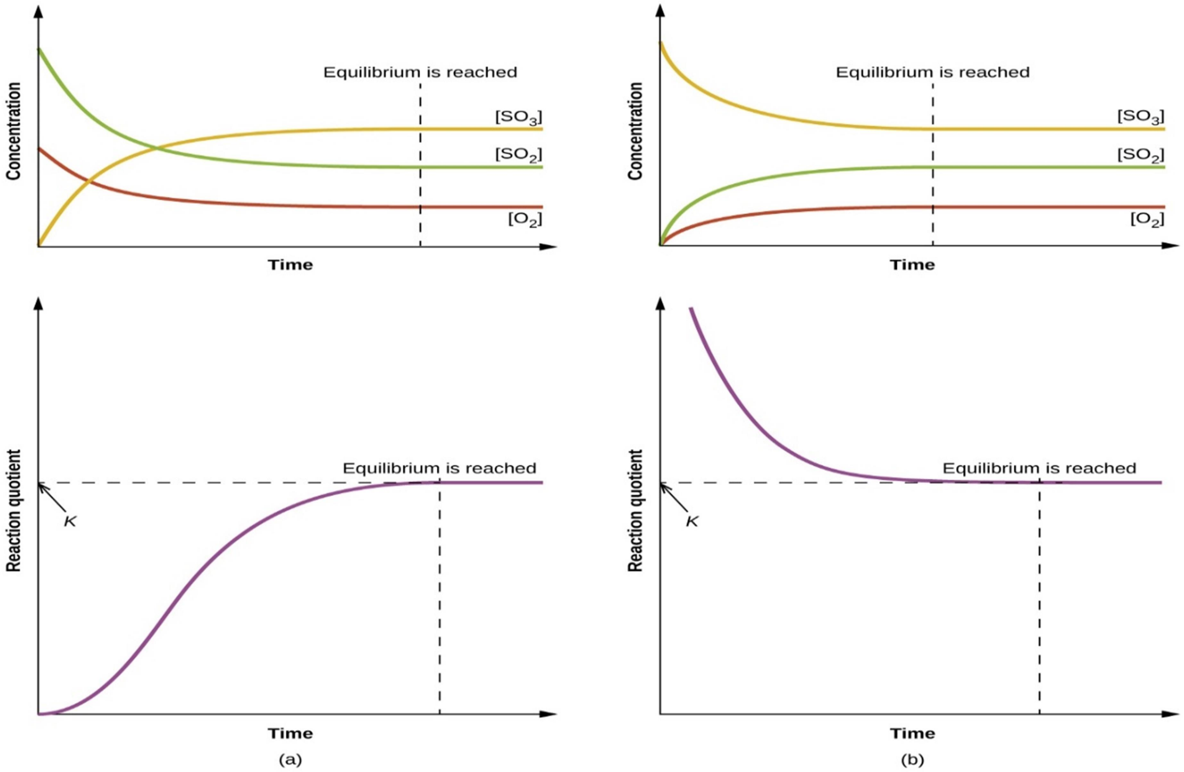


Figure 7.2: Changes in concentrations and Q_c for a chemical equilibrium achieved beginning with (a) a mixture of reactants only and (b) products only.

The numerical value of Q varies as a reaction proceeds towards equilibrium; therefore, it can serve as a useful indicator of the reaction's status. To illustrate this point, consider the oxidation of sulfur dioxide:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

Two different experimental scenarios are depicted in Figure 7.2 one in which this reaction is initiated with a mixture of reactants only, SO_2 and O_2, and another that begins with only product, SO_3. For the reaction that begins with a mixture of reactants only, Q is initially equal to zero:

$$\boldsymbol{Q_C = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{[0]^2}{[SO_2]^2[O_2]} = 0}$$

As the reaction proceeds toward equilibrium in the forward direction, reactant concentrations decrease (as does the denominator of Q_c), product concentration increases (as does the numerator of Q_c), and the reaction quotient consequently increases. When equilibrium is achieved, the concentrations of reactants and product remain constant, as does the value of Q_c.

If the reaction begins with only product present, the value of Q_c is initially undefined (immeasurably large, or infinite):

$$\boldsymbol{Q_C = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{[SO_3]^2}{0 \rightarrow \infty}}$$

In this case, the reaction proceeds toward equilibrium in the reverse direction. The product concentration and the numerator of Q_c decrease with time, the reactant concentrations and the denominator of Q_c increase, and the reaction quotient consequently decreases until it becomes constant at equilibrium.

The constant value of Q exhibited by a system at equilibrium is called the **equilibrium constant,** K: $\boldsymbol{K = Q}$, at equilibrium

Comparison of the data plots in Figure 7.2 shows that both experimental scenarios resulted in the same value for the equilibrium constant. This is a general observation for all equilibrium systems, known as the law of mass action: At a given temperature, the reaction quotient for a system at equilibrium is constant.

Example 7.2

Evaluating a Reaction Quotient

Gaseous nitrogen dioxide forms dinitrogen tetroxide according to this equation:

$$\boldsymbol{2NO2(g) \rightleftharpoons N2O4(g)}$$

When 0.10 mol NO_2 is added to a 1.0-L flask at 25°C, the concentration changes so that at equilibrium, $[NO_2] = 0.016\ M$ and $[N_2O_4] = 0.042\ M$.

a. What is the value of the reaction quotient before any reaction occurs?

b. What is the value of the equilibrium constant for the reaction?

Solution As for all equilibrium calculations in this text, use the simplified equations for Q and K and disregard any concentration or pressure units, as noted previously in this section.

(a) Before any product is formed, $[NO_2] = \frac{\mathbf{0.10}\boldsymbol{mol}}{\mathbf{1.0}\boldsymbol{L}} = 0.10M$, and $[N_2O_4] \ = \ 0\ M$. Thus,

$$\frac{[N_2O_4]}{[NO_2]^2} = \frac{0}{0.10^2} = 0$$

(b) At equilibrium, $Kc = Qc = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0.42}{0.016^2} = 1.6X10^2$. The equilibrium constant is 1.6 × 10^2.

✍**Check Your Learning**

For the reaction

$2SO_2(g)+O_2(g)\rightleftharpoons 2SO_3(g)$, the concentrations at equilibrium are $[SO_2] = 0.90\ M$, $[O_2] = 0.35\ M$, and $[SO_3] = 1.1\ M$. What is the value of the equilibrium constant, K_c?

By its definition, the magnitude of equilibrium constant explicitly reflects the composition of a reaction mixture at equilibrium, and it may be interpreted with regard to the extent of the forward reaction. A reaction exhibiting a large K will reach equilibrium when most of the reactant has been converted to product, whereas a small K indicates the reaction achieves equilibrium after very little reactant has been converted. It's important to keep in mind that the magnitude of K does *not* indicate how rapidly or slowly equilibrium will be reached. Some equilibria are established so quickly as to be nearly instantaneous, and others so slowly that no perceptible change is observed over the course of days, years, or longer.

The equilibrium constant for a reaction can be used to predict the behavior of mixtures containing its reactants and/or products. As demonstrated by the sulfur dioxide oxidation process described above, a chemical reaction will proceed in whatever direction is necessary to achieve equilibrium. Comparing Q to K for an equilibrium system of interest allows prediction of what reaction (forward or reverse), if any, will occur.

Example 7.3

Predicting the Direction of Reaction

Given here are the starting concentrations of reactants and products for three experiments involving in this reaction:

$$\boldsymbol{CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)}$$

$$\boldsymbol{K_C = 0.64}$$

Determine in which direction the reaction proceeds as it goes to equilibrium in each of the three experiments shown.

Reactants/Products	**Experiment 1**	**Experiment 2**	**Experiment 3**
$[CO]_i$	0.020 *M*	0.011 *M*	0.0094 *M*
$[H_2O]_i$	0.020 *M*	0.0011 *M*	0.0025 *M*
$[CO_2]_i$	0.0040 *M*	0.037 *M*	0.0015 *M*
$[H_2]_i$	0.0040 *M*	0.046 *M*	0.0076 *M*

Solution

Experiment 1:

$$Q_C = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.004)(0.004)}{(0.02)(0.02)} = 0.04$$

$$Qc < Kc\ (0.040 < 0.64)$$

The reaction will proceed in the forward direction.

Experiment 2:

$$Q_C = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.037)(0.046)}{(0.011)(0.0011)} = 1.4X10^2$$

$$Qc > Kc\ (140 > 0.64)$$

The reaction will proceed in the reverse direction.

Experiment 3:

$$Q_C = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.0015)(0.00.0076)}{(0.0094)(0.000.0025)} = 0.48$$

$$Qc < Kc\ (0.48 < 0.64)$$

The reaction will proceed in the forward direction.

✍Check Your Learning

Calculate the reaction quotient and determine the direction in which each of the following reactions will proceed to reach equilibrium.

A 1.00-L flask containing 0.0500 mol of NO(g), 0.0155 mol of Cl_2(g), and 0.500 mol of NOCl:

$$2NO(g) + Cl2(g) \rightleftharpoons 2NOCl(g) \quad Kc = 4.6 \times 10^4$$

A 5.0-L flask containing 17 g of NH_3, 14 g of N_2, and 12 g of H_2:

$$N2(g) + 3H2(g) \rightleftharpoons 2NH3(g) \quad Kc = 0.060$$

A 2.00-L flask containing 230 g of SO_3(g):

$$2SO3(g) \rightleftharpoons 2SO2(g) + O2(g)Kc = 0.230$$

Homogeneous Equilibria

A homogeneous equilibrium is one in which all reactants and products (and any catalysts, if applicable) are present in the same phase. By this definition, homogeneous equilibria take place in solutions. These solutions are most commonly either liquid or gaseous phases, as shown by the examples below:

$$\mathbf{C_2H_2(aq) + 2Br_2(aq) \rightleftharpoons C_2H_2Br_2(aq)} \qquad \mathbf{K_C = \frac{[C_2H_2Br_2]}{[C_2H_2][Br_2]^2}}$$

$$\mathbf{I_2(aq) + I^-(aq) \rightleftharpoons I_3{}^-(aq)} \qquad \mathbf{K_C = \frac{[I_3{}^-]}{[I_2][I^-]}}$$

$$\mathbf{HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)} \qquad \mathbf{K_C = \frac{[H_3O^+][F^-}{[HF]}}$$

$$\mathbf{NH_3(aq) + H_2O(l) \rightleftharpoons NH_4{}^+(aq) + OH^-(aq)} \qquad \mathbf{K_C = \frac{[NH_4{}^+][OH^-\ ]}{[NH_3]}}$$

These examples all involve aqueous solutions, those in which water functions as the solvent. In the last two examples, water also functions as a reactant, but its concentration is *not* included in the reaction quotient. The reason for this omission is related to the more rigorous form of the *Q* (or *K*) expression mentioned previously in this chapter, in which *relative concentrations for* *liquids and solids are equal to 1 and needn't be included*. Consequently, reaction quotients include concentration or pressure terms only for gaseous and solute species.

The equilibria below all involve gas-phase solutions:

$$\mathbf{C_2H_6(g) \rightleftharpoons C_2H_4(g) + (g)H_2} \qquad \mathrm{K_C} = \frac{[\mathrm{C_2H_4}][\mathrm{H_2}]}{[\mathrm{C_2H_6}]}$$

$$\mathbf{3O_2(g) \rightleftharpoons 2O_3(g)} \qquad \mathrm{K_C} = \frac{[\mathrm{O_3}]^2}{[\mathrm{O_2}]^3}$$

$$\mathbf{N_2(g) + 3H_2(aq) \rightleftharpoons 2NH_3(g)} \qquad \mathrm{K_C} = \frac{[\mathrm{NH_3}]^2}{[\mathrm{N_2}][\mathrm{H_2}]^3}$$

$$\mathbf{C_3H_8(g) + 5O_2(g) \rightleftharpoons 3CO_2(g) + 4H_2O(g)} \quad \mathrm{K_C} = \frac{[\mathrm{CO_2}]^3[\mathrm{H_2O}]^4}{[\mathrm{C_3H_8}][\mathrm{O_2}]^5}$$

For gas-phase solutions, the equilibrium constant may be expressed in terms of either the molar concentrations (K_c) or partial pressures (K_p) of the reactants and products. A relation between these two K values may be simply derived from the ideal gas equation and the definition of molarity:

$$\boldsymbol{PV = nRT}$$

$$\boldsymbol{P = \left(\frac{n}{V}\right)RT}$$

$$\boldsymbol{= MRT}$$

Where P is partial pressure, V is volume, n is molar amount, R is the gas constant, T is temperature, and M is molar concentration.

For the gas-phase reaction

$$\boldsymbol{mA + nB \rightleftharpoons xC + yD}:$$

$$\boldsymbol{K_P = \frac{(P_C)^x(P_D)^y}{(P_A)^m(P_B)^n}}$$

$$\boldsymbol{= \frac{([C]xRT)^x([D]xRT)^y}{([A]xRT)^m([BxRT)^n}}$$

$$= \frac{[C]^x[D]^x}{[A]^m[B]^n} x \frac{(RT)^{x+y}}{(RT)^{m+n}}$$

$$= K_C(RT)^{(x+y)-(m+n)}$$

$$= K_C(RT)^{\Delta n}$$

And so, the relationship between K_C and K_P is

$$K_P = K_C(RT)^{\Delta n}$$

Where Δn is the difference in the molar amounts of product and reactant gases, in this case:

$$\Delta n = (x + y) - (m + n)$$

Example 7.4

Calculation of K_P

Write the equations relating K_c to K_P for each of the following reactions:

a. $C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$
b. $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$
c. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
d. K_c is equal to 0.28 for the following reaction at 900 °C:

$CS_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2S(g)$

☞ What is K_P at this temperature?

Solution

a. $\Delta n = (2) - (1) = 1$

$KP = Kc\,(RT)^{\Delta n} = Kc\,(RT)^1 = Kc\,(RT)$

b. (*b*) $\Delta n = (2) - (2) = 0$

$KP = Kc\,(RT)^{\Delta n} = Kc\,(RT)^0 = Kc$

c. (*c*) $\Delta n = (2) - (1 + 3) = -2$

$KP = Kc(RT)^{\Delta n} = Kc\,(RT)^{-2} = \frac{Kc}{(RT)^2}$

$K_P = K_C(RT)^{\Delta n} = \frac{0.28}{[(0.0821)(1173)]^2} = 3.0X10^{-5}$

✍Check Your Learning

Write the equations relating K_c to K_P for each of the following reactions:

a. $2SO_2\,(g)+O_2(g) \rightleftharpoons 2SO_3(g)$

b. $N_2O_4\,(g) \rightleftharpoons 2NO_2(g)$

c. $C_3H_8\,(g)+5O_2(g) \rightleftharpoons 3CO_2(g)+4H_2O(g)$

d. At 227 °C, the following reaction has $K_c = 0.0952$:

$CH_3OH\,(g) \rightleftharpoons CO\,(g)+2H_2(g)$

☞ What would be the value of K_P at this temperature?

Heterogeneous Equilibria

A heterogeneous equilibrium involves reactants and products in two or more different phases, as illustrated by the following examples:

$$\mathrm{PbCl_2(s)} \rightleftharpoons \mathrm{Pb^{2+}(aq)} + \mathrm{2Cl^-(aq)} \qquad \mathrm{K_C} = [\mathrm{Pb^{2+}}][\mathrm{Cl^-}]^2$$

$$\mathrm{CaO(s)} + \mathrm{CO_2(g)} \rightleftharpoons \mathrm{CaCO_3(s)} \qquad \mathrm{K_C} = \frac{1}{[\mathrm{CO_2}]}$$

$$\mathrm{C(s)} + \mathrm{2S(g)} \rightleftharpoons \mathrm{CS_2(g)} \qquad \mathrm{K_C} = \frac{[\mathrm{CS_2}]}{[\mathrm{S}]^2}$$

$$\mathrm{br_2(l)} \rightleftharpoons \mathrm{Br_2(g)} \qquad \mathrm{K_C} = [\mathrm{Br_2}]$$

Again, note that concentration terms are only included for gaseous and solute species, as discussed previously.

Two of the above examples include terms for gaseous species only in their equilibrium constants, and so K_p expressions may also be written:

$$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) \qquad K_P = \frac{1}{P_{CO_2}}$$

$$C(s) + 2S(g) \rightleftharpoons CS_2(g) \qquad K_P = \frac{P_{CS_2}}{(P_S)^2}$$

7.1. Le Chatelier's principle

A system at equilibrium is in a state of dynamic balance, with forward and reverse reactions taking place at equal rates. If an equilibrium system is subjected to a change in conditions that affects these reaction rates differently (a stress), then the rates are no longer equal and the system is not at equilibrium. The system will subsequently experience a net reaction in the direction of greater rate (a shift) that will re-establish the equilibrium. This phenomenon is summarized by Le Châtelier's principle: if an equilibrium system is stressed, the system will experience a shift in response to the stress that re-establishes equilibrium.

Reaction rates are affected primarily by concentrations, as described by the reaction's rate law, and temperature, as described by the Arrhenius equation. Consequently, changes in concentration and temperature are the two stresses that can shift an equilibrium.

Effect of a Change in Concentration

If an equilibrium system is subjected to a change in the concentration of a reactant or product species, the rate of either the forward or the reverse reaction will change. As an example, consider the equilibrium reaction:

$$\boldsymbol{H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad K_C = 50\ at\ 400^0C}$$

The rate laws for the forward and reverse reactions are:

$$\boldsymbol{forward\ H_2(g) + I_2(g) \rightarrow 2HI(g) \qquad \mathbf{rate}_f = k_f[H_2]^m[I_2]^n}$$

$$\boldsymbol{reverse\ 2HI(g) \rightarrow H_2(g) + I_2(g) \qquad \mathbf{rate}_r = k_r[HI]^x}$$

When this system is at equilibrium, the forward and reverse reaction rates are equal.

$$\mathbf{rate}_{\boldsymbol{f}} = \mathbf{rat}\boldsymbol{e_r}$$

If the system is stressed by adding reactant, either H_2 or I_2, the resulting increase in concentration causes the rate of the forward reaction to increase, exceeding that of the reverse reaction:

$$\mathbf{rate}_{\boldsymbol{f}} > \mathbf{rat}\boldsymbol{e_r}$$

The system will experience a temporary net reaction in the forward direction to re-establish equilibrium (*the equilibrium will shift right*). This same shift will result if some product HI is removed from the system, which decreases the rate of the reverse reaction, again resulting in the same imbalance in rates.

The same logic can be used to explain the left shift that results from either removing reactant or adding product to an equilibrium system. These stresses both result in an increased rate for the reverse reaction

$$\boldsymbol{Q_C = \frac{[HI]^2}{[H_2][I_2]} = K_C}$$

If reactant is added (increasing the denominator of the reaction quotient) or product is removed (decreasing the numerator), then $Qc < Kc$ and the equilibrium will shift right. Note that the three different ways of inducing this stress result in three different changes in the composition of the equilibrium mixture. If H_2 is added, the right shift will consume I_2 and produce HI as equilibrium is re-established, yielding a mixture with a greater concentrations of H_2 and HI and a lesser concentration of I_2 than was present before. If I_2 is added, the new equilibrium mixture will have greater concentrations of I_2 and HI and a lesser concentration of H_2. Finally, if HI is removed, the new equilibrium mixture will have greater concentrations of H_2 and I_2 and a lesser concentration of HI. Despite these differences in composition, *the value of the equilibrium constant will be the same after the stress as it was before* (per the law of mass action). The same logic may be applied for stresses involving removing reactants or adding product, in which case $Qc > Kc$ and the equilibrium will shift left.

For gas-phase equilibria such as this one, some additional perspectives on changing the concentrations of reactants and products are worthy of mention. The partial pressure *P* of an ideal gas is proportional to its molar concentration *M*,

$$\boldsymbol{M = \frac{n}{V} = \frac{P}{RT}}$$

and so changes in the partial pressures of any reactant or product are essentially changes in concentrations and thus yield the same effects on equilibria. Aside from adding or removing reactant or product, the pressures (concentrations) of species in a gas-phase equilibrium can also be changed by *changing the volume occupied by the system*. Since all species of a gas-phase equilibrium occupy the same volume, a given change in volume will cause the same change in concentration for both reactants and products. In order to discern what shift, if any, this type of stress will induce the stoichiometry of the reaction must be considered.

At equilibrium, the reaction $\mathbf{H_2(g) + I_2(g) \rightleftharpoons 2HI(g)}$ is described by the reaction quotient

$$Q_p = \frac{P_{HI^2}}{P_{H_2}P_{I_2}} = K_P$$

If the volume occupied by an equilibrium mixture of these species is decreased by a factor of 3, the partial pressures of all three species will be increased by a factor of 3:

$$Q'_p = \frac{(3P_{HI})^2}{3P_{H_2}3P_{I_2}} = \frac{9{P_{HI}}^2}{9P_{H_2}P_{I_2}} = \frac{{P_{HI}}^2}{P_{H_2}P_{I_2}} = Q_p = K_p$$

$$Q'_p = Q_p = K_p$$

And so, changing the volume of this gas-phase equilibrium mixture does not results in a shift of the equilibrium.

A similar treatment of a different system, $\boldsymbol{2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)}$, however, yields a different result:

$$Q_p = \frac{P_{NO^2}P_{O_2}}{P_{NO_{2}2}} = K_p$$

$$Q'_p = \frac{(3P_{NO})^2 3P_{O_2}}{(3P_{NO_2})^2} = \frac{9P_{NO^2}3P_{O_2}}{9P_{NO_{2}2}} = \frac{27P_{NO^2}P_{O_2}}{9P_{NO_{2}2}} = 3Q_p > K_p$$

$$Q'_p = 3Q_p > K_p$$

In this case, the change in volume results in a reaction quotient greater than the equilibrium constant, and so the equilibrium will shift left.

These results illustrate the relationship between the stoichiometry of a gas-phase equilibrium and the effect of a volume-induced pressure (concentration) change. If the total molar amounts of reactants and products are equal, as in the first example, a change in volume does not shift the equilibrium. If the molar amounts of reactants and products are different, a change in volume will shift the equilibrium in a direction that better "accommodates" the volume change. In the second example, two moles of reactant (NO_2) yield three moles of product ($2NO + O_2$), and so decreasing the system volume causes the equilibrium to shift left since the reverse reaction produces less gas (2 mol) than the forward reaction (3 mol). Conversely, increasing the volume of this equilibrium system would result in a shift towards products.

Equilibrium and Soft Drinks

The connection between chemistry and carbonated soft drinks goes back to 1767, when Joseph Priestley (1733–1804) developed a method of infusing water with carbon dioxide to make carbonated water. Priestly's approach involved production of carbon dioxide reacting oil of vitriol (sulfuric acid) with chalk (calcium carbonate).

The carbon dioxide was then dissolved in water, reacting to produce hydrogen carbonate, a weak acid that subsequently ionized to yield bicarbonate and hydrogen ions:

$$\boldsymbol{dissolution\ CO_2 \rightleftharpoons CO_2(aq)}$$

$$\boldsymbol{hydrolysis\ CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)}$$

$$\boldsymbol{ionization\ H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)}$$

These same equilibrium reactions are the basis of today's soft-drink carbonation process. Beverages are exposed to a high pressure of gaseous carbon dioxide during the process to shift the first equilibrium above to the right, resulting in desirably high concentrations of dissolved carbon dioxide and, per similar shifts in the other two equilibria, its hydrolysis and ionization products. A bottle or can is then nearly filled with the carbonated beverage, leaving a relatively small volume of air in the container above the beverage surface (the *headspace*) before it is sealed. The pressure of carbon dioxide in the container headspace is very low immediately after sealing, but it rises as the dissolution equilibrium is re-established by shifting to the left. Since the volume of the beverage is significantly greater than the volume of the headspace, only a relatively small amount of dissolved carbon dioxide is lost to the headspace.

When a carbonated beverage container is opened, a hissing sound is heard as pressurized CO_2 escapes from the headspace. This causes the dissolution equilibrium to shift left, resulting in a decrease in the concentration of dissolved CO_2 and subsequent left-shifts of the hydrolysis and ionization equilibria. Fortunately for the consumer, the dissolution equilibrium is usually re-established slowly, and so the beverage may be enjoyed while its dissolved carbon dioxide concentration remains palatably high. Once the equilibria are re-established, the $CO_2(aq)$

concentration will be significantly lowered, and the beverage acquires a characteristic taste referred to as "flat."

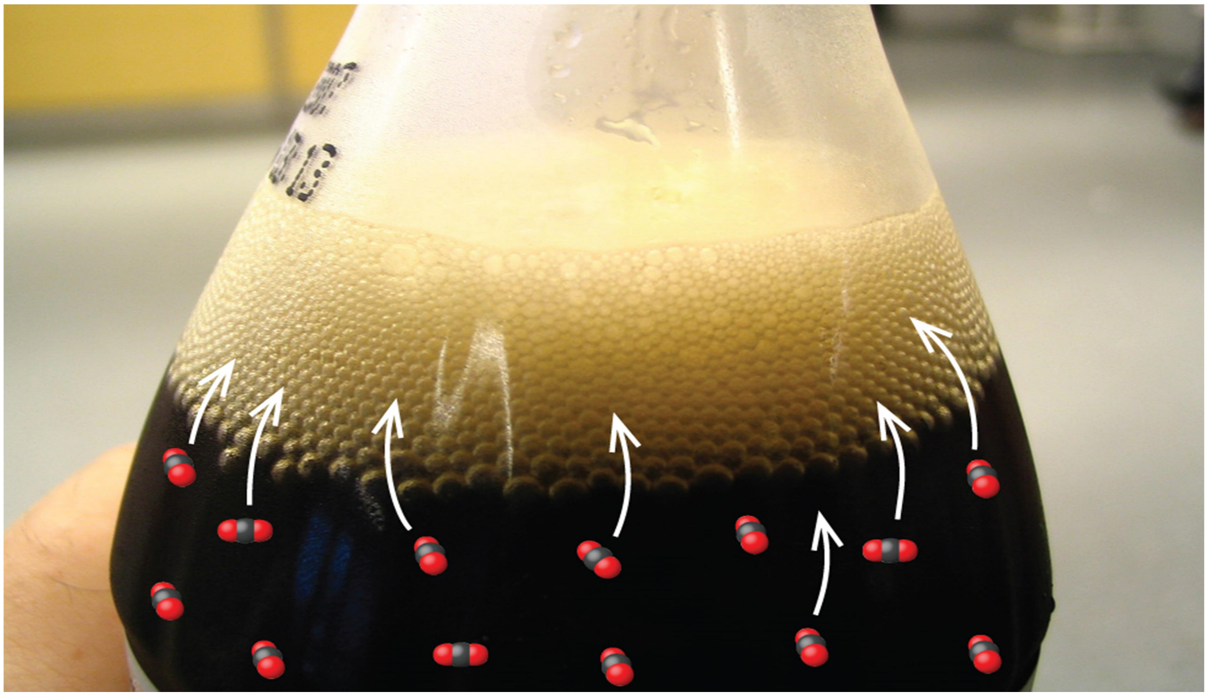


Figure 7.3: Opening a soft-drink bottle lowers the CO_2 pressure above the beverage, shifting the dissolution equilibrium and releasing dissolved CO_2 from the beverage.

Effect of a Change in Temperature

Consistent with the law of mass action, an equilibrium stressed by a change in concentration will shift to re-establish equilibrium without any change in the value of the equilibrium constant, *K*. When an equilibrium shifts in response to a temperature change, however, it is re-established with a different relative composition that exhibits a different value for the equilibrium constant.

To understand this phenomenon, consider the elementary reaction

$$\boldsymbol{A \rightleftharpoons B}$$

Since this is an elementary reaction, the rates laws for the forward and reverse may be derived directly from the balanced equation's stoichiometry:

$$\mathbf{rate}_{\boldsymbol{f}} = \boldsymbol{k_f}[\boldsymbol{A}]$$

$$\mathbf{rate}_{\boldsymbol{r}} = \boldsymbol{k_r}[\boldsymbol{B}]$$

When the system is at equilibrium,

$$\mathbf{rate}_{\boldsymbol{r}} = \mathbf{rate}_{\boldsymbol{f}}$$

Substituting the rate laws into this equality and rearranging gives

$$\boldsymbol{k_f[A] = k_r[B]}$$

$$\boldsymbol{\frac{[B]}{[A]} = \frac{k_f}{k_r} = K_C}$$

The equilibrium constant is seen to be a mathematical function of the rate constants for the forward and reverse reactions. Since the rate constants vary with temperature as described by the Arrhenius equation, is stands to reason that the equilibrium constant will likewise vary with temperature (assuming the rate constants are affected to different extents by the temperature change). For more complex reactions involving multistep reaction mechanisms, a similar but more complex mathematical relation exists between the equilibrium constant and the rate constants of the steps in the mechanism. Regardless of how complex the reaction may be, the temperature-dependence of its equilibrium constant persists.

Predicting the shift an equilibrium will experience in response to a change in temperature is most conveniently accomplished by considering the enthalpy change of the reaction. For example, the decomposition of dinitrogen tetroxide is an endothermic (heat-consuming) process:

$$\boldsymbol{N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = +57.20\ kJ}$$

For purposes of applying Le Chatelier’s principle, heat (*q*) may be viewed as a reactant:

$$\boldsymbol{heat + N_2O_4(g) \rightleftharpoons 2NO_2(g)}$$

Raising the temperature of the system is causing to increasing the amount of a product, and so the equilibrium will shift to the right. Lowering the system temperature will likewise cause the equilibrium to shift left. For exothermic processes, heat is viewed as a product of the reaction and so the opposite temperature dependence is observed.

Effect of Change in Pressure

According to Le Chatelier’s principle, if the pressure at equilibrium is increased then the reaction will proceed in that direction where the pressure is reduced. Since the pressure depends upon the number of moles, on increasing the pressure the reaction will proceed in that direction where the number of moles are reduced. If the pressure at equilibrium is decreased then the reaction will proceed in that direction where the number of moles is more. For a general reaction,

$$\mathbf{aA + bB \rightleftharpoons mM + nN}$$

The effect of pressure is decided by Δn. $\mathbf{\Delta n = (m + n) - (a + b)}$

If $\mathbf{\Delta n > 0}$**,** that means the total moles of products is greater than the total moles of reactants. Lowering of pressure will favour the reaction in forward direction. That is, more products will be formed at equilibrium if the pressure is lowered.

If $\mathbf{\Delta n < 0}$, that means the total moles of products is less than the total moles of reactants. Increasing the pressure will favour the reaction in forward direction. That is, more products will be formed at equilibrium if the pressure is increased.

If $\mathbf{\Delta n = 0}$, then the change in pressure has no effect on the position of equilibrium. For example, in the formation of ammonia, $\boldsymbol{N_2(g) + 3H_2(g) \rightleftharpoons 2N\ {}_3(g)}$, $\mathbf{\Delta n}$ = 2-(1+3) = -2

Therefore, an increase in pressure at equilibrium will favour the forward reaction.

For the dissociation of dinitrogen tetroxide, $\mathbf{N_2O_4(g) \rightleftharpoons 2NO_2(g)}$**,** Δn = 2 – 1= 1

The decrease in pressure at equilibrium, favours the forward reaction.

✍**Check your learning**

Consider the following reaction at 400°C:

$\boldsymbol{H_2(g) + I_2(g) \rightleftharpoons 2HI(g)}$, explain the effect of change in pressure on position of equilibrium?

Effect of a Catalyst

Catalysts are substances that enable a reaction to proceed via a different mechanism with an accelerated rate. The catalyzed reaction mechanism involves a lower energy transition state than the uncatalyzed reaction, resulting in lower activation energy, E_a, and a correspondingly greater rate constant.

To discern the effect of catalysis on an equilibrium system, consider the reaction diagram for a simple one-step (elementary) reaction shown in Figure 7.4. The lowered transition state energy of the catalyzed reaction results in lowered activation energies for both the forward and the reverse reactions. Consequently, both forward and reverse reactions are accelerated, and equilibrium is achieved more quickly *but without a change in the equilibrium constant*.

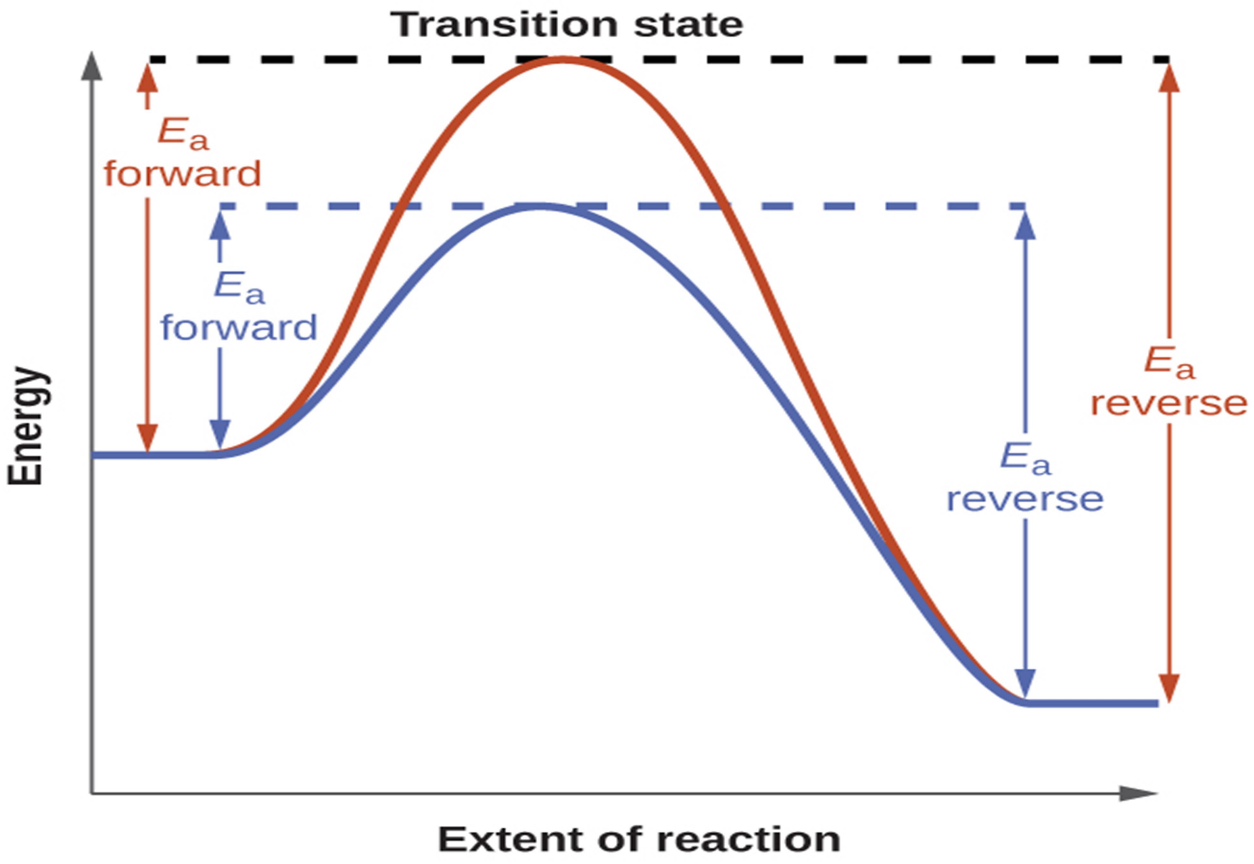


Figure 7.4: Reaction diagrams for an elementary process in the absence (red) and presence (blue) of a catalyst. The presence of catalyst lowers the activation energies of both the forward and reverse reactions but does not affect the value of the equilibrium constant.

An interesting case study highlighting these equilibrium concepts is the industrial production of ammonia, NH_3. This substance is among the “top 10” industrial chemicals with regard to production, with roughly two billion pounds produced annually in the US. Ammonia is used as a chemical feedstock to synthesize a wide range of commercially useful compounds, including fertilizers, plastics, dyes, and explosives.

Most industrial production of ammonia uses the *Haber-Bosch process* based on the following equilibrium reaction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92.2\ kJ$$

The traits of this reaction present challenges to its use in an efficient industrial process. The equilibrium constant is relatively small (K_p on the order of 10^{-5} at 25 °C), meaning very little ammonia is present in an equilibrium mixture. Also, the rate of this reaction is relatively slow at low temperatures. To raise the yield of ammonia, the industrial process is designed to operate under conditions favoring product formation:

- High pressures (concentrations) of reactants are used, ~150−250 atm, to shift the equilibrium right, favoring product formation.
- Ammonia is continually removed (collected) from the equilibrium mixture during the process, lowering its concentration and also shifting the equilibrium right.
- Although low temperatures favor product formation for this exothermic process, the reaction rate at low temperatures is inefficiently slow. A catalyst is used to accelerate the reaction to reasonable rates at relatively moderate temperatures (400−500 °C).

A diagram illustrating a typical industrial setup for production of ammonia via the Haber-Bosch process is shown in Figure 7.5.

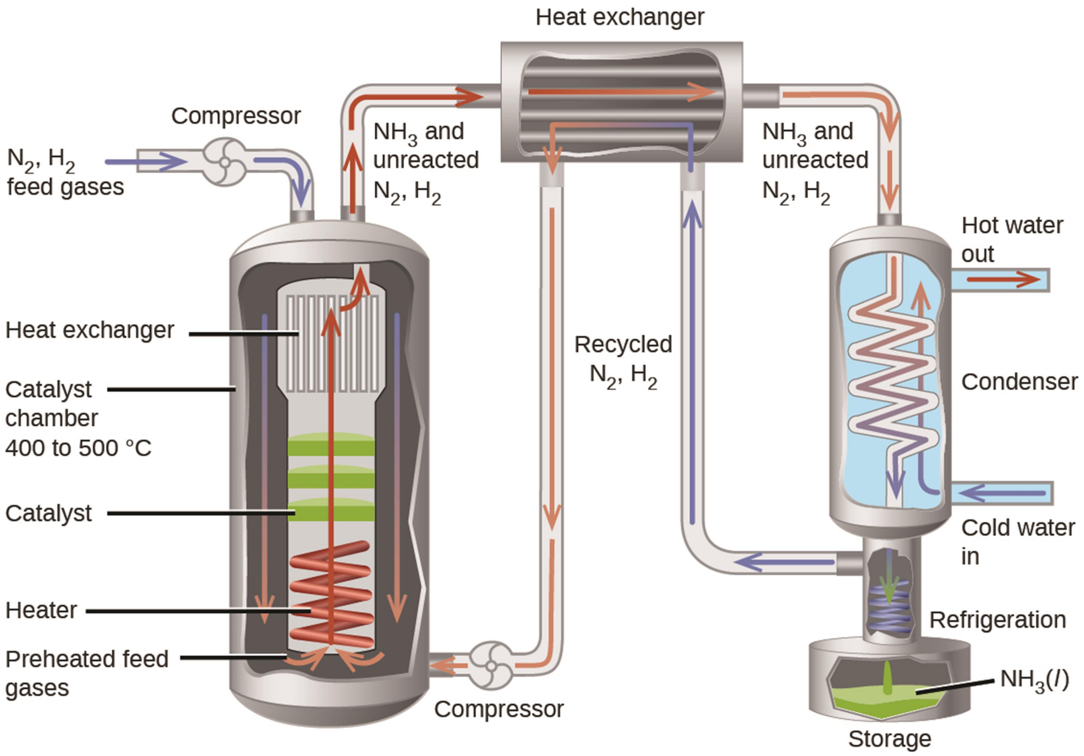


Figure 7.5: The figure shows a typical industrial setup for the commercial production of ammonia by the Haber-Bosch process. The process operates under conditions that stress the chemical equilibrium to favor product formation.

7.2. Equilibrium calculation

Having covered the essential concepts of chemical equilibria in the preceding sections of this chapter, this final section will demonstrate the more practical aspect of using these concepts and appropriate mathematical strategies to perform various equilibrium calculations. These types of computations are essential to many areas of science and technology-for example, in the formulation and dosing of pharmaceutical products. After a drug is ingested or injected, it is typically involved in several chemical equilibria that affect its ultimate concentration in the body system of interest. Knowledge of the quantitative aspects of these equilibria is required to compute a dosage amount that will solicit the desired therapeutic effect.

Many of the useful equilibrium calculations that will be demonstrated here require terms representing changes in reactant and product concentrations. These terms are derived from the stoichiometry of the reaction, as illustrated by decomposition of ammonia:

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$$

As shown earlier in this chapter, this equilibrium may be established within a sealed container that initially contains either NH_3 only, or a mixture of any two of the three chemical species involved in the equilibrium. Regardless of its initial composition, a reaction mixture will show the same relationships between changes in the concentrations of the three species involved, as dictated by the reaction stoichiometry.

Calculation of an Equilibrium Constant

The equilibrium constant for a reaction is calculated from the equilibrium concentrations (or pressures) of its reactants and products. If these concentrations are known, the calculation simply involves their substitution into the K expression. The reaction stoichiometry is used to derive equilibrium concentrations from the information provided. The basic strategy of this computation is helpful for many types of equilibrium computations and relies on the use of terms for the reactant and product concentrations *initially* present, for how they *change* as the reaction proceeds, and for what they are when the system reaches *equilibrium*.

Example 7.5

Calculation of an equilibrium constant

Iodine molecules react reversibly with iodine ions to produce triiodide ions.

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

If a solution with the concentrations of I_2 and I^- both equal to $1.000\text{x}10^{-3}$M before reaction gives an equilibrium concentration of $6.61\text{x}10^{-4}$M, what is the equilibrium constant for the reaction?

Solution

To calculate the equilibrium constants, constant are needed for all the reactant and products:

$$\boldsymbol{K_c = \frac{[I^{3-}]}{[I_2][I^-]}}$$

Provided are the initial concentrations of the reactants and the equilibrium concentration of the product. Use this information to derive terms for the equilibrium concentrations of reactants, presenting all the information in the reaction table.

	$\boldsymbol{I_2(aq)}$ $+$	$\boldsymbol{I^-(aq)}$ $\rightleftharpoons$	$\boldsymbol{I_3^-(aq)}$
Initial concentration (M)	$1.000\text{x}10^{-3}$	$1.000\text{x}10^{-3}$	0
Change (M)	-x	-x	+x
Equilibrium conc.(M)	$1.000\text{x}10^{-3}$-x	$1.000\text{x}10^{-3}$-x	X

At equilibrium the concentration of $I_2$is $6.61\text{x}10^{-4}$M so that

$$1.000\text{x}10^{-3}\text{-x} = 6.61\text{x}10^{-4}$$

$$\text{X} = 1.000\text{x}10^{-3} - 6.61\text{x}10^{-4}$$

$$= 3.39\text{x}10^{-4}\text{M}$$

The table may now be update with numerical values for all its concentrations:

	$I_2(aq)$ +	$I^-(aq)$	⇌ $I_3^-(aq)$
Initial concentration (M)	$1.000x10^{-3}$	$1.000x10^{-3}$	0
Change (M)	$-3.39x10^{-4}$	$-3.39x10^{-4}$	$+3.39x10^{-4}$
Equilibrium conc.(M)	$6.61x10^{-4}$	$6.61x10^{-4}$	$3.39x10^{-4}$

Finally, substitute the equilibrium concentrations into the K expression and solve:

$$K_c = \frac{[I^{3-}]}{[I_2][I^-]}$$

$$= \frac{3.39x10^{-4}M}{(6.61x10^{-4}M)(6.61x10^{-4}M)} = 776$$

✍**Check your learning**

Ethanol and acetic acid react and form water and ethyl acetate, the solvent responsible for the odor of some nail polish removers.

$$C_2H_5OH + CH_3CO_2H \rightleftharpoons CH_3CO_2C_2H_5$$

When 1 mol each of C_2H_5OH and CH_3CO_2H are allowed to react in 1L of the solvent dioxane, equilibrium is established when $\frac{1}{3}$ mole of each of the reactants remains. Calculate the equilibrium constant for the reaction. (Note: water is a solute in this reaction)

Calculation of a Missing Equilibrium Concentration

When the equilibrium constant and all but one equilibrium concentration are provided, the other equilibrium concentration(s) may be calculated. A computation of this sort is illustrated in the next example.

Example 7.6

Calculation of missing equilibrium concentration nitrogen oxides are air pollutants produced by the reaction of nitrogen and oxygen at high temperatures. At 2000 ^{0}c, the value of the Kc for the reaction, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, is $4.1x10^{-4}$. Calculate the equilibrium concentration of NO(g) in air at 1 atm pressure and 2000 ^{0}c. The equilibrium concentrations of N_2 and O_2 at this pressure and temperature are 0.036 M and 0.0089 M respectively.

Solution

Substitute the provided quantities in to the equilibrium constant expression and solve for [NO]:

$$K_C = \frac{[NO]^2}{[N_2][O_2]}$$

$$[NO]^2 = K_C[N_2][O_2]$$

$$[NO] = \sqrt{K_C[N_2][O_2]}$$

$$= \sqrt{(4.1x10^{-4})(0.036)(0.0089)}$$

$$= \sqrt{1.31x10^{-7}}$$

$$= 3.6x10^{-4}$$

Thus, [NO] is 3.6 × 10^{-4} mol/L at equilibrium under these conditions.

To confirm this result, it may be used along with the provided equilibrium concentrations to calculate a value for *K*:

$$K_C = \frac{[NO]^2}{[N_2][O_2]}$$

$$= \frac{(3.6x10^{-4})^2}{(0.036)(0.0089)}$$

$$= 4.0x10^{-4}$$

This result is consistent with the provided value for *K* within nominal uncertainty, differing by just 1 in the least significant digit's place.

✍Check Your Learning

The equilibrium constant K_c for the reaction of nitrogen and hydrogen to produce ammonia at a certain temperature is 6.00 × 10^{-2}. Calculate the equilibrium concentration of ammonia if the equilibrium concentrations of nitrogen and hydrogen are 4.26 *M* and 2.09 *M*, respectively.

Calculation of Equilibrium Concentrations from Initial Concentrations

Perhaps the most challenging type of equilibrium calculation can be one in which equilibrium concentrations are derived from initial concentrations and an equilibrium constant. For these calculations, a four-step approach is typically useful:

1. Identify the direction in which the reaction will proceed to reach equilibrium.
2. Develop a table.
3. Calculate the concentration changes and, subsequently, the equilibrium concentrations.
4. Confirm the calculated equilibrium concentrations.

Example 7.7

Calculation of equilibrium concentrations:

Under certain conditions, the equilibrium constant K_c for the decomposition of $PCl_5(g)$ in to $PCl_3(g)$ and $Cl_2(g)$ is 0.0211. What are the equilibrium concentrations of PCl5, PCl_3 and Cl_2 in a mixture that initially contained only PCl_5 at a concentration of 0.1 M?

Solution

Use the stepwise process described earlier

Step 1: Determine the direction of the reaction proceeds.

The balanced equation for the decomposition of PCl_5 is

$$\boldsymbol{PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)}$$

Because only the reactant is present initially $Q_c = 0$ and the reaction will proceed to the right

Step 2: Develop the reaction table

	$PCl_5(g)$ $\rightleftharpoons$	$PCl_3(g)$ +	$Cl_2(g)$
Initial concentration (M)	1.00	0	0
Change (M)	-x	+x	+x
Equilibrium concentration (M)	1.00-x	X	X

Step 3: Solve for the change and the equilibrium concentrations

Substituting the equilibrium concentrations into the equilibrium constant equation gives

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = 0.0221$$

$$= \frac{(x)(x)}{(1.00 - x)}$$

$$\mathbf{0.0211 = \frac{(x)(x)}{(1.00 - x)}}$$

$$\mathbf{0.0211(1.00 - x) = x^2}$$

$$\mathbf{x^2 + 0.0211x - 0.0211 = 0}$$

The quadratic equation form $\mathbf{ax^2 + bx + c = 0}$ can be rearranged to solve for x:

In this case, a = 1, b =0.0211, and c = -0.0211. Substituting the appropriate values for a, b, and c yields:

$$\mathbf{x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}}$$

$$\mathbf{x = \frac{-0.0211 \pm \sqrt{(0.0211)^2 - 4(1)(-0.0211)}}{(1)}}$$

$$\mathbf{= \frac{\sqrt{(4.45x10^{-4}) + (8.44x10^{-2})}}{2}}$$

$$\mathbf{= \frac{-0.0211 \pm 0.291}{2}}$$

The two roots of the quadratic are, therefore,

$$\mathbf{x = \frac{-0.0211 + \ .291}{2} = 0.135} \text{ and}$$

$$\mathbf{x = \frac{-0.0211 - 0.291}{2}}$$

For this situation, only the positive root is physically meaningful (concentrations are either zero or positive e), and so x = 0.135 M.

The equilibrium concentrations are

$$\mathbf{[PCl_5] = 1.00 - 0.135 = 0.87\ M}$$

$$\mathbf{[Cl_3] = x = 0.135M}$$

$$\mathbf{[Cl_2] = x = 0.135\ M}$$

Step 4: Confirm the calculated equilibrium concentrations.

Substitution into the expression for K_c (to check the calculation) gives

$$\mathbf{K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(0.135)(0.135)}{0.87} = 0.021}$$

The equilibrium constant calculated from the equilibrium concentrations is equal to the value of K_c given in the problem (when round to the proper number of significant figures).

✍Check Your Learning

A 1.00-L flask is filled with 1.00 mole of H_2 and 2.00 moles of I_2. The value of the equilibrium constant for the reaction of hydrogen and iodine reacting to form hydrogen iodide is 50.5 under the given conditions. What are the equilibrium concentrations of H_2, I_2, and HI in moles/L?

$$\boldsymbol{H2(g) + I2(g) \rightleftharpoons 2HI(g)}$$

Example 7.8

What are the concentrations at equilibrium of a 0.15 M solution of HCN?

$$\boldsymbol{HCN(g) \rightleftharpoons H^+(aq) + CN^-(aq)} \qquad K_c = 4.9x10^{-10}$$

Solution

Using "X" to represent the concentration of each product at equilibrium gives this the following reaction table.

	$\boldsymbol{HCN(g)} \rightleftharpoons$	$\boldsymbol{H^+(aq)}$ +	$\boldsymbol{CN^-(aq)}$
Initial concentration (M)	0.15	0	0
Change (M)	-x	+x	+x
Equilibrium concentration (M)	0.15-x	X	X

Substitute the equilibrium concentration terms into the K_c expression

$$K_c = \frac{(x)(x)}{0.15 - x}$$

Rearrange to the quadratic form and solve for x

$$x^2 - 4.9x10^{-1}\ x + 7.35x10^{-11} = 0$$

$$x = 8.56x10^{-6}M\ (3sig.figs) = 8.6x10^{-6}M\ (\ 2sig.figs.$$

Thus, $[H^+] = [CN^-] = x = 8.6x10^6\ M\ and\ [HCN] = 0.15 - x = 0.15\ M$

Note in this case that the change in concentration is significantly less than the initial concentration (a consequence of the small K), and so the initial concentration experiences a negligible change:

$$if\ x \ll 0.15\ M, then\ (0.15 - x) \approx 0.15$$

This approximation allows for a more expedient mathematical approach to the calculation that avoids the need to solve for the roots of a quadratic equation:

$$K_c = \frac{(x)(x)}{0.15 - x} \approx x\frac{x^2}{0.15}$$

$$4.9x10^{-10} = \frac{x^2}{0.15}$$

$$x^2 = (0.15)(4.9x10^{-10}) = 7.4x10^{-11}$$

$$x = \sqrt{7.4x10^{-1}} = 8.6x10^{-6}M$$

The value x calculated is, indeed, much less than the initial concentration

$$8.6x10^{-6} \ll 0.15$$

And also the approximation was justified. If this simplified approach were to yield a value for x that did not justify the approximation, the calculation would need to be repeated without making the approximation.

✍ **Check Your Learning**

What are the equilibrium concentrations in a 0.25 *M* NH_3 solution?

$$\boldsymbol{NH_3(aq) + H_2O(l) \rightleftharpoons NH_4{}^+(aq) + OH^-(aq) \quad Kc = 1.8 \times 10^{-5}}$$

7.3. Concepts of acid-base

7.3.1. Arrhenius concept

An Arrhenius acid dissociates in water to form hydrogen ions, while an Arrhenius base dissociates in water to form hydroxide ions.

- An Arrhenius acid increases the concentration of hydrogen (H^+) ions in an aqueous solution, while an Arrhenius base increases the concentration of hydroxide (OH^-) ions in an aqueous solution.
- The Arrhenius definitions of acidity and alkalinity are restricted to aqueous solutions and refer to the concentration of the solvent ions.
- The universal aqueous acid–base definition of the Arrhenius concept is described as the formation of a water molecule from a proton and hydroxide ion. Therefore, in Arrhenius acid–base reactions, the reaction between an acid and a base is a neutralization reaction.

An acid-base reaction is a chemical reaction that occurs between an acid and a base. Several concepts exist that provide alternative definitions for the reaction mechanisms involved and their application in solving related problems. Despite several differences in definitions, their importance as different methods of analysis becomes apparent when they are applied to acid-base reactions for gaseous or liquid species, or when acid or base character may be somewhat less apparent.

The Arrhenius definition of acid-base reactions, which was devised by Svante Arrhenius, is a development of the hydrogen theory of acids. It was used to provide a modern definition of acids and bases, and followed from Arrhenius's work with Friedrich Wilhelm Ostwald in establishing the presence of ions in aqueous solution in 1884. This led to Arrhenius receiving the Nobel Prize in Chemistry in 1903.

As defined by Arrhenius:

- An Arrhenius acid is a substance that dissociates in water to form hydrogen ions (H^+). In other words, an acid increases the concentration of H^+ ions in an aqueous solution. This protonation of water yields the hydronium ion (H_3O^+); in modern times, H^+ is used as a shorthand for H_3O^+ because it is now known that a bare proton (H^+) does not exist as a free species in aqueous solution.
- An Arrhenius base is a substance that dissociates in water to form hydroxide (OH^-) ions. In other words, a base increases the concentration of OH^- ions in an aqueous solution.

Limitations of the Arrhenius Definition

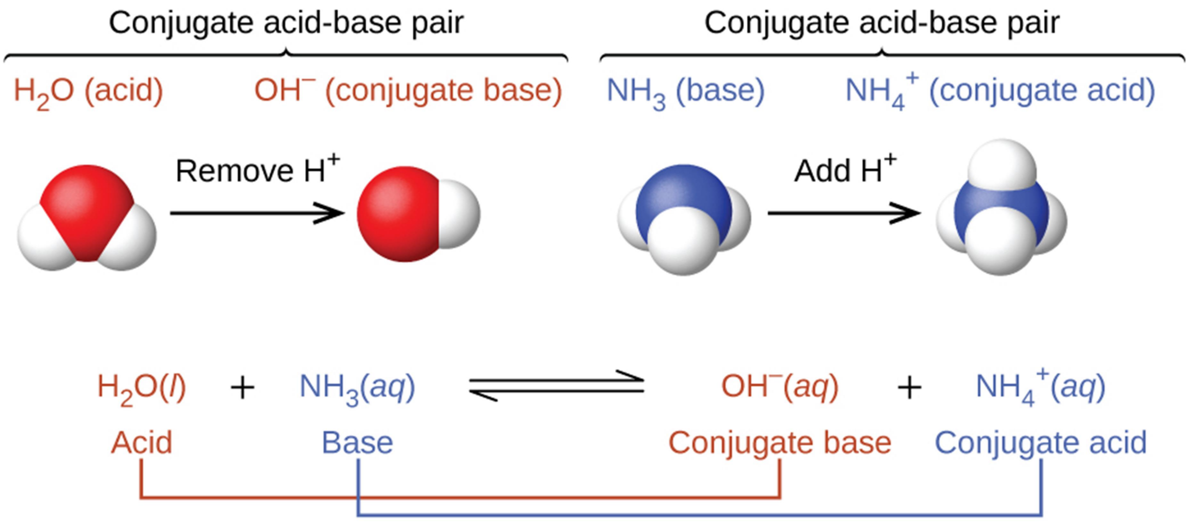
The Arrhenius definitions of acidity and alkalinity are restricted to aqueous solutions and refer to the concentration of the solvated ions. Under this definition, pure H_2SO_4 or HCl dissolved in toluene are not acidic, despite the fact that both of these acids will donate a proton to toluene. In addition, under the Arrhenius definition, a solution of sodium amide ($NaNH_2$) in liquid ammonia is not alkaline, despite the fact that the amide ion (NH_2^-) will readily deprotonate ammonia. Thus, the Arrhenius definition can only describe acids and bases in an aqueous environment.

7.3.2. BrØnsted-Lowery concept

The significance of hydrogen was reemphasized in 1884 when Svante Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

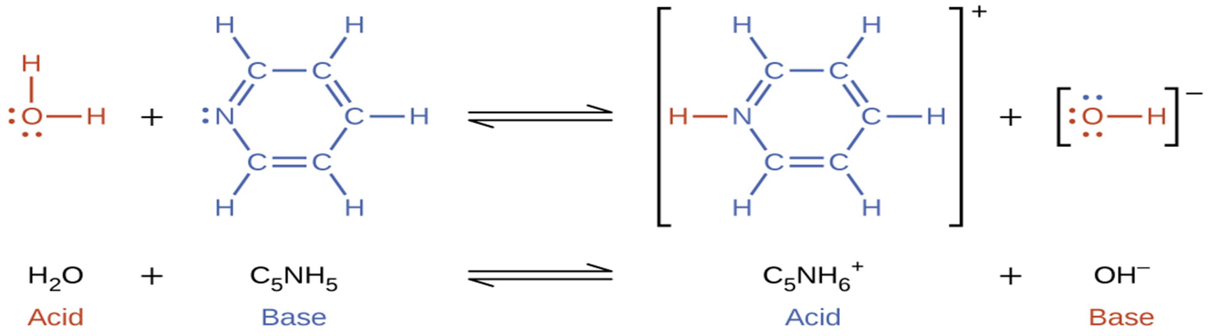
Johannes BrØnsted and **Thomas Lowry** proposed a more general description in 1923 in which acids and bases were defined in terms of the transfer of hydrogen ions, H^+. (Note that, these hydrogen ions are often referred to simply as *protons*, since that subatomic particle is the only component of cations derived from the most abundant hydrogen isotope, ^1H). A compound that donates a proton to another compound is called a BrØnsted-Lowry acid, and a compound that accepts a proton is called a Brønsted-Lowry base. An acid-base reaction is, thus, the transfer of a proton from a donor (acid) to an acceptor (base).

The concept of ***conjugate pairs*** is useful in describing BrØnsted-Lowry acid-base reactions (and other reversible reactions, as well). When an acid donates H^+, the species that remains is called the **conjugate base** of the acid because it reacts as a proton acceptor in the reverse reaction. Likewise, when a base accepts H^+, it is converted to its **conjugate acid**. The reaction between water and ammonia illustrates this idea. In the forward direction, water acts as an acid by donating a proton to ammonia and subsequently becoming a hydroxide ion, OH^-, the conjugate base of water. The ammonia acts as a base in accepting this proton, becoming an ammonium ion, NH_4^+, the conjugate acid of ammonia. In the reverse direction, a hydroxide ion acts as a base in accepting a proton from ammonium ion, which acts as an acid.



The reaction between a BrØnsted-Lowry acid and water is called acid ionization. For example, when hydrogen fluoride dissolves in water and ionizes, protons are transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions.

Base ionization of a species occurs when it accepts protons from water molecules. In the example below, pyridine molecules, C_5NH_5, undergo base ionization when dissolved in water, yielding hydroxide and pyridinium ions.



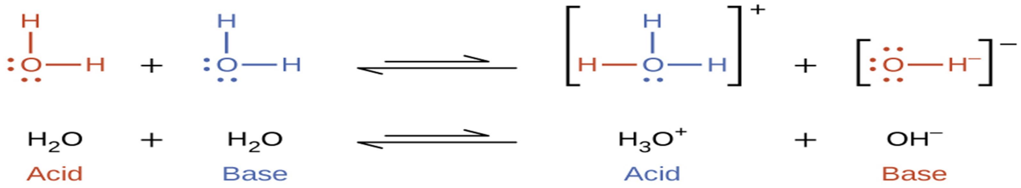
The preceding ionization reactions suggest that water may function as both a base (as in its reaction with hydrogen fluoride) and an acid (as in its reaction with ammonia). Species capable of either donating or accepting protons are called amphiprotic, or more generally, amphoteric, a term that may be used for acids and bases per definitions other than the BrØnsted-Lowry one. The equations below show the two possible acid-base reactions for two amphiprotic species, bicarbonate ion and water:

$$\mathbf{HCO_3^-(\mathit{aq}) + H_2O(\mathit{l}) \rightleftharpoons CO_3^{2-}(\mathit{aq}) + H_3O^+(\mathit{aq})}$$

$$\mathbf{HCO_3^-(\mathit{aq}) + H_2O(\mathit{l}) \rightleftharpoons H_2CO_3(\mathit{aq}) + OH^-(\mathit{aq})}$$

The first equation represents the reaction of bicarbonate as an acid with water as a base, whereas the second represents reaction of bicarbonate as a base with water as an acid. When bicarbonate is added to water, both these equilibria are established simultaneously and the composition of the resulting solution may be determined through appropriate equilibrium calculations.

In the liquid state, molecules of an amphiprotic substance can react with one another as illustrated for water in the equations below



The process in which like molecules react to yield ions is called autoionization. Liquid water undergoes autoionization to a very slight extent; at 25 °C, approximately two out of every billion water molecules are ionized. The extent of the water autoionization process is reflected in the value of its equilibrium constant, the ion-product constant for water, K_w:

$$\mathbf{H_2O(\mathit{l}) + H_2O(\mathit{l}) \rightleftharpoons H_3O^+(\mathit{aq}) + OH^-(\mathit{aq}) \qquad \mathit{K}_w = [H_3O^+][OH^-]}$$

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, K_w has a value of 1.0×10^{-14}. The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and hydroxide ion increase with temperature. For example, at 100 °C, the value for K_w is about 5.6×10^{-13}, roughly 50 times larger than the value at 25 °C.

7.3.3. Lewis concept

Lewis Acid base theory is more general than the Bronsted-Lowery theory, and will be used extensively in organic chemistry. A Lewis acid is defined as an **electron pair acceptor**, and a Lewis base as an **electron pair donor**.

Examples of Lewis Acids: H^+, K^+, Mg^{2+}, Fe^{3+}, BF_3, , $AlCl_3$, Br_2.

Examples of Lewis Bases: OH^-, F^-, H_2O, ROH, NH_3, SO_4^{2-}, H^-, CO, C_6H_6.

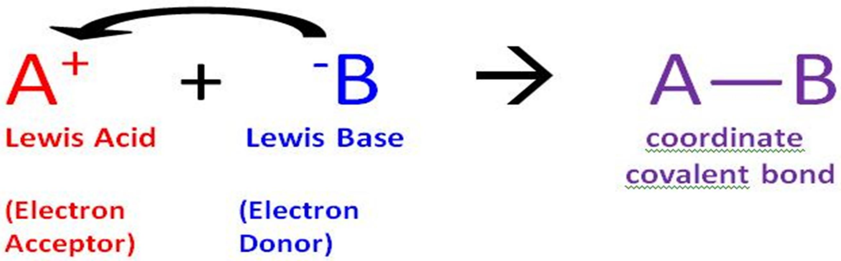


Figure 7.6: General schema for Lewis acid base reaction.

- Lewis Acid: a species that accepts an electron pair (i.e., an **electrophile**) and will have vacant orbitals, or the ability to form a vacant orbital.
- Lewis Base: a species that donates an electron pair (i.e., a **nucleophile**) and will have lone-pair electrons

In a Lewis Acid-Base reaction a bond is formed where both electrons come from the Lewis base, and this is called a coordinate covalent bond (or dative covalent bond).

Lewis Acids

There are three general types of Lewis Acids, that is, chemical species that can accept electrons.

1. Molecules with an incomplete octet
2. Molecules with double bonds
3. metal ions with vacant d-orbitals.

Incomplete Octets

Boron Trifluoride is an exception to the octet rule and has an incomplete octet, and can thus accept electrons to form a bond. In the process it goes from sp^2 hybrid to sp^3 hybrid.

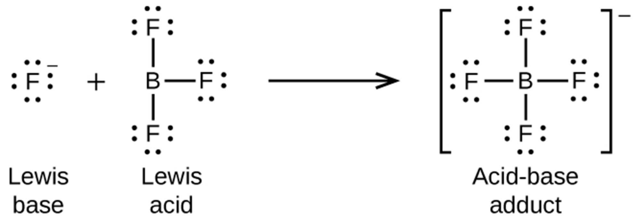


Figure 7.7: General reaction scheme where a molecule with an incomplete octet functions as a Lewis Acid

Double Bonds

A double bond has 4 electrons shared between 2 atoms in a PI and sigma orbital. If you break the pi bond and move the two electrons to a non-bonding orbital on one atom, the other atom develops an incomplete octet and can function as a Lewis acid. This is shown in figure 7.8 where the pi electrons move onto the oxygen, allowing the sulfur to receive electrons from a Lewis base.

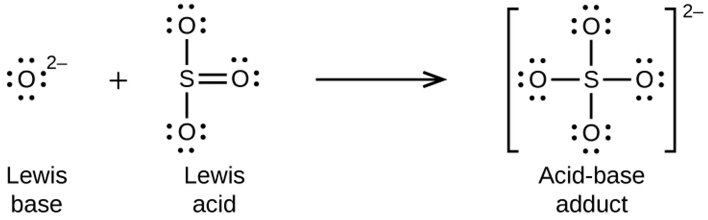


Figure 7.8: General reaction scheme where a molecule with a double bond functions as a Lewis Acid

Metal Cations

Many metals have vacant d-orbitals that can accept electrons and thus behave as Lewis Acids. In fact, most metals react with water when they dissolve in water to form what is called a complex ion. For example, aluminum(III) is not a free ion, but a complex with 6 water molecules

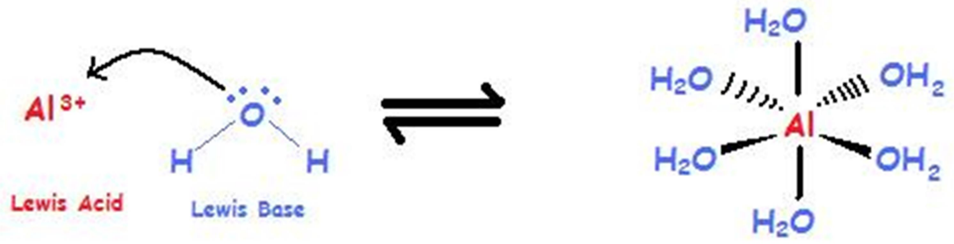


Figure 7.9: General reaction scheme where a molecule with a metal cation functions as a Lewis Acid

7.5. pH and pOH

As discussed earlier, hydronium and hydroxide ions are present both in pure water and in all aqueous solutions, and their concentrations are inversely proportional as determined by the ion product of water (K_w). The concentrations of these ions in a solution are often critical determinants of the solution's properties and the chemical behaviors of its other solutes, and specific vocabulary has been developed to describe these concentrations in relative terms.

A solution is neutral if it contains equal concentrations of hydronium and hydroxide ions; acidic if it contains a greater concentration of hydronium ions than hydroxide ions; and basic if it contains a lesser concentration of hydronium ions than hydroxide ions.

A common means of expressing quantities that may span many orders of magnitude is to use a logarithmic scale. One such scale that is very popular for chemical concentrations and equilibrium constants is based on the p-function, defined as shown where "X" is the quantity of interest and "log" is the base-10 logarithm:

$$\boldsymbol{pX = -logX}$$

The pH of a solution is therefore defined as shown here, where $[H_3O^+]$ is the molar concentration of hydronium ion in the solution:

$$\boldsymbol{pH = -log[H_3O^+]}$$

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

$$\boldsymbol{[H_3O^+] = 10^{-p}}$$

Likewise, the hydroxide ion molarity may be expressed as a p-function, or pOH:

$$\boldsymbol{pOH = -\log[OH^-]}$$

Or

$$[OH^-] = 10^{-pO}$$

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the K_w expression:

$$K_\mathrm{w} = [\mathrm{H_3O^+}]\,[\mathrm{OH^-}]$$

$$-\log K_\mathrm{w} = -\log\left([\mathrm{H_3O^+}]\,[\mathrm{OH^-}]\right) = -\log[\mathrm{H_3O^+}] + -\log[\mathrm{OH^-}]$$

$$\mathrm{p}K_\mathrm{w} = \mathrm{pH} + \mathrm{pOH}$$

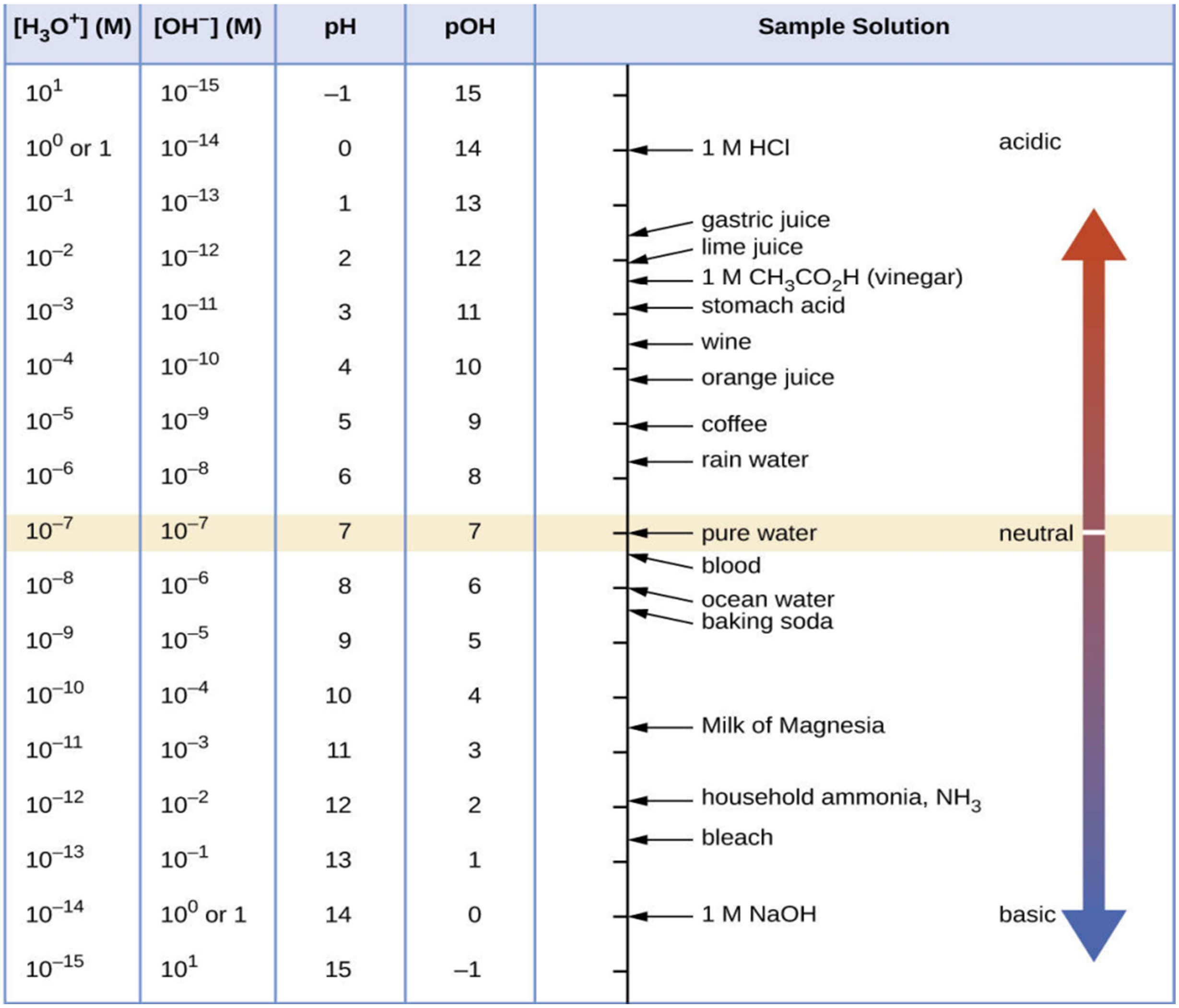
At 25 °C, the value of K_w is 1.0×10^{-14}, and so:

$$\boldsymbol{14.00 = pH + pOH}$$

Table 7.1: Summary of Relations for Acidic, Basic and Neutral Solutions

Classification	**Relative Ion Concentrations**	**pH at 25 °C**
Acidic	$[H_3O^+] > [OH^-]$	pH < 7
Neutral	$[H_3O^+] = [OH^-]$	pH = 7
Basic	$[H_3O^+] < [OH^-]$	pH > 7

Figure 7.9 shows the relationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH for solutions classified as acidic, basic, and neutral.



$[H_3O^+]$ (M)	$[OH^-]$ (M)	pH	pOH
10^1	10^{-15}	–1	15
10^0 or 1	10^{-14}	0	14
10^{-1}	10^{-13}	1	13
10^{-2}	10^{-12}	2	12
10^{-3}	10^{-11}	3	11
10^{-4}	10^{-10}	4	10
10^{-5}	10^{-9}	5	9
10^{-6}	10^{-8}	6	8
10^{-7}	10^{-7}	7	7
10^{-8}	10^{-6}	8	6
10^{-9}	10^{-5}	9	5
10^{-10}	10^{-4}	10	4
10^{-11}	10^{-3}	11	3
10^{-12}	10^{-2}	12	2
10^{-13}	10^{-1}	13	1
10^{-14}	10^0 or 1	14	0
10^{-15}	10^1	15	–1

Figure 7.9: The pH and pOH scales represent concentrations of H_3O^+ and OH^-, respectively. The pH and pOH values of some common substances at 25 °C are shown in this chart.

Example 7.9

Calculation of pH from $[H_3O^+]$

What is th pH of stomach acid, a solution of HCl with a hydronium ion concentration of $1.2\text{x}10^{-3}$ M?

Solution

$$\mathbf{pH = -log[H_3O^+]}$$

$$\mathbf{= -log(1.2x10^{-3})}$$

$$\mathbf{= -(-2.92) = 2.92}$$

✍Check Your Learning

Water exposed to air contains carbonic acid, H_2CO_3, due to the reaction between carbon dioxide and water:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

Air-saturated water has a hydronium ion concentration caused by the dissolved CO_2 of $2.0 \times 10^{-6} M$, about 20-times larger than that of pure water. Calculate the pH of the solution at 25 °C.

Example 7.10

Calculate the hydronium ion concentration of blood, the pH of which is 7.3

Solution

$$\text{pH} = -\log[H_3O^+]$$

$$\log[H_3O^+] = 7.3$$

$$[H_3O^+] = 10^{-7.3} \text{ or } [H_3O^+] = \text{antilog of } -7.3$$

$$[H_3O^+] = 5\text{x}10^{-8} \text{ M}$$

✍Check Your Learning

Calculate the hydronium ion concentration of a solution with a pH of −1.07.

7.6. Relative Strength of Acids and Base

The relative strength of an acid or base is the extent to which it ionizes when dissolved in water. If the ionization reaction is essentially complete, the acid or base is termed *strong*; if relatively little ionization occurs, the acid or base is weak. As will be evident throughout the remainder of this chapter, there are many more weak acids and bases than strong ones. The most common strong acids and bases are listed in Table 7.2.

Table 7.2: Some of the common strong acids and bases are listed here

Strong acids	Strong bases
$HClO_4$ perchloric acid	LiOH lithium hydroxide
HCl hydrochloric acid	NaOH sodium hydroxide
HBr hydrobromic acid	KOH potassium hydroxide
HI hydroiodic acid	$Ca(OH)_2$ calcium hydroxide
HNO_3 nitric acid	Sr(OH)2 strontium hydroxide
H_2SO_4 sulfuric acid	Ba(OH)2 barium hydroxide

The relative strengths of acids may be quantified by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions than do weaker acids. The equilibrium constant for an acid is called the acid-ionization constant, K_a. For the reaction of an acid HA:

$\boldsymbol{HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)}$, the ionization constant is written

$$\boldsymbol{K_a = \frac{[H_3O^+][A^-]}{[HA]}}$$

Where, the concentrations are those at equilibrium. Although water is a reactant in the reaction, it is the solvent as well, so we do not include $[H_2O]$ in the equation. The larger the K_a value of an acid, the larger the concentration of H_3O^+ and A^- relative to the concentration of the nonionized acid, HA, in an equilibrium mixture, and the stronger the acid. An acid is classified as “strong” when it undergoes complete ionization, in which case the concentration of HA is zero and the acid ionization constant is immeasurably large ($K_a \approx \infty$). Acids that are partially ionized are called "weak," and their acid ionization constants may be experimentally measured.

To illustrate this idea, three acid ionization equations and K_a values are shown below. The ionization constants increase from first to last of the listed equations, indicating the relative acid strength increases in the order $CH_3CO_2H < HNO_2 < HSO_4^-$:

$$\boldsymbol{CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq) \quad K_a = 1.8x10^{-5}}$$

$$\boldsymbol{HNO_2(aq) + H_2O(aq) \rightleftharpoons H_3O^+(aq) + NO_2^- \qquad K_a = 4.6x10^{-4}}$$

$$\boldsymbol{HSO_4^-(aq) + H_2O(aq) \rightleftharpoons H_3O^+(aq) + SO_4^{2-} \qquad K_a = 1.2x10^{-2}}$$

Another measure of the strength of an acid is its percent ionization. The percent ionization of a weak acid is defined in terms of the composition of an equilibrium mixture:

$$\%ionization = \frac{[H_3O^+]_{eq}}{[HA]_0} x100$$

Where the numerator is equivalent to the concentration of the acid's conjugate base (per stoichiometry, $[A^-] = [H_3O^+]$). Unlike the K_a value, the percent ionization of a weak acid varies with the initial concentration of acid, typically decreasing as concentration increases. Equilibrium calculations of the sort described later in this chapter can be used to confirm this behavior.

Example 7.11

Calculation of percent ionization from pH

Calculate the percent ionization of a 0.125 M solution of nitrous acid (a weak acid), with a pH of 2.09.

Solution

The percent ionization for an acid is

$$\boldsymbol{\frac{[H_3O^+]_{eq}}{[HNO_2]_0} x10}$$

Converting the provided pH to hydronium ion concentration yields

$$[H_3O^+] = 10^{-2.09} = 0.0081$$

Substituting this value and the provided initial acid concentration into the percent ionization equation gives

$$\frac{8.1x10^{-3}}{0.125}x100 = 6.5\%$$

(Recall the provided pH value of 2.09 is logarithmic, and so it contains just two significant digits, limiting the certainty of the computed percent ionization.)

Just as for acids, the relative strength of a base is reflected in the magnitude of its base-ionization constant (K_b) in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, B:

$$\mathbf{B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)}$$

The ionization constant is written as

$$\mathbf{K_b = \frac{[HB^+][OH^-]}{[B]}}$$

Inspection of the data for three weak bases presented below shows the base strength increases in the order $NO_2^- < CH_2CO_2^- < NH_3$.

$$\mathbf{NO_2{}^-(aq) + H_2O(l) \rightleftharpoons HNO_2(aq) + OH^- \qquad K_b = 2.17x10^{-1}}$$

$$\mathbf{CH_3CO_2{}^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq) \qquad \boldsymbol{K_b = 5.6x10^{-10}}}$$

$$\mathbf{NH_3(aq) + H_2O(l) \rightleftharpoons NH_4{}^+(aq) + OH^- \qquad K_b = 1.8x10^{-5}}$$

As for acids, the relative strength of a base is also reflected in its percent ionization, computed as

$$\mathbf{\%ionization = \frac{[OH^-]_{eq}}{[B]_0}x100\%}$$

but will vary depending on the base ionization constant and the initial concentration of the solution.

Relative Strengths of Conjugate Acid-Base Pairs

Brønsted-Lowry acid-base chemistry is the transfer of protons; thus, logic suggests a relation between the relative strengths of conjugate acid-base pairs. The strength of an acid or base is quantified in its ionization constant, K_a or K_b, which represents the extent of the acid or base ionization reaction. For the conjugate acid-base pair HA / A^-, ionization equilibrium equations and ionization constant expressions are:

$$\mathbf{HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \quad K_a = \frac{[H_3O^+][A^-]}{[HA]}}$$

$$\mathbf{A^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HA\,(aq) \quad K_b = \frac{[HA][OH^-]}{[A^-]}}$$

Adding these two chemical equations yields the equation for the autoionization for water:

$$\mathbf{\cancel{HA(aq)} + H_2O(l) + \cancel{A^-(aq)} + H_2O(l) \rightleftharpoons H_3O^+(aq) + \cancel{A^-(aq)} + OH^-(aq) + \cancel{HA\,(aq)}}$$

$$\mathbf{2H_2H(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)}$$

The equilibrium constant for a summed reaction is equal to the mathematical product of the equilibrium constants for the added reactions, and so

$$\boldsymbol{K_a x K_a} = \frac{\mathbf{[H_3O^+][OH^-]}}{[HA]} x \frac{[\boldsymbol{HA}]\mathbf{[OH^-]}}{[\boldsymbol{A^-}]} = \mathbf{[H_3O^+][OH^-]} = \boldsymbol{K_w}$$

This equation states the relation between ionization constants for any conjugate acid-base pair, namely, their mathematical product is equal to the ion product of water, K_w. By rearranging this equation, a reciprocal relation between the strengths of a conjugate acid-base pair becomes evident:

$$\boldsymbol{K_a = K_w/K_b \text{ or } K_b = K_w/K_5}$$

The inverse proportional relation between K_a and K_b means the stronger the acid or base, the weaker its conjugate partner. Figure 7.10 illustrates this relation for several conjugate acid-base pairs.

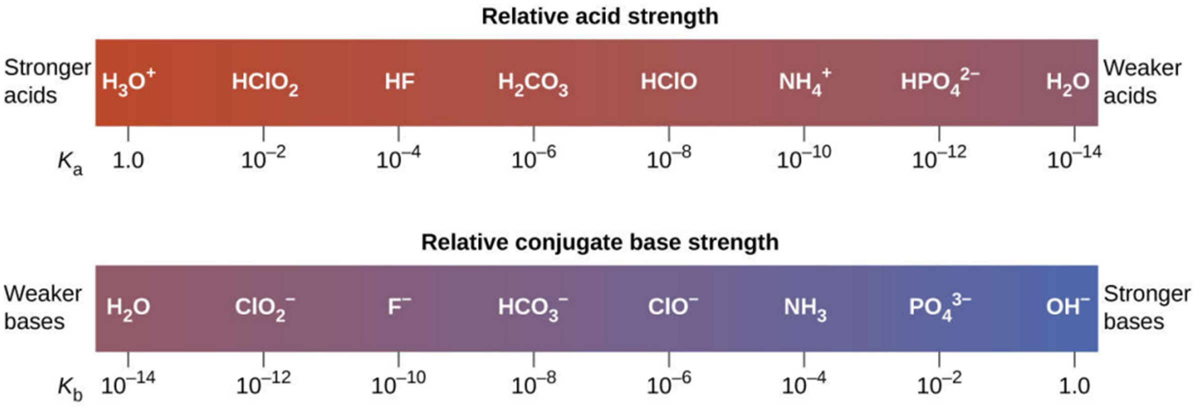
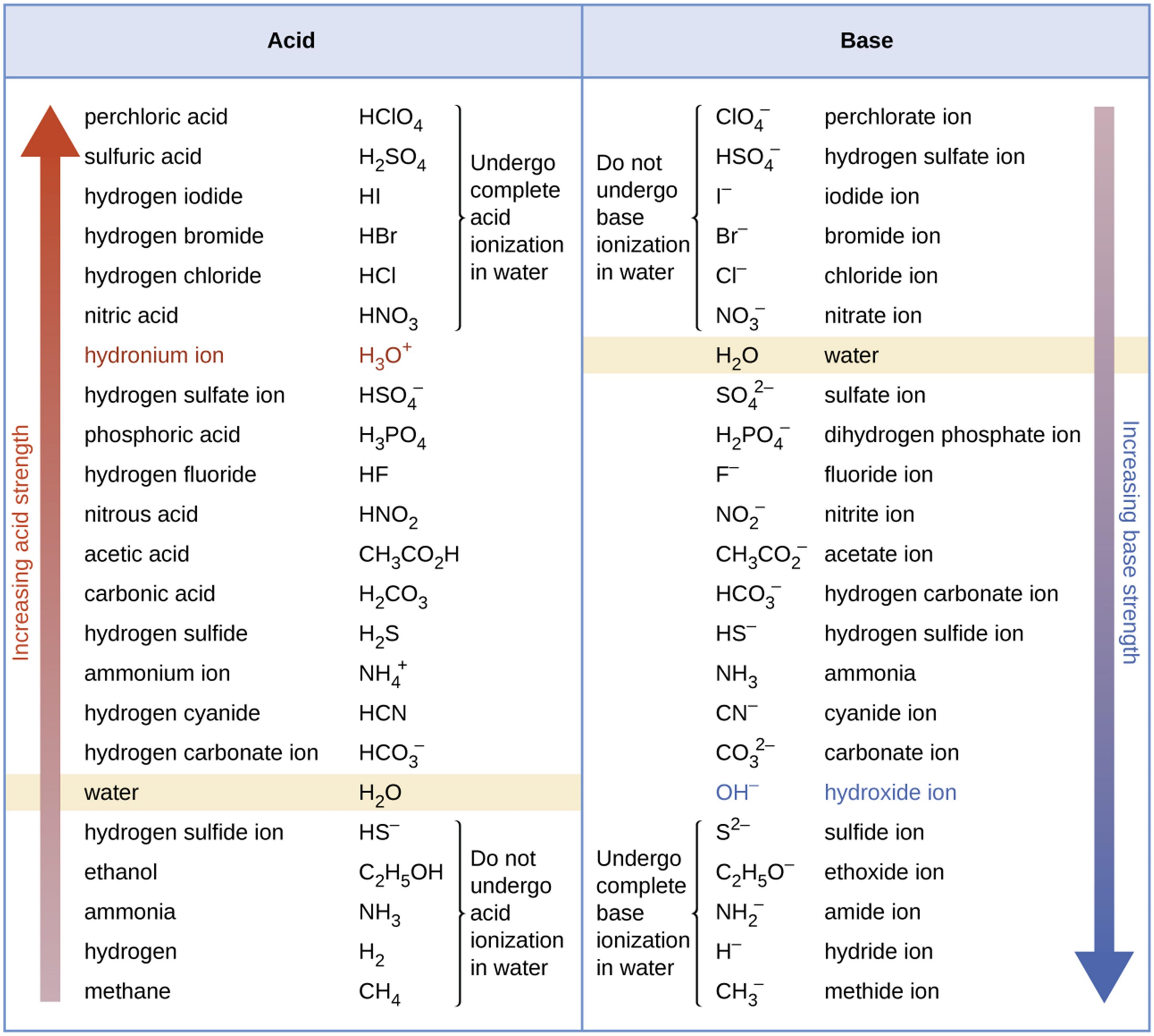


Figure 7.10: Relative strengths of several conjugate acid-base pairs are shown.



Acid				Base	
perchloric acid	$HClO_4$	Undergo complete acid ionization in water	Do not undergo base ionization in water	ClO_4^-	perchlorate ion
sulfuric acid	H_2SO_4			HSO_4^-	hydrogen sulfate ion
hydrogen iodide	HI			I^-	iodide ion
hydrogen bromide	HBr			Br^-	bromide ion
hydrogen chloride	HCl			Cl^-	chloride ion
nitric acid	HNO_3			NO_3^-	nitrate ion
hydronium ion	H_3O^+			H_2O	water
hydrogen sulfate ion	HSO_4^-			SO_4^{2-}	sulfate ion
phosphoric acid	H_3PO_4			$H_2PO_4^-$	dihydrogen phosphate ion
hydrogen fluoride	HF			F^-	fluoride ion
nitrous acid	HNO_2			NO_2^-	nitrite ion
acetic acid	CH_3CO_2H			$CH_3CO_2^-$	acetate ion
carbonic acid	H_2CO_3			HCO_3^-	hydrogen carbonate ion
hydrogen sulfide	H_2S			HS^-	hydrogen sulfide ion
ammonium ion	NH_4^+			NH_3	ammonia
hydrogen cyanide	HCN			CN^-	cyanide ion
hydrogen carbonate ion	HCO_3^-			CO_3^{2-}	carbonate ion
water	H_2O			OH^-	hydroxide ion
hydrogen sulfide ion	HS^-	Do not undergo acid ionization in water	Undergo complete base ionization in water	S^{2-}	sulfide ion
ethanol	C_2H_5OH			$C_2H_5O^-$	ethoxide ion
ammonia	NH_3			NH_2^-	amide ion
hydrogen	H_2			H^-	hydride ion
methane	CH_4			CH_3^-	methide ion

Figure 7.11: This figure shows strengths of conjugate acid-base pairs relative to the strength of water as the reference substance.

The listing of conjugate acid–base pairs shown in Figure 7.11 is arranged to show the relative strength of each species as compared with water, whose entries are highlighted in each of the table's columns. In the acid column, those species listed below water are weaker acids than water. These species do not undergo acid ionization in water; they are not BrØnsted-Lowry acids. All the species listed above water are stronger acids, transferring protons to water to some extent when dissolved in an aqueous solution to generate hydronium ions. Species above water but below hydronium ion are *weak acids*, undergoing partial acid ionization, where as those above hydronium ion are *strong acids* that are completely ionized in aqueous solution.

If all these strong acids are completely ionized in water, why does the column indicate they vary in strength, with nitric acid being the weakest and perchloric acid the strongest? Notice that the sole acid species present in an aqueous solution of any strong acid is $H_3O^+(aq)$, meaning that hydronium ion is the strongest acid that may exist in water; any stronger acid will react completely with water to generate hydronium ions. This limit on the acid strength of solutes in a solution is called a **leveling effect**. To measure the differences in acid strength for "strong" acids, the acids must be dissolved in a solvent that is *less basic* than water. In such solvents, the acids will be "weak," and so any differences in the extent of their ionization can be determined. For example, the binary hydrogen halides HCl, HBr, and HI are strong acids in water but weak acids in ethanol (strength increasing HCl < HBr < HI).

The right column of Figure 7.11 lists a number of substances in order of increasing base strength from top to bottom. Following the same logic as for the left column, species listed above water are weaker bases and so they don't undergo base ionization when dissolved in water. Species listed between water and its conjugate base, hydroxide ion, are weak bases that partially ionize. Species listed below hydroxide ion are strong bases that completely ionize in water to yield hydroxide ions (i.e., they are *leveled* to hydroxide). A comparison of the acid and base columns in this table supports the reciprocal relation between the strengths of conjugate acid-base pairs. For example, the conjugate bases of the strong acids (top of table) are all of negligible strength. A strong acid exhibits an immeasurably large K_a, and so its conjugate base will exhibit a K_b that is essentially zero:

Strong acid: $\boldsymbol{K_a \approx \infty}$

Conjugate base: $\boldsymbol{K_b = \frac{K_w}{K_a} = K_a/\infty \approx 0}$

A similar approach can be used to support the observation that conjugate acids of strong bases ($K_b \approx \infty$) are of negligible strength ($K_a \approx 0$).

Example 7.12

Calculating ionization constants for conjugate acid-base pairs

Use the K_b for the nitrite ion, to calculate the K_a for its conjugate acid.

Solution

$\boldsymbol{K_a}$ for $NO_2{}^-$ is given in this section as $2.17\text{x}10^{11}$. The conjugate acid of $NO_2{}^-$ is HNO_2; HNO_2 can be calculated using the relationship:

$$\boldsymbol{K_A x K_b = 1.0x10^{-1} \quad = K_w}$$

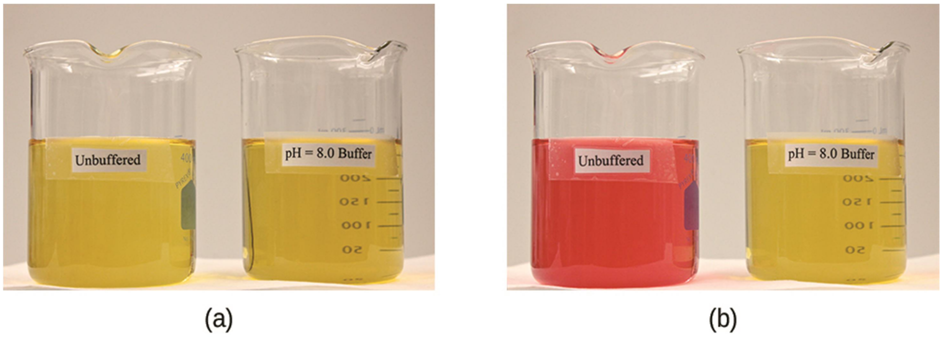
Solving for $\boldsymbol{K_a = \frac{K_w}{K_b} = \frac{1.0x10^{-10}}{2.17x10^{-11}} = 4.6x10^{-4}}$

✍**Check Your Learning**

Determine the relative acid strengths of $NH_4{}^+$ and HCN by comparing their ionization constants. The ionization constant of HCN is 4.9×10^{-10}. The ionization constant of $NH_4{}^+$ is not listed, but the ionization constant of its conjugate base, NH_3, is listed as 1.8×10^{-5}.

7.7. Buffers Solution

A solution containing appreciable amounts of a weak conjugate acid-base pair is called a buffer solution, or a buffer. Buffer solutions resist a change in pH when small amounts of a strong acid or a strong base are added Figure 7.12. A solution of acetic acid and sodium acetate (CH_3COOH + CH_3COONa) is an example of a buffer that consists of a weak acid and its salt. An example of a buffer that consists of a weak base and its salt is a solution of ammonia and ammonium chloride ($NH_3(aq)$ + $NH_4Cl(aq)$).



(a)

(b)

Figure 7.12: (a) The buffered solution on the left and the unbuffered solution on the right have the same pH (pH 8); they are basic, showing the yellow color of the indicator methyl orange at this pH. (b) After the addition of 1 mL of a 0.01-M HCl solution, the buffered solution has not detectably changed its pH but the unbuffered solution has become acidic, as indicated by the change in color of the methyl orange, which turns red at a pH of about 4.

How Buffers Work

To illustrate the function of a buffer solution, consider a mixture of roughly equal amounts of acetic acid and sodium acetate. The presence of a weak conjugate acid-base pair in the solution imparts the ability to neutralize modest amounts of added strong acid or base. For example, adding strong base to this solution will neutralize hydronium ion and shift the acetic acid ionization equilibrium to the right, partially restoring the decreased H_3O^+ concentration:

$$\mathbf{CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2{}^-(aq)}$$

Likewise, adding strong acid to this buffer solution will neutralize acetate ion, shifting the above ionization equilibrium right and returning $[H_3O^+]$ to near its original value. Figure 7.13 provides a graphical illustration of the changes in conjugate-partner concentration that occur in this buffer solution when strong acid and base are added. The buffering action of the solution is essentially a result of the added strong acid and base being converted to the weak acid and base that make up the buffer's conjugate pair. The weaker acid and base undergo only slight ionization, as compared with the complete ionization of the strong acid and base, and the solution pH, therefore, changes much less drastically than it would in an unbuffered solution.

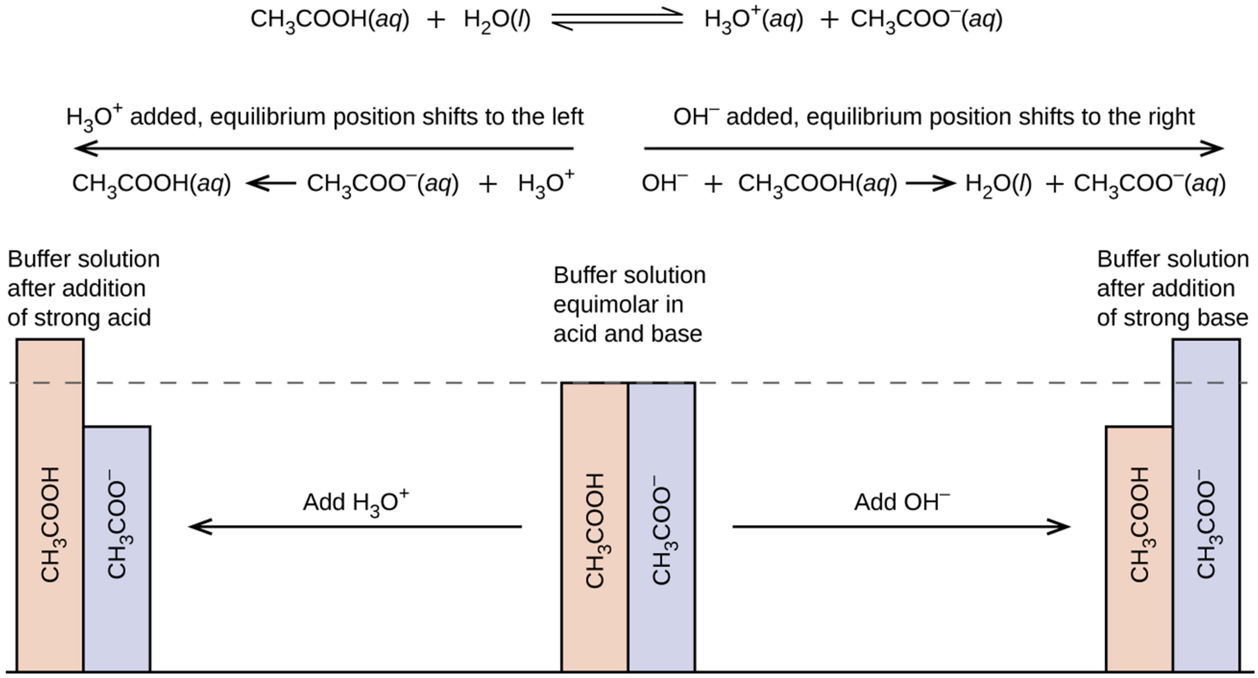


Figure 7.13: Buffering action in a mixture of acetic acid and acetate salt.

Example 7.13

pH changes in buffer and unbuffered solutions

Acetate buffers are used in biochemical studies of enzymes and other chemical components of cells to prevent pH changes that might affect the biochemical activity of these compounds.

a. Calculate the pH of an acetate buffer that is a mixture with 0.1 M acetic acid and 0.10 M sodium acetate.
b. Calculate the pH after 1.0 mL of 0.10 M NaOH is added to 100 mL of this buffer.
c. For comparison, calculate the pH after 1.0 mL of 0.10 M NaOH is added to100 mL of a solution of an unbuffered solution with a pH of 4.74.

Solution

a. Following the reaction table approach to this equilibrium calculation yields the following:

	$\mathbf{CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2{}^-(aq)}$			
Initial concentration (M)	0.10		0	0.10
Change (M)	-x		+x	+x
Equilibrium concentration (M)	0.10-x		x	0.10+x

Substituting the equilibrium concentration terms into the K_a expression, assuming x<<0.10, and solving the simplified equation for x yields

$$\boldsymbol{x = 1.8x10^{-5}\,M}$$

$$\mathbf{[H_3O^+] = 0 + x = \boldsymbol{x} = 1.8\boldsymbol{x}10^{-5}\,\boldsymbol{M}}$$

$$\boldsymbol{pH = -\log[H_3O^+] \ = -l0g(1.8x10^{-5}\,) = 4.74}$$

b. Calculate the pH after 1 mL of 0.10 M NaOH is added to 100 mL of this buffer.
Adding strong acid will neutralize some of the acetic acid, yielding the conjugate base acetate ion. Compute the new concentrations of these two buffer components, then repeat the equilibrium calculation of part (a) using these new concentrations.

$$\boldsymbol{0.0010\,\cancel{L}x\left(\frac{0.10\,mol\,NaOH}{1\,\cancel{L}}\right) = 1.0x10^{-4}\ \ mol\,NaOH}$$

The initial molar amount of acetic acid is

$$\boldsymbol{0.10\,\cancel{L}x\left(\frac{0.100\,mol\,CH_3CO_2H}{1\,\cancel{L}}\right) = 1.00x10^{-2}\,mol\,CH_3CO_2H}$$

The amount of acetic acid remaining after some neutralized by the added base is

$$\mathbf{(1.00x10^{-2}) - (0.01.00x10^{-2}) = 0.99x10^{-2}\quad mol\ CH_3CO_2H}$$

The newly formed acetate ion, along with the initially present acetate, gives a final acetate concentration of

$$\boldsymbol{1.00x10^{-2} + 0.01.00x10^{-2} = 1.0100x10^{-2}}\ \ \mathrm{mol\ NaCH_3CO_2H}$$

Compute molar concentrations for the two buffer components:

$$\mathbf{[\,CH_3CO_2H] = \frac{9.9x10^{-3}mol}{0.101\ L} = 0.098\ M}$$

$$\mathbf{[\,CH_3CO_2H] = \frac{1.01\boldsymbol{x}10^{-2}\,\boldsymbol{mol}}{0.101\,\boldsymbol{L}} = 0.100\,\boldsymbol{M}}$$

Using these concentrations, the pH of the solution may be computed as in part (a) above, yielding pH = 4.75 (only slightly different from that prior to adding the strong base). (c) for comparison, calculate the pH after 1.0 L of 0.10 M NaOH is added to 100 mL of a solution of an unbuffered solution with a pH of 4.74.

The amount of hydrogen ion initially present in the solution is

$$\boldsymbol{[H_3H^+] = 10^{-4.74} = 1.8x10^{-5}\,M}$$

$$\boldsymbol{mol\,H_3O^+ = ((0.100\,L)(1.8x10^{-5}\,M) = 1.8x10^{-6}\,mol\,H_3O^+}$$

The amount of hydroxide ion added to the solution is

$$mol\ OH^- = (0.0010\ L)(0.1\ M) = 1.0x10^{-4}\ mol\ OH^-$$

The added hydroxide will neutralize hydronium ion via the reaction

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2H_2O(l)$$

The 1:1 stoichiometry of this reaction shows that an excess of hydroxide has been added (greater molar amount than the initially present hydronium ion).

The amount of hydroxide ion remaining of

$$1.0x10^{-4}\ mol - 1.8x10^{-6}\ mol = 9.8x10^{-5}\ mol\ OH^-$$

Corresponding to a hydroxide molarity of

$$\frac{9.8x10^{-5} mol}{0.101\ L} = 9.7x10^{-4} M$$

The pH of the solution is then calculated to be

$$pH = 14 - pOH = 14 \text{—} \log(9.7x10^{-4}) = 10.99$$

In this unbuffered solution, addition of the base results in a significant rise in pH (from 4.74 t0 10.99) compared with the very slight increase observed for the buffer solution in part (b) (from 4.74 to 4.75).

Review Exercise

1. Write equations that show NH_3 as both a conjugate acid and a conjugate base.
2. Write equations that show $H_2PO_4^-$ acting both as an acid and as a base.
3. Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:
    a. $H3O^+$
    b. HCl
    c. NH_3
    d. CH_3CO_2H
    e. $NH4^+$
    f. $HSO4^-$
4. What is the conjugate acid of each of the following? What is the conjugate base of each?
    a. OH^-
    b. H_2O
    c. $HCO3^-$
    d. NH_3
    e. HSO4–
    f. H_2O_2
    g. HS^-
    h. $H5N2^+$
5. Identify and label the Brønsted-Lowry acid, its conjugate base, the Brønsted-Lowry base, and its conjugate acid in each of the following equations:

a. $HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-$

b. $CN^- + H_2O \longrightarrow HCN + OH^-$

c. $H_2SO_4 + Cl^- \longrightarrow HCl + HSO_4^-$

d. $HSO_4^- + OH^- \longrightarrow SO_4^{2-} + H_2O$

6. What are amphiprotic species? Illustrate with suitable equations.
7. State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species:

a. H_2O

b. $H_2PO_4^-$

c. S^{2-}

d. CO_3^{2-}

e. HSO_4^-

8. Is the self-ionization of water endothermic or exothermic? The ionization constant for water (K_w) is 2.9×10^{-14} at 40 °C and 9.3×10^{-14} at 60 °C.
9. Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:

(a) 0.200 *M* HCl

(b) 0.0143 *M* NaOH

(c) 3.0 *M* HNO_3

(d) 0.0031 *M* $Ca(OH)_2$

10. What are the hydronium and hydroxide ion concentrations in a solution whose pH is 6.52?
11. The hydronium ion concentration in a sample of rainwater is found to be $1.7 \times 10^{-6} M$ at 25 °C. What is the concentration of hydroxide ions in the rainwater?
12. Explain why the neutralization reaction of a strong acid and a weak base gives a weakly acidic solution.
13. Explain why the neutralization reaction of a weak acid and a strong base gives a weakly basic solution.
14. Explain why the ionization constant, K_a, for H_2SO_4 is larger than the ionization constant for H_2SO_3.
15. Explain why the ionization constant, K_a, for HI is larger than the ionization constant for HF.
16. What is the ionization constant at 25 °C for the weak acid $CH_3NH_3^+$, the conjugate acid of the weak base CH_3NH_2, $K_b = 4.4 \times 10^{-4}$.
17. Predict which acid in each of the following pairs is the stronger and explain your reasoning for each.

a) H_2O or HF

(b) $B(OH)_3$ or $Al(OH)_3$

(c) HSO_3^- or HSO_4^-

(d) NH_3 or H_2S

(e) H_2O or H_2Te

18. Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.

(a) acidity: HCl, HBr, HI

(b) basicity: H_2O, OH^-, H^-, Cl^-

(c) acidity: HF, H_2O, NH_3, CH_4

19. What is the effect on the concentrations of NO_2^-, HNO_2, and OH^- when the following are added to a solution of KNO_2 in water:

(a) HCl

(b) HNO_2

(c) NaOH

(d) NaCl

(e) KNO

20. Why is the hydronium ion concentration in a solution that is 0.10 *M* in HCl and 0.10 *M* in HCOOH determined by the concentration of HCl?

21. From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.

    a. CH_3CO_2H: [H3O+] = $1.34 \times 10^{-3} M$; [$CH_3CO_2^-$] = $1.34 \times 10^{-3} M$; [CH_3CO_2H] = $9.866 \times 10^{-2} M$;

    b. ClO^-: [OH^-] = $4.0 \times 10^{-4} M$; [HClO] = $2.38 \times 10^{-4} M$; [ClO^-] = 0.273 *M*

    c. HCO_2H: [HCO_2H] = 0.524 *M*; [H_3O^+] = $9.8 \times 10^{-3} M$; [HCO_2^-] = $9.8 \times 10^{-3} M$;

22. Determine K_b for the nitrite ion, NO_2^-. In a 0.10-*M* solution this base is 0.0015% ionized.

23. Determine K_a for hydrogen sulfate ion, HSO_4^-. In a 0.10-*M* solution the acid is 29% ionized.

24. Propionic acid, $C_2H_5CO_2H$ ($K_a = 1.34 \times 10^{-5}$), is used in the manufacture of calcium propionate, a food preservative. What is the pH of a 0.698-*M* solution of $C_2H_5CO_2H$?

25. White vinegar is a 5.0% by mass solution of acetic acid in water. If the density of white vinegar is 1.007 g/cm^3, what is the pH?

26. Nicotine, $C_{10}H_{14}N_2$, is a base that will accept two protons ($K_{b1} = 7 \times 10^{-7}$, $K_{b2} = 1.4 \times 10^{-11}$). What is the concentration of each species present in a 0.050-*M* solution of nicotine?

27. The pH of a 0.23-*M* solution of HF is 1.92. Determine K_a for HF from these data.

28. The pH of a 0.10-*M* solution of caffeine is 11.70. Determine K_b for caffeine from these data:

    C8H10N4O2(*aq*)+H2O(*l*)⇌C8H10N4O2H+(*aq*)+OH−(*aq*)

29. The pH of a solution of household ammonia, a 0.950 M solution of NH_3, is 11.612. Determine K_b for NH_3 from these data.

30. Explain why a buffer can be prepared from a mixture of NH_4Cl and NaOH but not from NH_3 and NaOH.

31. Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the acid H_3PO_4 and a salt of its conjugate base NaH_2PO_4.

32. What is $[H_3O^+]$ in a solution of 0.25 *M* CH_3CO_2H and 0.030 *M* $NaCH_3CO_2$?

    $CH_3CO_2H(aq)+H_2O(l)\rightleftharpoons H_3O^+(aq)+CH_3CO_2^-(aq)$ K_a = 1.8×10−5

33. What is $[OH^-]$ in a solution of 0.125 *M* CH_3NH_2 and 0.130 *M* CH_3NH_3Cl?

    $CH_3NH_2(aq)+H_2O(l)\rightleftharpoons CH_3NH_3^+(aq)+OH^-(aq)$ K_b = .4×10−4

34. What is the effect on the concentration of acetic acid, hydronium ion, and acetate ion when the following are added to an acidic buffer solution of equal concentrations of acetic acid and sodium acetate:

    (a) HCl

    (b) KCH_3CO_2

    (c) NaCl

    (d) KOH

    (e) CH_3CO_2H

35. What will be the pH of a buffer solution prepared from 0.20 mol NH_3, 0.40 mol NH_4NO_3, and just enough water to give 1.00 L of solution?

36. Calculate the pH of a buffer solution prepared from 0.155 mol of phosphoric acid, 0.250 mole of KH_2PO_4, and enough water to make 0.500 L of solution.

37. What mass of NH_4Cl must be added to 0.750 L of a 0.100-*M* solution of NH_3 to give a buffer solution with a pH of 9.26? (Hint: Assume a negligible change in volume as the solid is added.)

38. A buffer solution is prepared from equal volumes of 0.200 *M* acetic acid and 0.600 *M* sodium acetate. Use 1.80×10^{-5} as K_a for acetic acid.
    a. What is the pH of the solution?
    b. Is the solution acidic or basic?
    c. What is the pH of a solution that results when 3.00 mL of 0.034 *M* HCl is added to 0.200 L of the original buffer?

CHAPTER EIGHT

ORGANIC CHEMISTRY

Introduction

All living things on earth are formed mostly of carbon compounds. The prevalence of carbon compounds in living things has led to the epithet “carbon-based” life. The truth is we know of no other kind of life. Early chemists regarded substances isolated from *organisms* (plants and animals) as a different type of matter that could not be synthesized artificially, and these substances were thus known as *organic compounds*. The widespread belief called vitalism held that organic compounds were formed by a vital force present only in living organisms. The German chemist Friedrich Wohler was one of the early chemists to refute this aspect of vitalism, when, in 1828, he reported the synthesis of urea, a component of many body fluids, from nonliving materials. Since then, it has been recognized that organic molecules obey the same natural laws as inorganic substances, and the category of organic compounds has evolved to include both natural and synthetic compounds that contain carbon. Some carbon-containing compounds are *not* classified as organic, for example, carbonates and cyanides, and simple oxides, such as CO and CO_2. Although a single, precise definition has yet to be identified by the chemistry community, most agree that a defining trait of organic molecules is the presence of carbon as the principal element, bonded to hydrogen and other carbon atoms.

Today, organic compounds are key components of plastics, soaps, perfumes, sweeteners, fabrics, pharmaceuticals, and many other substances that we use every day. The value to us of organic compounds ensures that organic chemistry is an important discipline within the general field of chemistry. In this module, we discuss why the element carbon gives rise to a vast number and variety of compounds, how those compounds are classified, and the role of organic compounds in representative biological and industrial settings.

Learning Objective of the Chapter: At the end of this chapter you will be able to

- Explain the importance of hydrocarbons and the reason for their diversity
- Name saturated and unsaturated hydrocarbons, and molecules derived from them
- Describe the reactions characteristic of saturated and unsaturated hydrocarbons
- Describe the structure and properties of alcohols and ethers

- Describe the structure and properties of aldehydes, ketones, carboxylic acids and esters
- Describe the structure and properties of an amine and amides

8.1. Hydrocarbons

The largest database of organic compounds lists about 10 million substances, which include compounds originating from living organisms and those synthesized by chemists. The number of potential organic compounds has been estimated at 10^{60} an astronomically high number. The existence of so many organic molecules is a consequence of the ability of carbon atoms to form up to four strong bonds to other carbon atoms, resulting in chains and rings of many different sizes, shapes, and complexities.

The simplest organic compounds contain only the elements carbon and hydrogen, and are called hydrocarbons. Even though they are composed of only two types of atoms, there is a wide variety of hydrocarbons because they may consist of varying lengths of chains, branched chains, and rings of carbon atoms, or combinations of these structures. In addition, hydrocarbons may differ in the types of carbon-carbon bonds present in their molecules. Many hydrocarbons are found in plants, animals, and their fossils; other hydrocarbons have been prepared in the laboratory. We use hydrocarbons every day, mainly as fuels, such as natural gas, acetylene, propane, butane, and the principal components of gasoline, diesel fuel, and heating oil. The familiar plastics polyethylene, polypropylene, and polystyrene are also hydrocarbons. We can distinguish several types of hydrocarbons by differences in the bonding between carbon atoms. This leads to differences in geometries and in the hybridization of the carbon orbitals.

8.1.1. Alkanes

Alkanes, or saturated hydrocarbons, contain only single covalent bonds between carbon atoms. Each of the carbon atoms in an alkane has sp^3 hybrid orbitals and is bonded to four other atoms, each of which is either carbon or hydrogen. The Lewis structures and models of methane, ethane, and pentane are illustrated in Figure 8.1. Carbon chains are usually drawn as straight lines in Lewis structures, but one has to remember that Lewis structures are not intended to indicate the geometry of molecules. Notice that the carbon atoms in the structural models (the ball-and-stick and space-filling models) of the pentane molecule do not lie in a straight line. Because of the sp^3

hybridization, the bond angles in carbon chains are close to 109.5°, giving such chains in an alkane a zigzag shape.

The structures of alkanes and other organic molecules may also be represented in a less detailed manner by condensed structural formulas (or simply, *condensed formulas*). Instead of the usual format for chemical formulas in which each element symbol appears just once, a condensed formula is written to suggest the bonding in the molecule. These formulas have the appearance of a Lewis structure from which most or all of the bond symbols have been removed. Condensed structural formulas for ethane and pentane are shown at the bottom of Figure 8.1, and several additional examples are provided in the exercises at the end of this chapter.

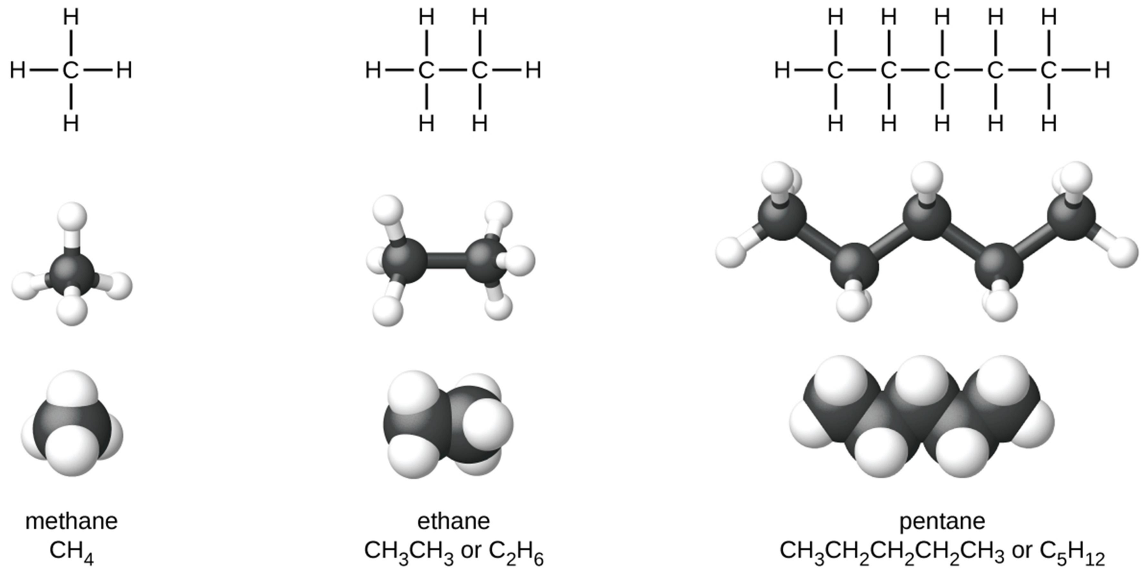
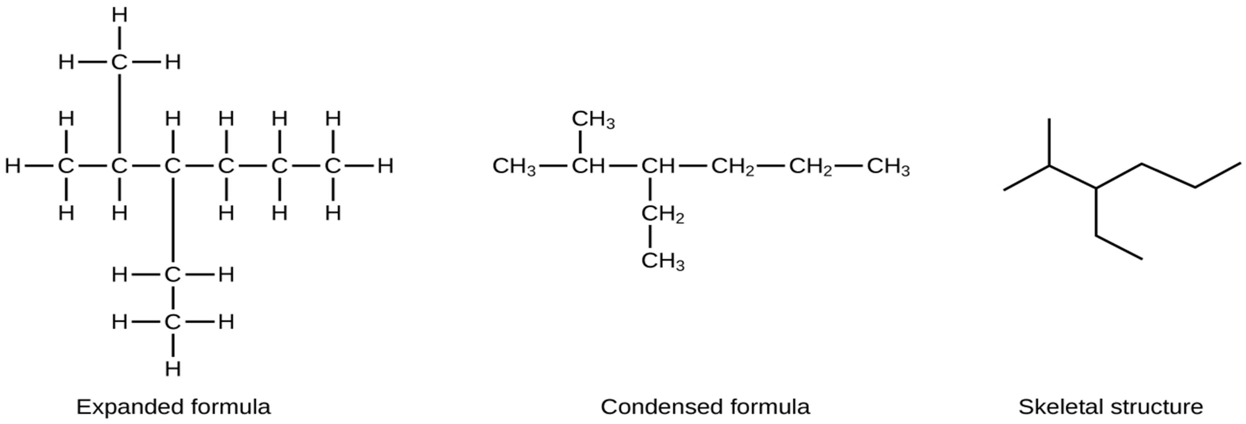


Figure 8.1:- Pictured are the Lewis structures, ball-and-stick models, and space-filling models for molecules of methane, ethane, and pentane.

A common method used by organic chemists to simplify the drawings of larger molecules is to use a skeletal structure (also called a line-angle structure). In this type of structure, carbon atoms are not symbolized with a C, but represented by each end of a line or bend in a line. Hydrogen atoms are not drawn if they are attached to a carbon. Other atoms besides carbon and hydrogen are represented by their elemental symbols. Figure 8.2 shows three different ways to draw the same structure.


Expanded formula

Condensed formula

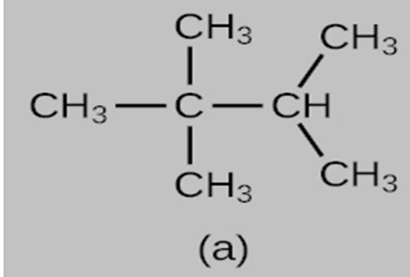
Skeletal structure

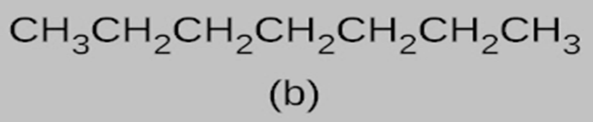
Figure 8.2:- The same structure can be represented three different ways: an expanded formula, a condensed formula, and a skeletal structure.

Example 8.1

Drawing Skeletal Structures

Draw the skeletal structures for these two molecules:

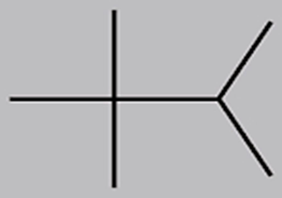

(a)

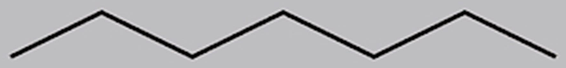

$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$

(b)

Solution

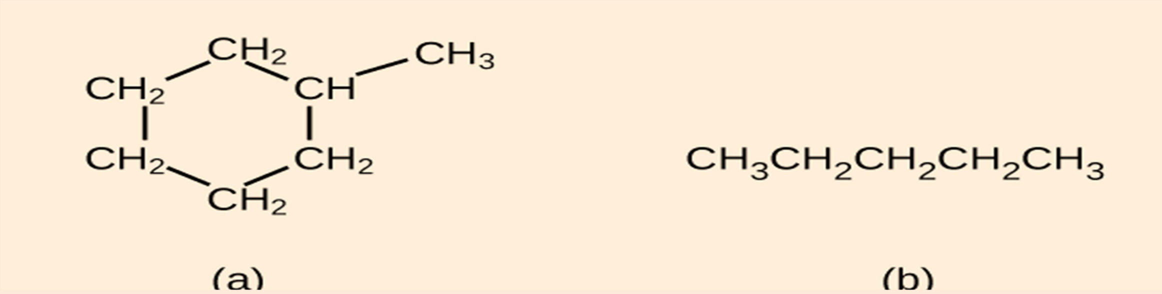
Each carbon atom is converted into the end of a line or the place where lines intersect. All hydrogen atoms attached to the carbon atoms are left out of the structure (although we still need to recognize they are there):


(a)


(b)

Check Your Learning

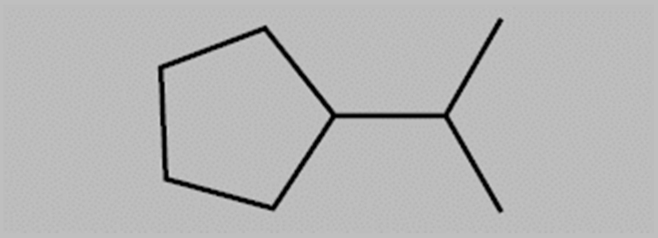
Draw the skeletal structures for these two molecules:



Example 8.2

Interpreting Skeletal Structures

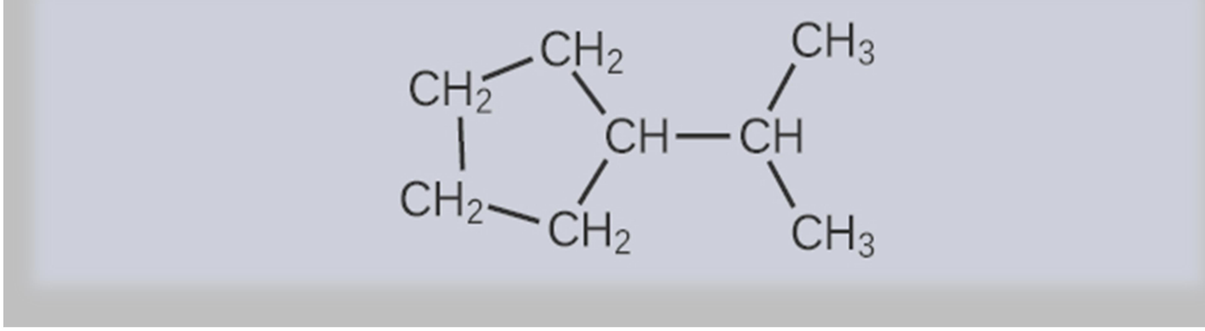
Identify the chemical formula of the molecule represented here:



Solution

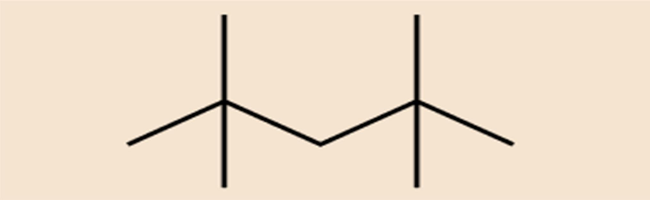
There are eight places where lines intersect or end, meaning that there are eight carbon atoms in the molecule. Since we know that carbon atoms tend to make four bonds, each carbon atom will have the number of hydrogen atoms that are required for four bonds. This compound contains 16 hydrogen atoms for a molecular formula of C_8H_{16}.

Location of the hydrogen atoms:



✍ **Check Your Learning**

Identify the chemical formula of the molecule represented here:



All alkanes are composed of carbon and hydrogen atoms, and have similar bonds, structures, and formulas; noncyclic alkanes all have a formula of C_nH_{2n+2}. The number of carbon atoms present in an alkane has no limit. Greater numbers of atoms in the molecules will lead to stronger intermolecular attractions (dispersion forces) and correspondingly different physical properties of the molecules. Properties such as melting point and boiling point (Table 8.1) usually change smoothly and predictably as the number of carbon and hydrogen atoms in the molecules change.

Table 8.1:- Properties of Some Alkanes

Alkane	Molecular Formula	Melting Point (°C)	Boiling Point (°C)	Phase at STP	Number of Structural Isomers
methane	CH_4	–182.5	–161.5	gas	1
ethane	C_2H_6	–183.3	–88.6	gas	1
propane	C_3H_8	–187.7	–42.1	gas	1
butane	C_4H_{10}	–138.3	–0.5	gas	2
pentane	C_5H_{12}	–129.7	36.1	liquid	3
hexane	C_6H_{14}	–95.3	68.7	liquid	5
heptane	C_7H_{16}	–90.6	98.4	liquid	9
octane	C_8H_{18}	–56.8	125.7	liquid	18
nonane	C_9H_{20}	–53.6	150.8	liquid	35
decane	$C_{10}H_{22}$	–29.7	174.0	liquid	75
tetradecane	$C_{14}H_{30}$	5.9	253.5	solid	1858
octadecane	$C_{18}H_{38}$	28.2	316.1	solid	60,523

Hydrocarbons with the same formula, including alkanes, can have different structures. For example, two alkanes have the formula C_4H_{10}: They are called *n*-butane and 2-methylpropane (or isobutane) and have the following Lewis structures:

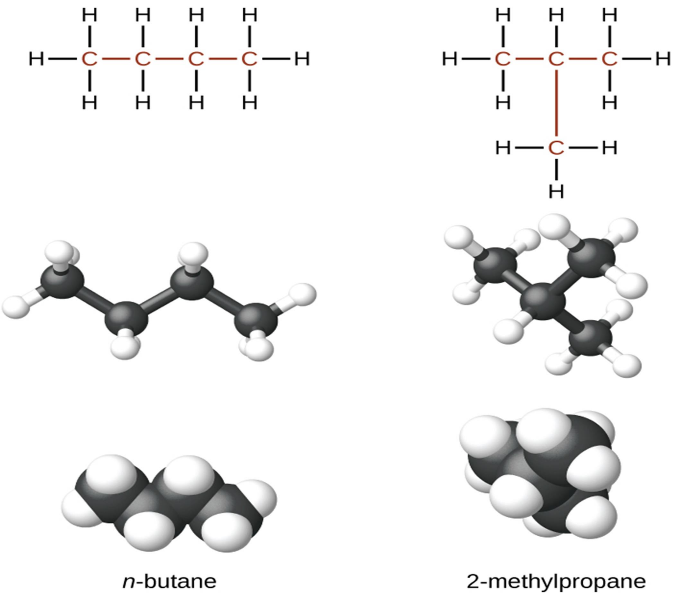


Figure 8.3:- Structure for *n*-butane and 2-methylpropane

The compounds *n*-butane and 2-methylpropane are structural isomers (the term constitutional isomers are also commonly used). Constitutional isomers have the same molecular formula but different spatial arrangements of the atoms in their molecules. The *n*-butane molecule contains an *unbranched chain*, meaning that no carbon atom is bonded to more than two other carbon atoms. We use the term *normal*, or the prefix *n*, to refer to a chain of carbon atoms without branching. The compound 2–methylpropane has a branched chain (the carbon atom in the center of the Lewis structure is bonded to three other carbon atoms)

Identifying isomers from Lewis structures is not as easy as it looks. Lewis structures that look different may actually represent the same isomers. For example, the three structures in Figure 8.4 all represent the same molecule, *n*-butane, and hence are not different isomers. They are identical because each contains an unbranched chain of four carbon atoms.

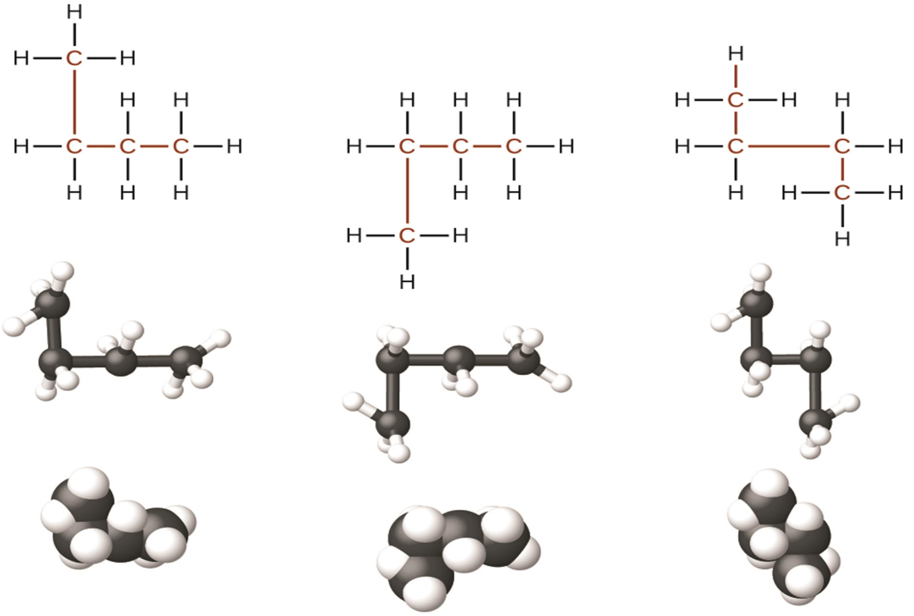
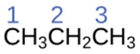


Figure 8.4:-These three representations of the structure of n-butane are not isomers because they all contain the same arrangement of atoms and bonds.

The Basics of Organic Nomenclature: Naming Alkanes

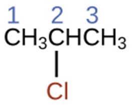
The International Union of Pure and Applied Chemistry (IUPAC) has devised a system of nomenclature that begins with the names of the alkanes and can be adjusted from there to account for more complicated structures. The nomenclature for alkanes is based on two rules:

1. To name an alkane, first identify the longest chain of carbon atoms in its structure. A two-carbon chain is called ethane; a three-carbon chain, propane; and a four-carbon chain, butane. Longer chains are named as follows: pentane (five-carbon chain), hexane (6), heptane (7), octane (8), nonane (9), and decane (10). These prefixes can be seen in the names of the alkanes described in Table 8.1.
2. Add prefixes to the name of the longest chain to indicate the positions and names of substituents. Substituents are branches or functional groups that replace hydrogen atoms on a chain. The position of a substituent or branch is identified by the number of the carbon atom it is bonded to in the chain. We number the carbon atoms in the chain by counting from the end of the chain nearest the substituents. Multiple substituents are named individually and placed in alphabetical order at the front of the name.



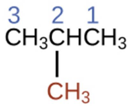
$\overset{1}{CH_3}\overset{2}{CH_2}\overset{3}{CH_3}$

propane



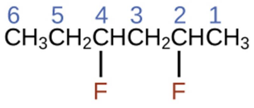
$\overset{1}{CH_3}\underset{\substack{|\\ Cl}}{\overset{2}{C}}H\overset{3}{CH_3}$

2-chloropropane



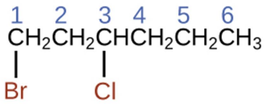
$\overset{3}{CH_3}\underset{\substack{|\\ CH_3}}{\overset{2}{C}}H\overset{1}{CH_3}$

2-methylpropane



$\overset{6}{CH_3}\overset{5}{CH_2}\underset{\substack{|\\ F}}{\overset{4}{C}}H\overset{3}{CH_2}\underset{\substack{|\\ F}}{\overset{2}{C}}H\overset{1}{CH_3}$

2,4-difluorohexane



$\underset{\substack{|\\ Br}}{\overset{1}{CH_2}}\overset{2}{CH_2}\underset{\substack{|\\ Cl}}{\overset{3}{C}}H\overset{4}{CH_2}\overset{5}{CH_2}\overset{6}{CH_3}$

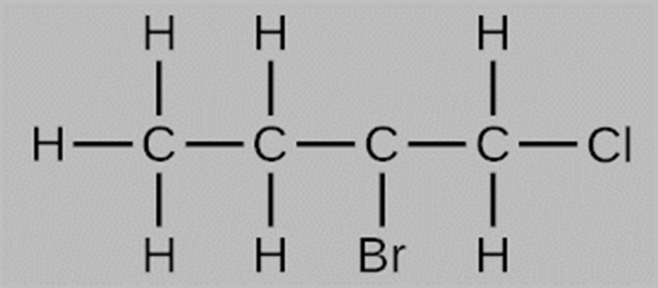
1-bromo-3-chlorohexane

When more than one substituent is present, either on the same carbon atom or on different carbon atoms, the substituents are listed alphabetically. Because the carbon atom numbering begins at the end closest to a substituent, the longest chain of carbon atoms is numbered in such a way as to produce the lowest number for the substituents. The ending *-o* replaces *-ide* at the end of the name of an electronegative substituent (in ionic compounds, the negatively charged ion ends with *-ide* like chloride; in organic compounds, such atoms are treated as substituents and the *-o* ending is used). The number of substituents of the same type is indicated by the prefixes *di-* (two), *tri-* (three), *tetra-* (four), and so on (for example, *difluoro-* indicates two fluoride substituents).

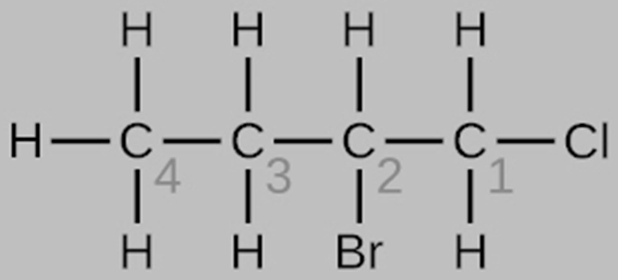
Example 8.3

Naming Halogen-substituted Alkanes

Name the molecule whose structure is shown here:



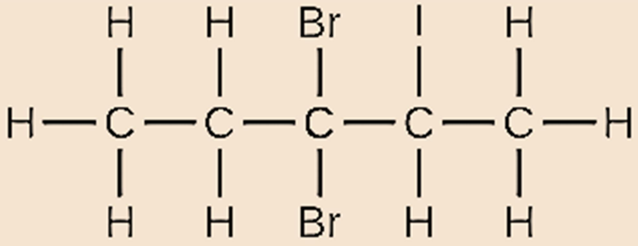
Solution



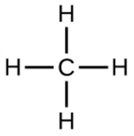
The four-carbon chain is numbered from the end with the chlorine atom. This puts the substituents on positions 1 and 2 (numbering from the other end would put the substituents on positions 3 and 4). Four carbon atoms means that the base name of this compound will be butane. The bromine at position 2 will be described by adding 2-bromo-; this will come at the beginning of the name, since bromo- comes before chloro- alphabetically. The chlorine at position 1 will be described by adding 1-chloro-, resulting in the name of the molecule being 2-bromo-1-chlorobutane.

Check Your Learning

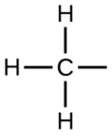
Name the following molecule:



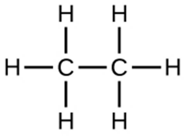
We call a substituent that contains one less hydrogen than the corresponding alkane an alkyl group. The name of an alkyl group is obtained by dropping the suffix *-ane* of the alkane name and adding *–yl*.



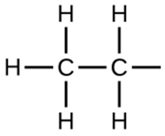
methane



methyl group



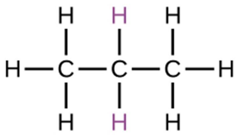
ethane



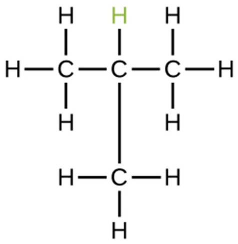
ethyl group

The open bonds in the methyl and ethyl groups indicate that these alkyl groups are bonded to another atom.

Some hydrocarbons can form more than one type of alkyl group when the hydrogen atoms that would be removed have different “environments” in the molecule. This diversity of possible alkyl groups can be identified in the following way: The four hydrogen atoms in a methane molecule are equivalent; they all have the same environment. They are equivalent because each is bonded to a carbon atom (the same carbon atom) that is bonded to three hydrogen atoms. (It may be easier to see the equivalency in the ball and stick models in Figure 8.1. Removal of any one of the four hydrogen atoms from methane forms a methyl group. Likewise, the six hydrogen atoms in ethane are equivalent (Figure 8.1) and removing any one of these hydrogen atoms produces an ethyl group. Each of the six hydrogen atoms is bonded to a carbon atom that is bonded to two other hydrogen atoms and a carbon atom. However, in both propane and 2–methylpropane, there are hydrogen atoms in two different environments, distinguished by the adjacent atoms or groups of atoms:



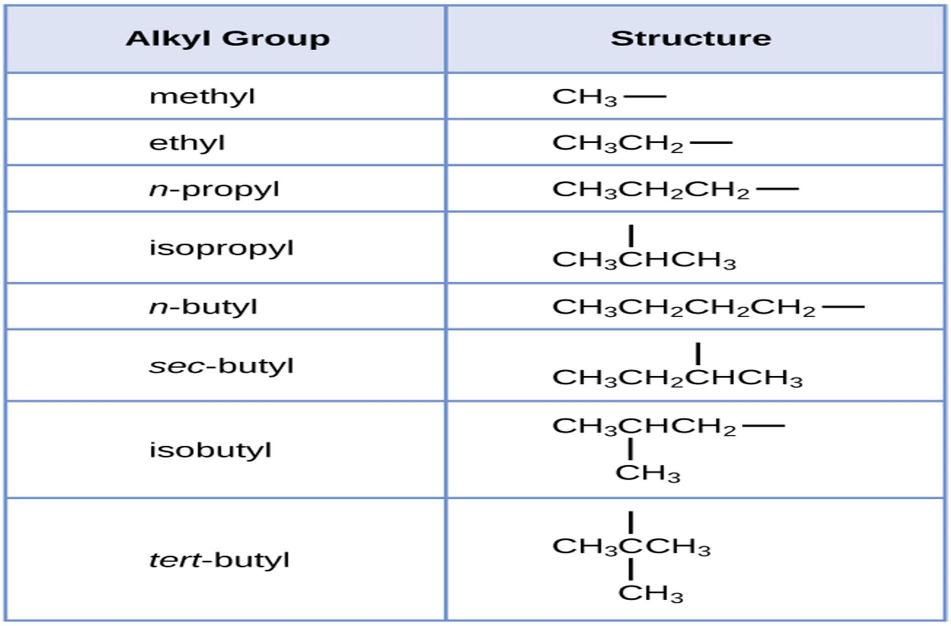
propane



2-methylpropane

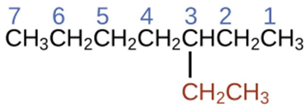
Each of the six equivalent hydrogen atoms of the first type in propane and each of the nine equivalent hydrogen atoms of that type in 2-methylpropane (all shown in black) are bonded to a carbon atom that is bonded to only one other carbon atom. The two purple hydrogen atoms in propane are of a second type. They differ from the six hydrogen atoms of the first type in that they are bonded to a carbon atom bonded to two other carbon atoms. The green hydrogen atom in 2-methylpropane differs from the other nine hydrogen atoms in that molecule and from the purple hydrogen atoms in propane. The green hydrogen atom in 2-methylpropane is bonded to a carbon atom bonded to three other carbon atoms. Two different alkyl groups can be formed from each of these molecules, depending on which hydrogen atom is removed. The names and structures of these and several other alkyl groups are listed in Table 8.2.

Table 8.2:-This listing gives the names and formulas for various alkyl groups formed by the removal of hydrogen atoms from different locations.



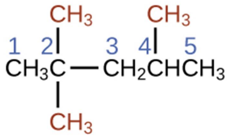
Alkyl Group	Structure
methyl	$CH_3—$
ethyl	$CH_3CH_2—$
n-propyl	$CH_3CH_2CH_2—$
isopropyl	$CH_3\overset{\vert}{C}HCH_3$
n-butyl	$CH_3CH_2CH_2CH_2—$
sec-butyl	$CH_3CH_2\overset{\vert}{C}HCH_3$
isobutyl	$CH_3\underset{\substack{\vert \\ CH_3}}{C}HCH_2—$
tert-butyl	$CH_3\overset{\vert}{\underset{\substack{\vert \\ CH_3}}{C}}CH_3$

Note that alkyl groups do not exist as stable independent entities. They are always a part of some larger molecule. The location of an alkyl group on a hydrocarbon chain is indicated in the same way as any other substituent:



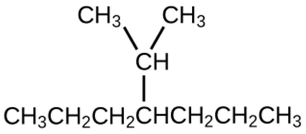
$CH_3CH_2CH_2CH_2\underset{\displaystyle |\atop \displaystyle CH_2CH_3}{C}HCH_2CH_3$

3-ethylheptane



$CH_3\overset{\displaystyle CH_3\atop \displaystyle |}{\underset{\displaystyle |\atop \displaystyle CH_3}{C}}-CH_2\overset{\displaystyle CH_3\atop \displaystyle |}{C}HCH_3$

2,2,4-trimethylpentane



4-isopropylheptane

Alkanes are relatively stable molecules, but heat or light will activate reactions that involve the breaking of C–H or C–C single bonds. Combustion is one such reaction:

$$CH_4(g)+2O_2(g)\longrightarrow CO_2(g)+2H_2O(g)$$

Alkanes burn in the presence of oxygen, a highly exothermic oxidation-reduction reaction that produces carbon dioxide and water. As a consequence, alkanes are excellent fuels. For example, methane, CH_4, is the principal component of natural gas. Butane, C_4H_{10}, used in camping stoves and lighters is an alkane. Gasoline is a liquid mixture of continuous- and branched-chain alkanes, each containing from five to nine carbon atoms, plus various additives to improve its performance as a fuel. Kerosene, diesel oil, and fuel oil are primarily mixtures of alkanes with higher molecular masses. The main source of these liquid alkane fuels is crude oil, a complex mixture that is separated by fractional distillation. Fractional distillation takes advantage of differences in the boiling points of the components of the mixture (see Figure 8.5). You may recall that boiling point is a function of intermolecular interactions.

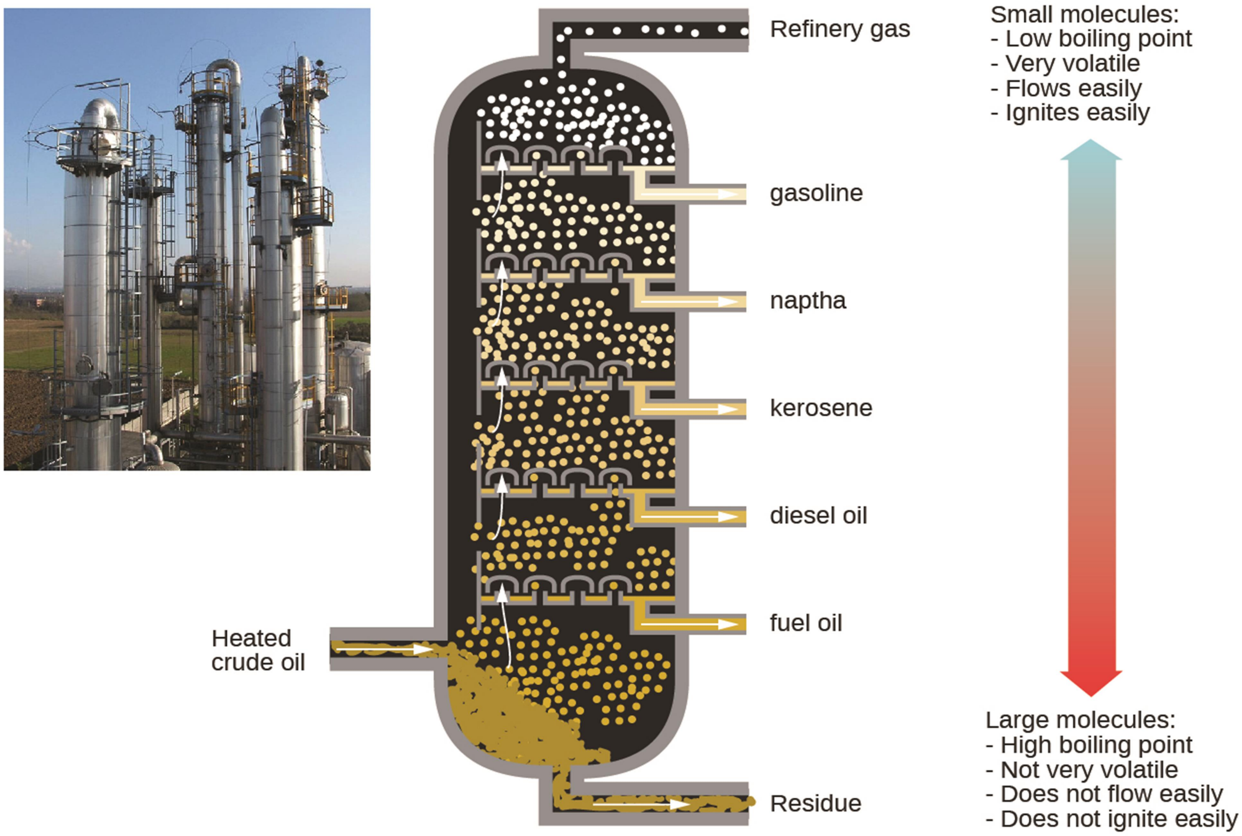
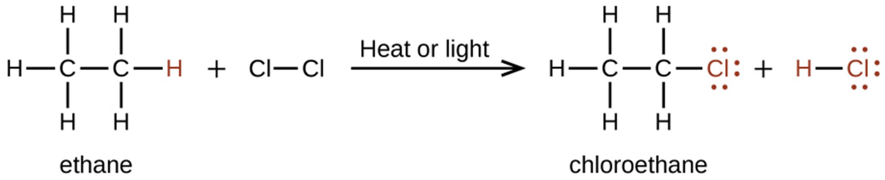


Figure 8.5: In a column for the fractional distillation of crude oil, oil heated to about 425 °C in the furnace vaporizes when it enters the base of the tower. The vapors rise through bubble caps in a series of trays in the tower. As the vapors gradually cool, fractions of higher, then of lower, boiling points condense to liquids and are drawn off.

In a **substitution reaction**, another typical reaction of alkanes, one or more of the alkane’s hydrogen atoms is replaced with a different atom or group of atoms. No carbon-carbon bonds are broken in these reactions, and the hybridization of the carbon atoms does not change. For example, the reaction between ethane and molecular chlorine depicted here is a substitution reaction:



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}H + Cl{-}Cl \xrightarrow{\text{Heat or light}} H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\ddot{\underset{..}{Cl}}{:} + H{-}\ddot{\underset{..}{Cl}}{:}}$$

The C–Cl portion of the chloroethane molecule is an example of a functional group, the part or moiety of a molecule that imparts a specific chemical reactivity. The types of functional groups present in an organic molecule are major determinants of its chemical properties and are used as a means of classifying organic compounds as detailed in the remaining sections of this chapter.

8.1.2. Alkenes

Organic compounds that contain one or more double or triple bonds between carbon atoms are described as **unsaturated**. You have likely heard of unsaturated fats. These are complex organic molecules with long chains of carbon atoms, which contain at least one double bond between carbon atoms. Unsaturated hydrocarbon molecules that contain one or more double bonds are called alkenes. Carbon atoms linked by a double bond are bound together by two bonds, one σ bond and one π bond. Double and triple bonds give rise to a different geometry around the carbon atom that participates in them, leading to important differences in molecular shape and properties. The differing geometries are responsible for the different properties of unsaturated versus saturated fats.

Ethene, C_2H_4, is the simplest alkene. Each carbon atom in ethene, commonly called ethylene, has a trigonal planar structure. The second member of the series is propene (propylene) (Figure 8.6); the butene isomers follow in the series. Four carbon atoms in the chain of butene allows for the formation of isomers based on the position of the double bond, as well as a new form of isomerism.

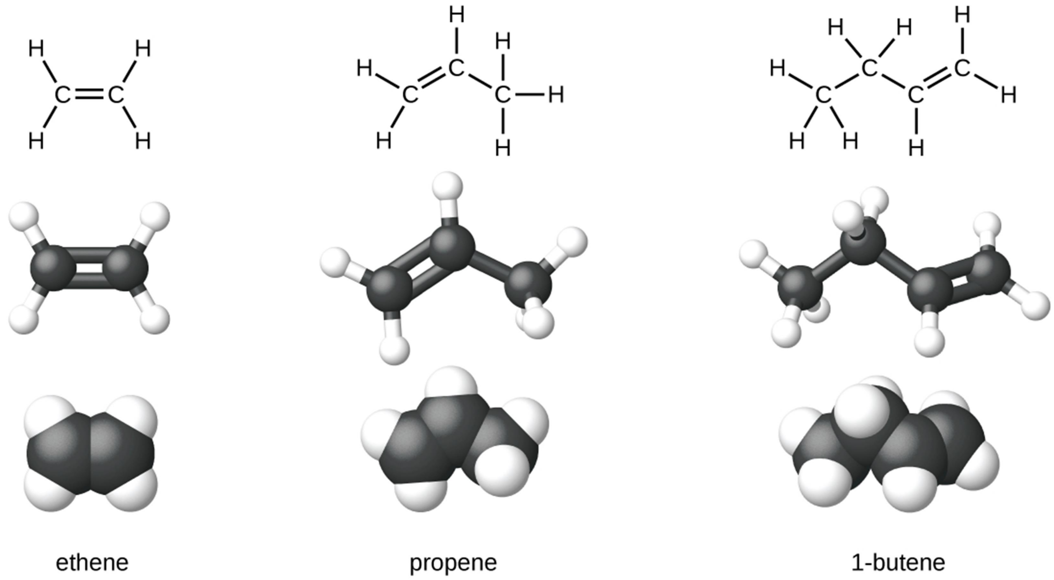
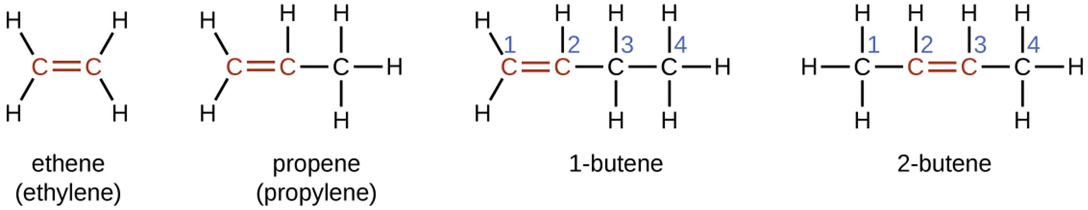


Figure 8.6: Expanded structures, ball-and-stick structures, and space-filling models for the alkenes ethene, propene, and 1-butene are shown.

Ethylene (the common industrial name for ethene) is a basic raw material in the production of polyethylene and other important compounds. Over 135 million tons of ethylene were produced worldwide in 2010 for use in the polymer, petrochemical, and plastic industries. Ethylene is produced industrially in a process called cracking, in which the long hydrocarbon chains in a petroleum mixture are broken into smaller molecules.

The name of an alkene is derived from the name of the alkane with the same number of carbon atoms. The presence of the double bond is signified by replacing the suffix *-ane* with the suffix *-ene*. The location of the double bond is identified by naming the smaller of the numbers of the carbon atoms participating in the double bond:



Isomers of Alkenes

Molecules of 1-butene and 2-butene are structural isomers; the arrangement of the atoms in these two molecules differs. As an example of arrangement differences, the first carbon atom in 1-butene is bonded to two hydrogen atoms; the first carbon atom in 2-butene is bonded to three hydrogen atoms.

The compound 2-butene and some other alkenes also form a second type of isomer called a geometric isomer. In a set of geometric isomers, the same types of atoms are attached to each other in the same order, but the geometries of the two molecules differ. Geometric isomers of alkenes differ in the orientation of the groups on either side of a C=C bond.

Carbon atoms are free to rotate around a single bond but not around a double bond; a double bond is rigid. This makes it possible to have two isomers of 2-butene, one with both methyl groups on the same side of the double bond and one with the methyl groups on opposite sides. When structures of butene are drawn with 120° bond angles around the sp^2-hybridized carbon atoms participating in the double bond, the isomers are apparent. The 2-butene isomer in which the two methyl groups are on the same side is called a *cis*-isomer; the one in which the two methyl groups are on opposite sides is called a *trans*-isomer (Figure 8.7). The different geometries produce different physical properties, such as boiling point, that may make separation of the isomers possible:

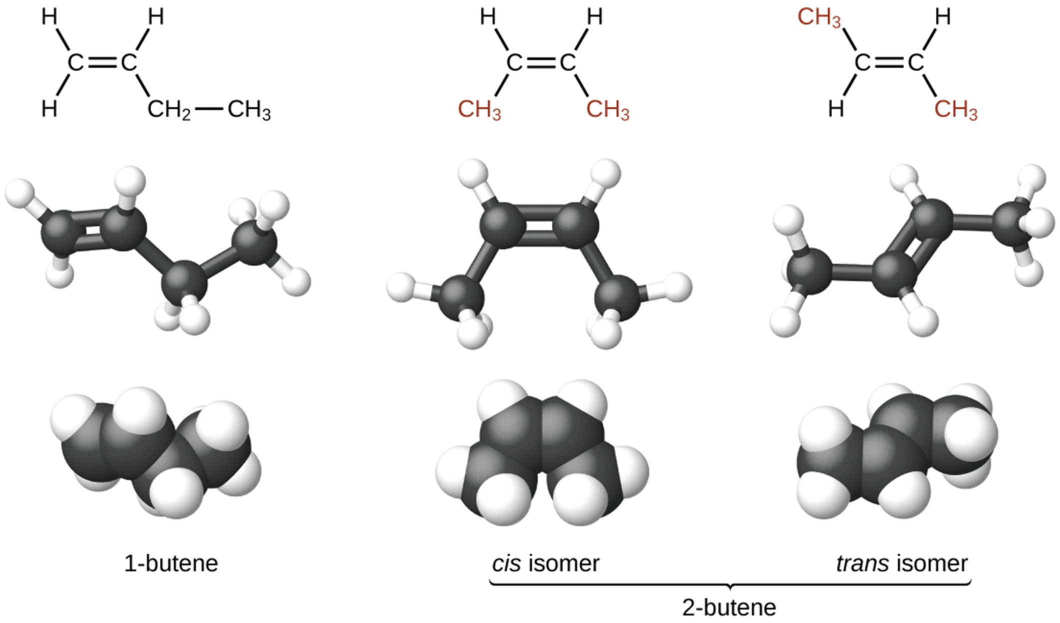
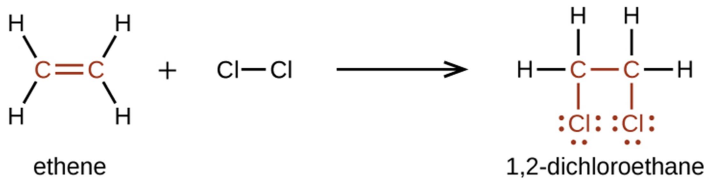


Figure 8.7: These molecular models show the structural and geometric isomers of butene.

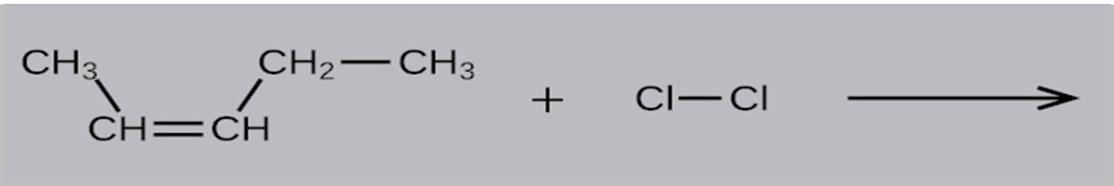
Alkenes are much more reactive than alkanes because the C=C moiety is a reactive functional group. A π bond, being a weaker bond, is disrupted much more easily than a σ bond. Thus, alkenes undergo a characteristic reaction in which the π bond is broken and replaced by two σ bonds. This reaction is called an **addition reaction**. The hybridization of the carbon atoms in the double bond in an alkene changes from *sp*^{2} to *sp*^{3} during an addition reaction. For example, halogens add to the double bond in an alkene instead of replacing hydrogen, as occurs in an alkane:



Example 8.4

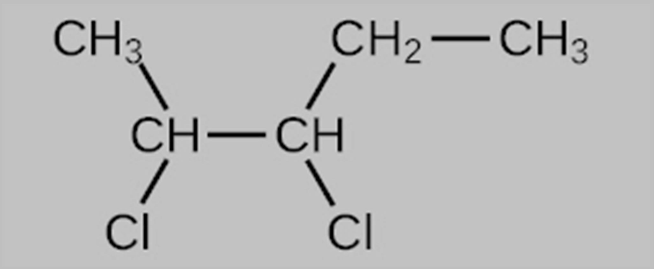
Alkene Reactivity and Naming

Provide the IUPAC names for the reactant and product of the halogenation reaction shown here:



Solution

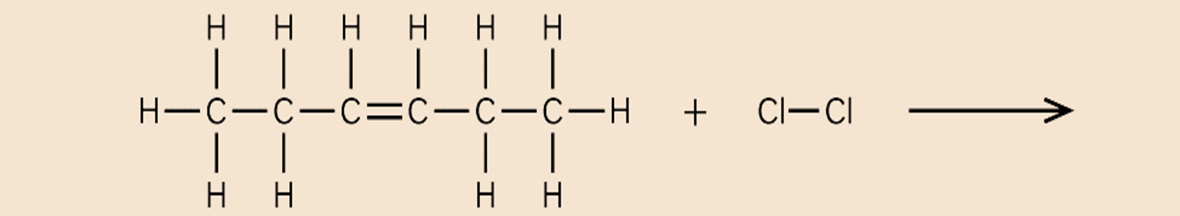
The reactant is a five-carbon chain that contains a carbon-carbon double bond, so the base name will be pentene. We begin counting at the end of the chain closest to the double bond—in this case, from the left—the double bond spans carbons 2 and 3, so the name becomes 2-pentene. Since there are two carbon-containing groups attached to the two carbon atoms in the double bond—and they are on the same side of the double bond—this molecule is the *cis*-isomer, making the name of the starting alkene *cis*-2-pentene. The product of the halogenation reaction will have two chlorine atoms attached to the carbon atoms that were a part of the carbon-carbon double bond:



This molecule is now a substituted alkane and will be named as such. The base of the name will be pentane. We will count from the end that numbers the carbon atoms where the chlorine atoms are attached as 2 and 3, making the name of the product 2,3-dichloropentane.

✍**Check Your Learning**

Provide names for the reactant and product of the reaction shown:



8.1.3. Alkynes

Hydrocarbon molecules with one or more triple bonds are called alkynes; they make up another series of unsaturated hydrocarbons. Two carbon atoms joined by a triple bond are bound together by one σ bond and two π bonds. The *sp*-hybridized carbons involved in the triple bond have bond angles of 180°, giving these types of bonds a linear, rod-like shape.

The simplest member of the alkyne series is ethyne, C_2H_2, commonly called acetylene. The Lewis structure for ethyne, a linear molecule, is:

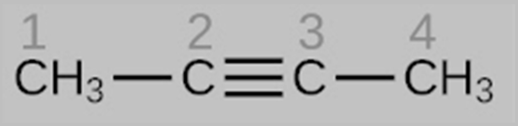
ethyne (acetylene)

The IUPAC nomenclature for alkynes is similar to that for alkenes except that the suffix *-yne* is used to indicate a triple bond in the chain. For example, $CH_3CH_2C{\equiv}CH$ is called 1-butyne.

Example 8.5

Structure of Alkynes

Describe the geometry and hybridization of the carbon atoms in the following molecule:

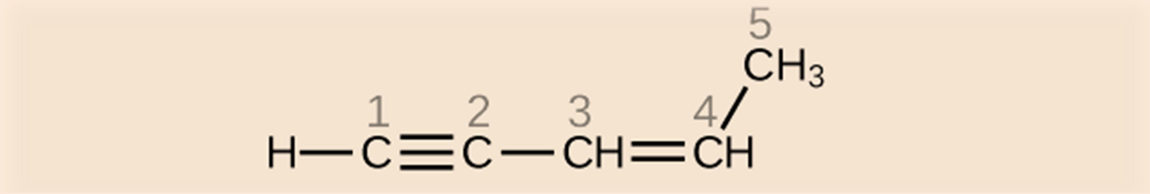


Solution

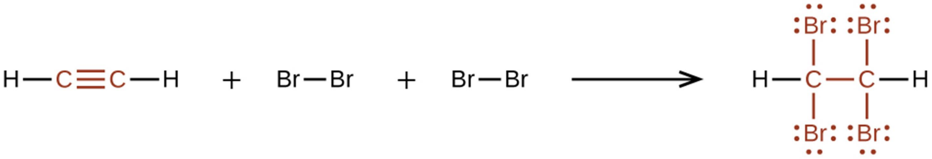
Carbon atoms 1 and 4 have four single bonds and are thus tetrahedral with sp^3 hybridization. Carbon atoms 2 and 3 are involved in the triple bond, so they have linear geometries and would be classified as *sp* hybrids.

Check Your Learning

Identify the hybridization and bond angles at the carbon atoms in the molecule shown:



Chemically, the alkynes are similar to the alkenes. Since the C≡C functional group has two π bonds, alkynes typically react even more readily, and react with twice as much reagent in addition reactions. The reaction of acetylene with bromine is a typical example:

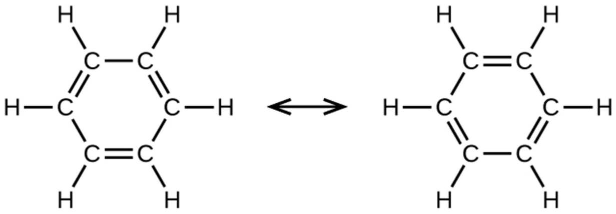


1,1,2,2-tetrabromoethane

Acetylene and the other alkynes also burn readily. An acetylene torch takes advantage of the high heat of combustion for acetylene.

8.2. Aromatic Hydrocarbons

Benzene, C_6H_6, is the simplest member of a large family of hydrocarbons, called aromatic hydrocarbons. These compounds contain ring structures and exhibit bonding that must be described using the resonance hybrid concept of valence bond theory or the delocalization concept of molecular orbital theory. (To review these concepts, refer to the earlier chapters on chemical bonding). The resonance structures for benzene, C_6H_6, are:



Valence bond theory describes the benzene molecule and other planar aromatic hydrocarbon molecules as hexagonal rings of sp^2-hybridized carbon atoms with the unhybridized p orbital of each carbon atom perpendicular to the plane of the ring. Three valence electrons in the sp^2 hybrid orbitals of each carbon atom and the valence electron of each hydrogen atom form the framework of σ bonds in the benzene molecule. The fourth valence electron of each carbon atom is shared with an adjacent carbon atom in their unhybridized p orbitals to yield the π bonds. Benzene does not, however, exhibit the characteristics typical of an alkene. Each of the six bonds between its carbon atoms is equivalent and exhibits properties that are intermediate between those of a C–C single bond and a C=C double bond. To represent this unique bonding, structural formulas for benzene and its derivatives are typically drawn with single bonds between the carbon atoms and a circle within the ring as shown in Figure 8.8.

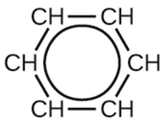
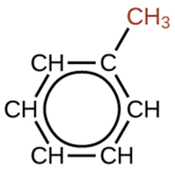
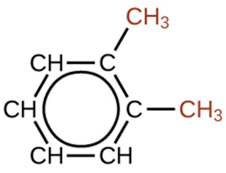


Figure 8.8:This condensed formula shows the unique bonding structure of benzene.

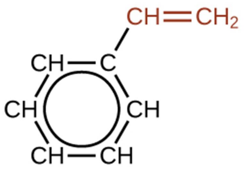
There are many derivatives of benzene. The hydrogen atoms can be replaced by many different substituents. Aromatic compounds more readily undergo substitution reactions than addition reactions; replacement of one of the hydrogen atoms with another substituent will leave the delocalized double bonds intact. The following are typical examples of substituted benzene derivatives:



toluene



xylene



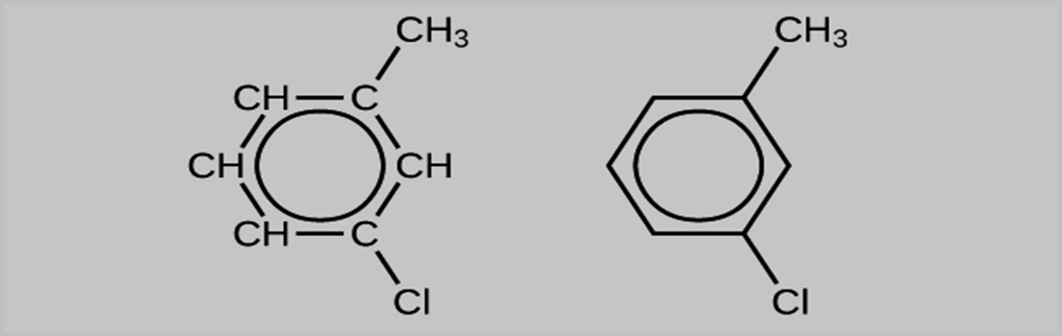
styrene

Toluene and xylene are important solvents and raw materials in the chemical industry. Styrene is used to produce the polymer polystyrene.

Example 8.6

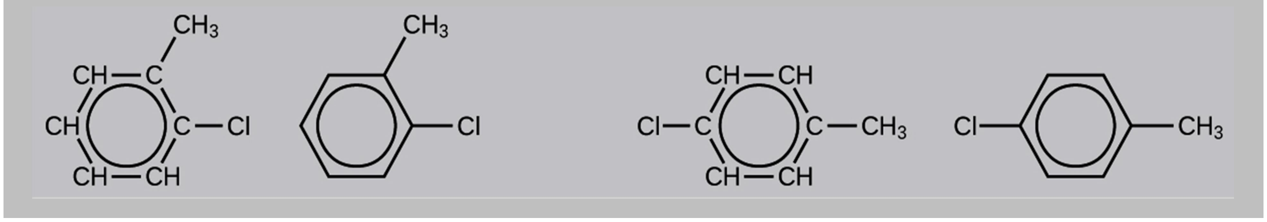
Structure of Aromatic Hydrocarbons

One possible isomer created by a substitution reaction that replaces a hydrogen atom attached to the aromatic ring of toluene with a chlorine atom is shown here. Draw two other possible isomers in which the chlorine atom replaces a different hydrogen atom attached to the aromatic ring:



Solution

Since the six-carbon ring with alternating double bonds is necessary for the molecule to be classified as aromatic, appropriate isomers can be produced only by changing the positions of the chloro-substituent relative to the methyl-substituent:



Check Your Learning

Draw three isomers of a six-membered aromatic ring compound substituted with two bromines.

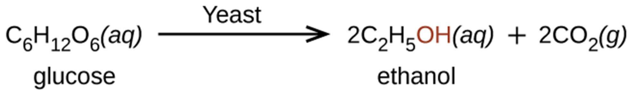
8.3. Alcohols and Ether

8.3.1. Alcohols

Incorporation of an oxygen atom into carbon- and hydrogen-containing molecules leads to new functional groups and new families of compounds. When the oxygen atom is attached by single bonds, the molecule is either an alcohol or ether.

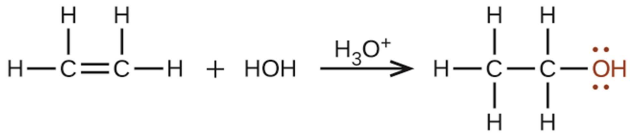
Alcohols are derivatives of hydrocarbons in which an –OH group has replaced a hydrogen atom. Although all alcohols have one or more hydroxyl (–OH) functional groups, they do not behave like bases such as NaOH and KOH. NaOH and KOH are ionic compounds that contain OH^- ions. Alcohols are covalent molecules; the –OH group in an alcohol molecule is attached to a carbon atom by a covalent bond.

Ethanol, CH_3CH_2OH, also called ethyl alcohol, is a particularly important alcohol for human use. Ethanol is the alcohol produced by some species of yeast that is found in wine, beer, and distilled drinks. It has long been prepared by humans harnessing the metabolic efforts of yeasts in fermenting various sugars:

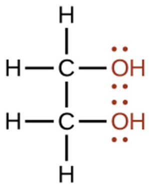


$$\underset{\text{glucose}}{C_6H_{12}O_6(aq)} \xrightarrow{\text{Yeast}} \underset{\text{ethanol}}{2C_2H_5OH(aq)} + 2CO_2(g)$$

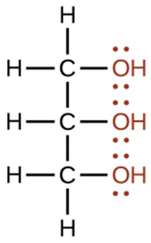
Large quantities of ethanol are synthesized from the addition reaction of water with ethylene using an acid as a catalyst:



Alcohols containing two or more hydroxyl groups can be made. Examples include 1,2-ethanediol (ethylene glycol, used in antifreeze) and 1,2,3-propanetriol (glycerine, used as a solvent for cosmetics and medicines):



1,2-ethanediol



1,2,3-propanetriol

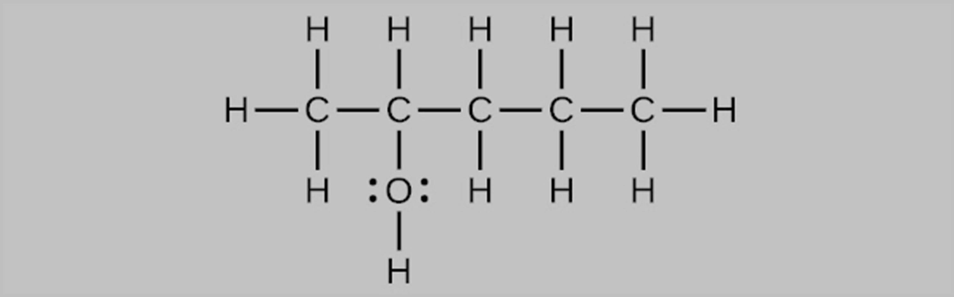
Naming Alcohols

The name of an alcohol comes from the hydrocarbon from which it was derived. The final *-e* in the name of the hydrocarbon is replaced by *-ol*, and the carbon atom to which the –OH group is bonded is indicated by a number placed before the name.

Example 8.7

Naming Alcohols

Consider the following example. How should it be named?

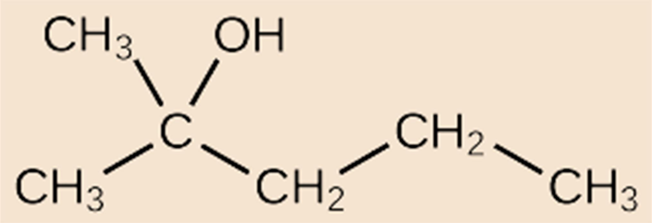


Solution

The carbon chain contains five carbon atoms. If the hydroxyl group was not present, we would have named this molecule pentane. To address the fact that the hydroxyl group is present, we change the ending of the name to *-ol*. In this case, since the –OH is attached to carbon 2 in the chain, we would name this molecule 2-pentanol.

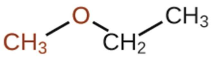
✍ **Check Your Learning**

Name the following molecule:



8.3.2. Ethers

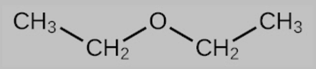
Ethers are compounds that contain the functional group –O–. Ethers do not have a designated suffix like the other types of molecules we have named so far. In the IUPAC system, the oxygen atom and the smaller carbon branch are named as an alkoxy substituent and the remainder of the molecule as the base chain, as in alkanes. As shown in the following compound, the red symbols represent the smaller alkyl group and the oxygen atom, which would be named "methoxy." The larger carbon branch would be ethane, making the molecule methoxyethane. Many ethers are referred to with common names instead of the IUPAC system names. For common names, the two branches connected to the oxygen atom are named separately and followed by "ether."



Example 8.8

Naming Ethers

Provide the IUPAC and common name for the ether shown here:



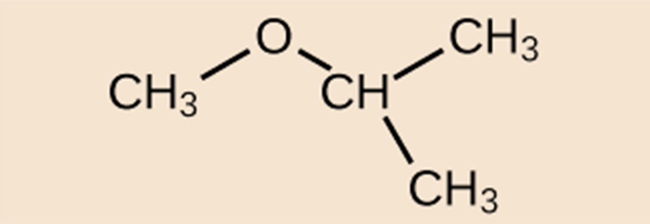
Solution

IUPAC: The molecule is made up of an ethoxy group attached to an ethane chain, so the IUPAC name would be ethoxyethane.

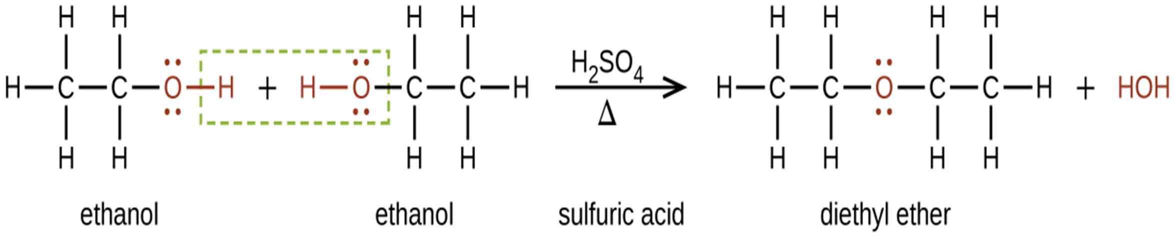
Common: The groups attached to the oxygen atom are both ethyl groups, so the common name would be diethyl ether.

Check Your Learning

Provide the IUPAC and common name for the ether shown:



Ethers can be obtained from alcohols by the elimination of a molecule of water from two molecules of the alcohol. For example, when ethanol is treated with a limited amount of sulfuric acid and heated to 140 °C, diethyl ether and water are formed:



In the general formula for ethers, R—**O**—R, the hydrocarbon groups (R) may be the same or different. Diethyl ether, the most widely used compound of this class, is a colorless, volatile liquid that is highly flammable. It was first used in 1846 as an anesthetic, but better anesthetics have now largely taken its place. Diethyl ether and other ethers are presently used primarily as solvents for gums, fats, waxes, and resins. *Tertiary*-butyl methyl ether, $C_4H_9OCH_3$ (abbreviated

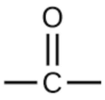
MTBE—italicized portions of names are not counted when ranking the groups alphabeticallyso butyl comes before methyl in the common name), is used as an additive for gasoline. MTBE belongs to a group of chemicals known as oxygenates due to their capacity to increase the oxygen content of gasoline.

8.4. Aldehydes, Ketones, Carboxylic acids and Esters

Another class of organic molecules contains a carbon atom connected to an oxygen atom by a double bond, commonly called a carbonyl group. The trigonal planar carbon in the carbonyl group can attach to two other substituents leading to several subfamilies (aldehydes, ketones, carboxylic acids and esters) described in this section.

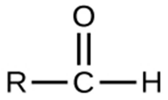
8.4.1. Aldehydes and Ketones

Both aldehydes and ketones contain a carbonyl group, a functional group with a carbon-oxygen double bond. The names for aldehyde and ketone compounds are derived using similar nomenclature rules as for alkanes and alcohols, and include the class-identifying suffixes *-al* and *-one*, respectively:

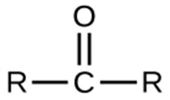


$$-\overset{\displaystyle O}{\overset{\|}{C}}-$$

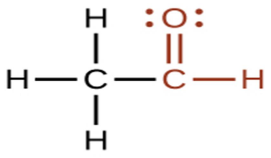
In an aldehyde, the carbonyl group is bonded to at least one hydrogen atom. In a ketone, the carbonyl group is bonded to two carbon atoms:



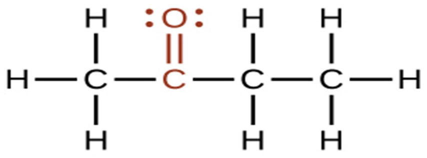
Functional group of an aldehyde



Functional group of a ketone



CH_3CHO
An aldehyde
ethanal (acetaldehyde)



$CH_3COCH_2CH_3$
A ketone
butanone

In both aldehydes and ketones, the geometry around the carbon atom in the carbonyl group is trigonal planar; the carbon atom exhibits sp^2 hybridization. Two of the sp^2 orbitals on the carbon atom in the carbonyl group are used to form σ bonds to the other carbon or hydrogen atoms in a molecule. The remaining sp^2 hybrid orbital forms a σ bond to the oxygen atom. The unhybridized *p* orbital on the carbon atom in the carbonyl group overlaps a *p* orbital on the oxygen atom to form the π bond in the double bond.

Like the C=O bond in carbon dioxide, the C=O bond of a carbonyl group is polar (recall that oxygen is significantly more electronegative than carbon, and the shared electrons are pulled toward the oxygen atom and away from the carbon atom). Many of the reactions of aldehydes and ketones start with the reaction between a Lewis base and the carbon atom at the positive end of the polar C=O bond to yield an unstable intermediate that subsequently undergoes one or more structural rearrangements to form the final product (Figure 8.9).

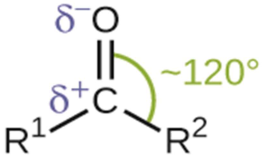
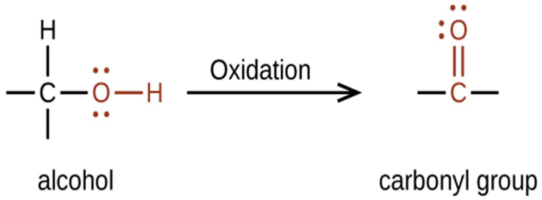


Figure 8.9**:** The carbonyl group is polar, and the geometry of the bonds around the central carbon is trigonal planar.

The importance of molecular structure in the reactivity of organic compounds is illustrated by the reactions that produce aldehydes and ketones. We can prepare a carbonyl group by oxidation of an alcohol for organic molecules, oxidation of a carbon atom is said to occur when a carbon-hydrogen bond is replaced by a carbon-oxygen bond. The reverse reaction replacing a carbon-oxygen bond by a carbon-hydrogen bond is a reduction of that carbon atom. Recall that oxygen is generally assigned a –2 oxidation number unless it is elemental or attached to fluorine. Hydrogen is generally assigned an oxidation number of +1 unless it is attached to a metal. Since carbon does not have a specific rule, its oxidation number is determined algebraically by factoring the atoms it is attached to and the overall charge of the molecule or ion. In general, a carbon atom attached to an oxygen atom will have a more positive oxidation number and a carbon atom attached to a hydrogen atom will have a more negative oxidation number. This should fit nicely with your understanding of the polarity of C–O and C–H bonds. The other reagents and possible products of these reactions are beyond the scope of this chapter, so we will focus only on the changes to the carbon atoms:



Example 8.9

Oxidation and Reduction in Organic Chemistry

Methane represents the completely reduced form of an organic molecule that contains one carbon atom. Sequentially replacing each of the carbon-hydrogen bonds with a carbon-oxygen bond would lead to an alcohol, then an aldehyde, then a carboxylic acid (discussed later), and, finally, carbon dioxide:

$$CH_4 \longrightarrow CH_3OH \longrightarrow CH_2O \longrightarrow HCO_2H \longrightarrow CO_2$$

What are the oxidation numbers for the carbon atoms in the molecules shown here?

Solution

In this example, we can calculate the oxidation number (review the chapter on oxidation-reduction reactions if necessary) for the carbon atom in each case (note how this would become difficult for larger molecules with additional carbon atoms and hydrogen atoms, which is why organic chemists use the definition dealing with replacing C–H bonds with C–O bonds described). For CH_4, the carbon atom carries a –4 oxidation number (the hydrogen atoms are assigned oxidation numbers of +1 and the carbon atom balances that by having an oxidation number of –4). For the alcohol (in this case, methanol), the carbon atom has an oxidation number of –2 (the oxygen atom is assigned –2, the four hydrogen atoms each are assigned +1, and the carbon atom balances the sum by having an oxidation number of –2; note that compared to the carbon atom in CH_4, this carbon atom has lost two electrons so it was oxidized); for the aldehyde, the carbon atom's oxidation number is 0 (–2 for the oxygen atom and +1 for each hydrogen atom already balances to 0, so the oxidation number for the carbon atom is 0); for the carboxylic acid, the carbon atom's oxidation number is +2 (two oxygen atoms each at –2 and two hydrogen atoms at +1); and for carbon dioxide, the carbon atom's oxidation number is +4 (here, the carbon atom needs to balance the –4 sum from the two oxygen atoms).

Aldehydes are commonly prepared by the oxidation of alcohols whose –OH functional group is located on the carbon atom at the end of the chain of carbon atoms in the alcohol:

$$\underset{\text{alcohol}}{\mathrm{CH_3CH_2CH_2OH}} \longrightarrow \underset{\text{aldehyde}}{\mathrm{CH_3CH_2CHO}}$$

Alcohols that have their –OH groups in the middle of the chain are necessary to synthesize a ketone, which requires the carbonyl group to be bonded to two other carbon atoms:

$$\underset{\text{alcohol}}{\mathrm{CH_3CH(OH)CH_3}} \longrightarrow \underset{\text{ketone}}{\mathrm{CH_3COCH_3}}$$

An alcohol with its –OH group bonded to a carbon atom that is bonded to no or one other carbon atom will form an aldehyde. An alcohol with its –OH group attached to two other carbon atoms will form a ketone. If three carbons are attached to the carbon bonded to the –OH, the molecule will not have a C–H bond to be replaced, so it will not be susceptible to oxidation.

Formaldehyde, an aldehyde with the formula HCHO, is a colorless gas with a pungent and irritating odor. It is sold in an aqueous solution called formalin, which contains about 37% formaldehyde by weight. Formaldehyde causes coagulation of proteins, so it kills bacteria (and any other living organism) and stops many of the biological processes that cause tissue to decay. Thus, formaldehyde is used for preserving tissue specimens and embalming bodies. It is also used to sterilize soil or other materials. Formaldehyde is used in the manufacture of Bakelite, a hard plastic having high chemical and electrical resistance.

Dimethyl ketone, CH_3COCH_3, commonly called acetone, is the simplest ketone. It is made commercially by fermenting corn or molasses, or by oxidation of 2-propanol. Acetone is a colorless liquid. Among its many uses are as a solvent for lacquer (including fingernail polish), cellulose acetate, cellulose nitrate, acetylene, plastics, and varnishes; as a paint and varnish remover; and as a solvent in the manufacture of pharmaceuticals and chemicals.

8.4.2. Carboxylic Acids and Esters

The odor of vinegar is caused by the presence of acetic acid, a carboxylic acid, in the vinegar. The odor of ripe bananas and many other fruits is due to the presence of esters, compounds that can be prepared by the reaction of a carboxylic acid with an alcohol. Because esters do not have hydrogen bonds between molecules, they have lower vapor pressures than the alcohols and carboxylic acids from which they are derived (see Figure 8.10).

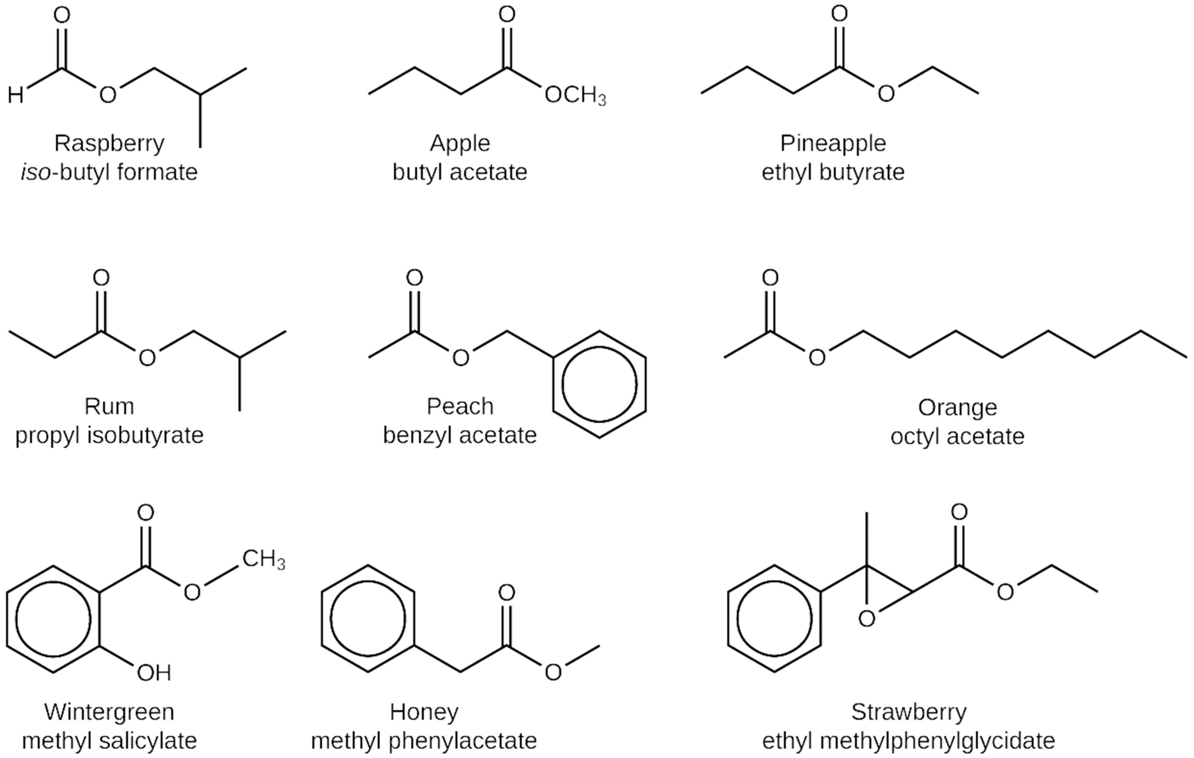
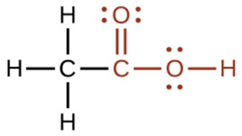
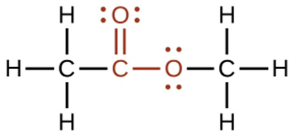


Figure 8.10**:** Esters are responsible for the odors associated with various plants and their fruits.

Both carboxylic acids and esters contain a carbonyl group with a second oxygen atom bonded to the carbon atom in the carbonyl group by a single bond. In a carboxylic acid, the second oxygen atom also bonds to a hydrogen atom. In an ester, the second oxygen atom bonds to another carbon atom. The names for carboxylic acids and esters include prefixes that denote the lengths of the carbon chains in the molecules and are derived following nomenclature rules similar to those for inorganic acids and salts (see these examples):



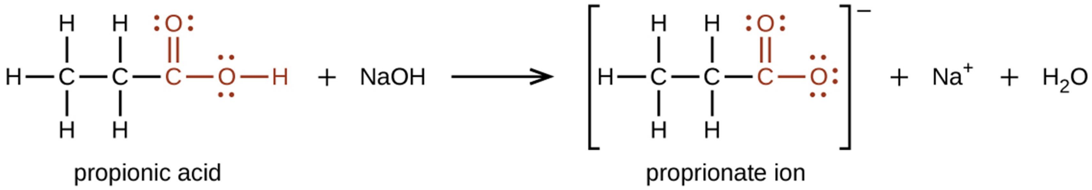
ethanoic acid
(acetic acid)



methyl ethanoate
(methyl acetate)

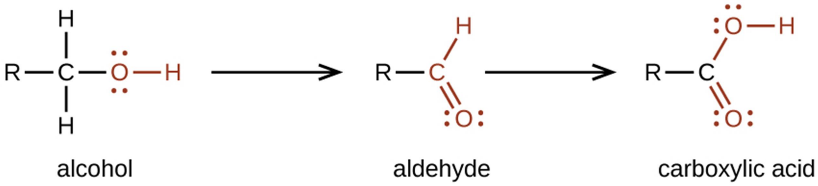
The functional groups for an acid and for an ester are shown in red in these formulas.

The hydrogen atom in the functional group of a carboxylic acid will react with a base to form an ionic salt:

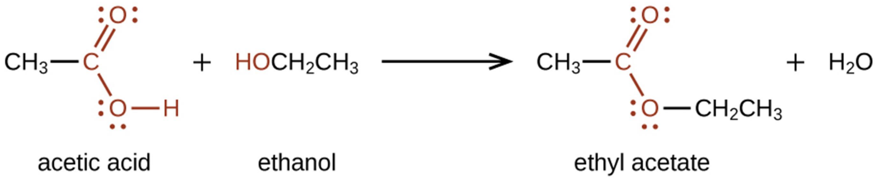


Carboxylic acids are weak acids (see the chapter on acids and bases), meaning they are not 100% ionized in water. Generally only about 1% of the molecules of a carboxylic acid dissolved in water are ionized at any given time. The remaining molecules are undissociated in solution.

We prepare carboxylic acids by the oxidation of aldehydes or alcohols whose –OH functional group is located on the carbon atom at the end of the chain of carbon atoms in the alcohol:



Esters are produced by the reaction of acids with alcohols. For example, the ester ethyl acetate, $CH_3CO_2CH_2CH_3$, is formed when acetic acid reacts with ethanol:



The simplest carboxylic acid is formic acid, HCO_2H, known since 1670. Its name comes from the Latin word *formicus*, which means “ant”; it was first isolated by the distillation of red ants. It is partially responsible for the pain and irritation of ant and wasp stings, and is responsible for a characteristic odor of ants that can be sometimes detected in their nests.

Acetic acid, CH_3CO_2H, constitutes 3–6% vinegar. Cider vinegar is produced by allowing apple juice to ferment without oxygen present. Yeast cells present in the juice carry out the fermentation reactions. The fermentation reactions change the sugar present in the juice to ethanol, then to acetic acid. Pure acetic acid has a penetrating odor and produces painful burns. It is an excellent solvent for many organic and some inorganic compounds, and it is essential in the production of cellulose acetate, a component of many synthetic fibers such as rayon.

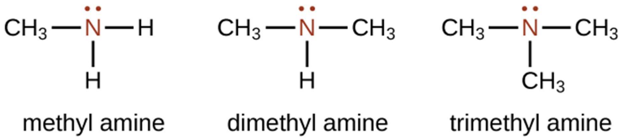
The distinctive and attractive odors and flavors of many flowers, perfumes, and ripe fruits are due to the presence of one or more esters (Figure 8.11). Among the most important of the natural esters are fats (such as lard, tallow, and butter) and oils (such as linseed, cottonseed, and olive oils), which are esters of the trihydroxyl alcohol glycerine, $C_3H_5(OH)_3$, with large carboxylic acids, such as palmitic acid, $CH_3(CH_2)_{14}CO_2H$, stearic acid, $CH_3(CH_2)_{16}CO_2H$, and oleic acid, $CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$. Oleic acid is an unsaturated acid; it contains a C=C double bond. Palmitic and stearic acids are saturated acids that contain no double or triple bonds.

Figure 8.11: Over 350 different volatile molecules (many members of the ester family) have been identified in strawberries.

8.5. Amines and Amides

8.5.1. Amines

Amines are molecules that contain carbon-nitrogen bonds. The nitrogen atom in an amine has a lone pair of electrons and three bonds to other atoms, either carbon or hydrogen. Various nomenclatures are used to derive names for amines, but all involve the class-identifying suffix –*ine* as illustrated here for a few simple examples:



In some amines, the nitrogen atom replaces a carbon atom in an aromatic hydrocarbon. Pyridine (Figure 8.12) is one such heterocyclic amine. A heterocyclic compound contains atoms of two or more different elements in its ring structure.

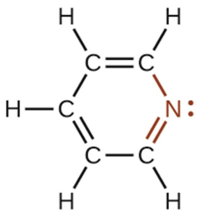
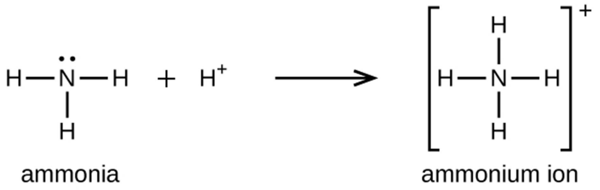
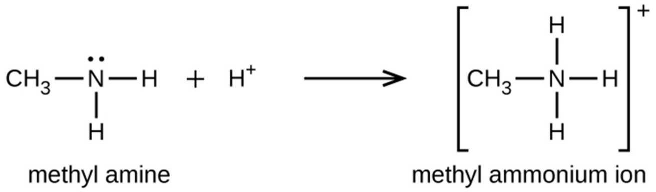


Figure 8.12:-The illustration shows one of the resonance structures of pyridine.

Like ammonia, amines are weak bases due to the lone pair of electrons on their nitrogen atoms:

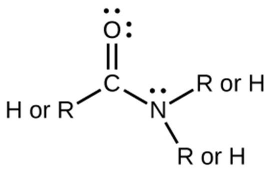


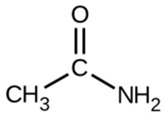


The basicity of an amine's nitrogen atom plays an important role in much of the compound's chemistry. Amine functional groups are found in a wide variety of compounds, including natural and synthetic dyes, polymers, vitamins, and medications such as penicillin and codeine. They are also found in many molecules essential to life, such as amino acids, hormones, neurotransmitters, and DNA.

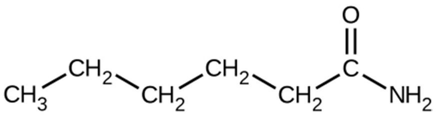
8.5.2. Amides

Amides are molecules that contain nitrogen atoms connected to the carbon atom of a carbonyl group. Like amines, various nomenclature rules may be used to name amides, but all include use of the class-specific suffix *-amide*:



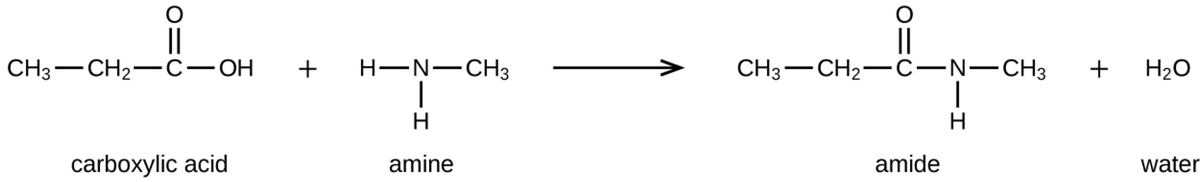


acetamide



hexanamide

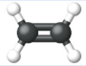
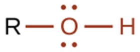
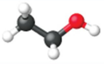
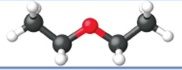
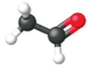
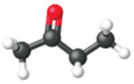
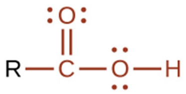
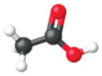
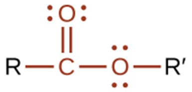
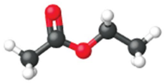
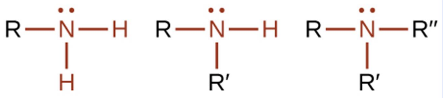
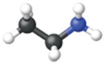
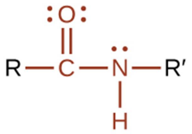
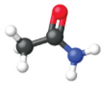
Amides can be produced when carboxylic acids react with amines or ammonia in a process called amidation. A water molecule is eliminated from the reaction, and the amide is formed from the remaining pieces of the carboxylic acid and the amine (note the similarity to formation of an ester from a carboxylic acid and an alcohol discussed in the previous section):



$$CH_3-CH_2-\overset{\overset{\large O}{\|}}{C}-OH + H-\underset{\underset{\large H}{|}}{N}-CH_3 \longrightarrow CH_3-CH_2-\overset{\overset{\large O}{\|}}{C}-\underset{\underset{\large H}{|}}{N}-CH_3 + H_2O$$

The reaction between amines and carboxylic acids to form amides is biologically important. It is through this reaction that amino acids (molecules containing both amine and carboxylic acid substituents) link together in a polymer to form proteins.

Table 8.3:-The table here summarizes the structures discussed in this chapter:

Compound Name	Structure of Compound and Functional Group (red)	Example	
		Formula	Name
alkene	$C=C$	C_2H_4 	ethene
alkyne	$C\equiv C$	C_2H_2 	ethyne
alcohol	 $R-\ddot{O}-H$	CH_3CH_2OH 	ethanol
ether	 $R-\ddot{O}-R'$	$(C_2H_5)_2O$ 	diethyl ether
aldehyde	 $R-\overset{\overset{O}{\|}}{C}-H$	CH_3CHO 	ethanal
ketone	 $R-\overset{\overset{O}{\|}}{C}-R'$	$CH_3COCH_2CH_3$ 	methyl ethyl ketone
carboxylic acid	 $R-\overset{\overset{O}{\|}}{C}-\ddot{O}-H$	CH_3COOH 	acetic acid
ester	 $R-\overset{\overset{O}{\|}}{C}-\ddot{O}-R'$	$CH_3CO_2CH_2CH_3$ 	ethyl acetate
amine	 $R-\underset{\underset{H}{\|}}{\ddot{N}}-H \quad R-\underset{\underset{R'}{\|}}{\ddot{N}}-H \quad R-\underset{\underset{R'}{\|}}{\ddot{N}}-R''$	$C_2H_5NH_2$ 	ethylamine
amide	 $R-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{\|}}{\ddot{N}}-R'$	CH_3CONH_2 	acetamide

Review Exercise

1. Write the chemical formula and Lewis structure of the following, each of which contains five carbon atoms:

   (a) an alkane(b) an alkene(c) an alkyne

2. What is the difference between the hybridization of carbon atoms' valence orbitals in saturated and unsaturated hydrocarbons?
3. On a microscopic level, how does the reaction of bromine with a saturated hydrocarbon differ from its reaction with an unsaturated hydrocarbon? How are they similar?

4. On a microscopic level, how does the reaction of bromine with an alkene differ from its reaction with an alkyne? How are they similar?
5. Explain why unbranched alkenes can form geometric isomers while unbranched alkanes cannot. Does this explanation involve the macroscopic domain or the microscopic domain?
6. How does the carbon-atom hybridization change when polyethylene is prepared from ethylene?
7. Write the Lewis structure and molecular formula for each of the following hydrocarbons:

   (a) hexane (c) *cis*-3-hexene (e) 3-hexyne

   (b) 3-methylpentane (d) 4-methyl-1-pentene (f) 4-methyl-2-pentyne
8. Write the chemical formula, condensed formula, and Lewis structure for each of the following hydrocarbons:

   (a) heptane (c) *trans*-3-heptene (e) 2-heptyne

   (b) 3-methylhexane (d) 4-methyl-1-hexene (f) 3,4-dimethyl-1-pentyne
9. Give the complete IUPAC name for each of the following compounds:

   (a) $CH_3CH_2CBr_2CH_3$(c) $(CH_3)_3CCl$ (e) $CH_3CHClCHClCH_3$

   (b) $CH_3CH_2C{\equiv}CH$ $CH_3CH_2C{\equiv}CH$(d) $(CH_3)_2CHCH_2CH{=}CH_2$(f) $(CH_3)_2CH$
10. Butane is used as a fuel in disposable lighters. Write the Lewis structure for each isomer of butane.
11. Write Lewis structures and name the five structural isomers of hexane.
12. Write Lewis structures for the *cis–trans* isomers of $CH_3CH{=}CHCl$.
13. Write structures for the three isomers of the aromatic hydrocarbon xylene, $C_6H_4(CH_3)_2$.
14. Write Lewis structures and IUPAC names for the alkyne isomers of C_4H_6.
15. Write Lewis structures and describe the molecular geometry at each carbon atom in the following compounds:

(a) *cis*-3-hexene (c) 2-pentyne

(b) *cis*-1-chloro-2-bromoethene (d) *trans*-6-ethyl-7-methyl-2-octene

16. Teflon is prepared by the polymerization of tetrafluoroethylene. Write the equation that describes the polymerization using Lewis symbols.
17. Write two complete, balanced equations for each of the following reactions, one using condensed formulas and one using Lewis structures.

   (a) 1 mol of 1-butyne reacts with 2 mol of iodine.(c) benzene burns in air.

   (b) Pentane is burned in air.(d) 2-butene reacts with chlorine.

18. What mass of 2-bromopropane could be prepared from 25.5 g of propene? Assume a 100% yield of product.

19. Ethylene can be produced by the pyrolysis of ethane:

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

How many kilograms of ethylene are produced by the pyrolysis of 1.000×10^3 kg of ethane, assuming a 100.0% yield?

20. Why do the compounds hexane, hexanol, and hexene have such similar names?

21. Write condensed formulas and provide IUPAC names for the following compounds:

(a) ethyl alcohol (in beverages)
(d) glycerine
(b) isopropyl alcohol (used in rubbing alcohol)
(e) ethylene glycol (antifreeze)
(c) methyl alcohol (used as a solvent, for example, in shell)

22. Give the complete IUPAC name and the common name for each of the following compounds:

(a) $CH_3—CH_2—O—CH_2—CH_2—CH_3$

(b) $CH_3—CH_2—O—CH_2—CH_2—CH_2—CH_3$

(c) $CH_3—O—CH_2—CH_2—CH_3$

23. Write the condensed structures of both isomers with the formula C_2H_6O. Label the functional group of each isomer.

24. Write the condensed structures of all isomers with the formula $C_2H_6O_2$. Label the functional group (or groups) of each isomer.

25. Draw the condensed formulas for each of the following compounds:

(a) dipropyl ether(b) 2,2-dimethyl-3-hexanol(c) 2-ethoxybutane

26. Write two complete balanced equations for each of the following reactions, one using condensed formulas and one using Lewis structures.

(a) propanol is converted to dipropyl ether

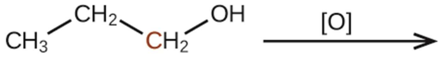
(b) propene is treated with water in dilute acid.

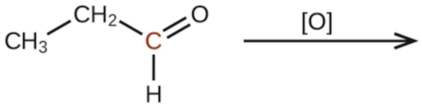
27. Write two complete balanced equations for each of the following reactions, one using condensed formulas and one using Lewis structures.

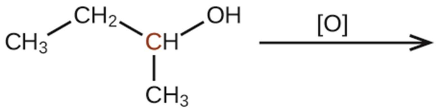
(a) 2-butene is treated with water in dilute acid

(b) ethanol is dehydrated to yield ethane

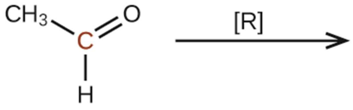
28. Predict the products of oxidizing the molecules shown in this problem. In each case, identify the product that will result from the minimal increase in oxidation state for the highlighted carbon atom:

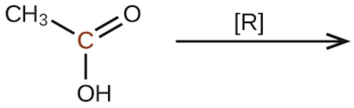
(a) 

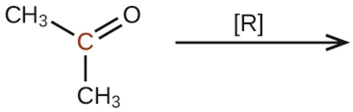
(b) 

(c) 

29. Predict the products of reducing the following molecules. In each case, identify the product that will result from the minimal decrease in oxidation state for the highlighted carbon atom:

(a) 

(b) 

(c) 

30. Explain why it is not possible to prepare a ketone that contains only two carbon atoms.

31. How does hybridization of the substituted carbon atom change when an alcohol is converted into an aldehyde? An aldehyde to a carboxylic acid?

32. Fatty acids are carboxylic acids that have long hydrocarbon chains attached to a carboxylate group. How does a saturated fatty acid differ from an unsaturated fatty acid? How are they similar?

33. Write a condensed structural formula, such as CH_3CH_3, and describe the molecular geometry at each carbon atom.

(a) propene
(b) 1-butanol
(g) 2-propanol
(h) acetone
(c) ethyl propyl ether
(d) *cis*-4-bromo-2-heptene
(i) dimethyl ether
(j) acetic acid
(e) 2,2,3-trimethylhexane
(f) formaldehyde
(e) 3-methyl-1-hexene

34. Write the two-resonance structures for the acetate ion.
35. Write two complete, balanced equations for each of the following reactions, one using condensed formulas and one using Lewis structures:
    (a) ethanol reacts with propionic acid
    (b) benzoic acid, $C_6H_5CO_2H$, is added to a solution of sodium hydroxide
    (c) 1-butanol reacts with acetic acid
    (d) propionic acid is poured onto solid calcium carbonate
36. Yields in organic reactions are sometimes low. What is the percent yield of a process that produces 13.0 g of ethyl acetate from 10.0 g of CH_3CO_2H?
37. Alcohols A, B, and C all have the composition $C_4H_{10}O$. Molecules of alcohol A contain a branched carbon chain and can be oxidized to an aldehyde; molecules of alcohol B contain a linear carbon chain and can be oxidized to a ketone; and molecules of alcohol C can be oxidized to neither an aldehyde nor a ketone. Write the Lewis structures of these molecules.
38. Write the Lewis structures of both isomers with the formula C_2H_7N.
39. What is the molecular structure about the nitrogen atom in trimethyl amine and in the trimethyl ammonium ion, $(CH_3)_3NH^+$? What is the hybridization of the nitrogen atom in trimethyl amine and in the trimethyl ammonium ion?
40. Write the two resonance structures for the pyridinium ion, $C_5H_5NH^+$.
41. Write the Lewis structures of all isomers with the formula C_3H_7ON that contain an amide linkage.
42. Write two complete balanced equations for the following reaction, one using condensed formulas and one using Lewis structures.
    (a) Methyl amine is added to a solution of HCl.
    (b) Ethylammonium chloride is added to a solution of sodium hydroxide.

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