TRU: FUNDAMENTALS AND PRINCIPLES OF CHEMISTRY (CHEM 1510 AND CHEM 1520)



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Thompson Rivers University

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This text was compiled on 06/08/2025

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SECTION OVERVIEW

1.1: Essential Ideas of Chemistry

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 course, you will learn many of the essential principles underlying the chemistry of modern-day life.

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1.1.1: Chemistry in Context

Learning Objectives

- Outline the historical development of chemistry
- Provide examples of the importance of chemistry in everyday life
- Describe the scientific method and informs the scientific process
- Differentiate among hypotheses, theories, and laws
- Provide examples illustrating macroscopic, microscopic, and symbolic domains

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 were 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 (Figure 1.1.1.1).



Figure 1.1.1.1: This portrayal shows an alchemist’s workshop circa 1580. Although alchemy made some useful contributions to how to manipulate matter, it was not scientific by modern standards. (credit: Chemical Heritage Foundation).

A sketch depicts 4 people stirring and handling chemicals. The chemicals are held in a variety of barrels and large cylinders. Several of the containers are being heated over burning embers. A large stove in the laboratory is filled with burning embers. There is also a large chest in the corner that is producing steam.

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. This effort has been so successful that many people do not realize either the central position of chemistry among the sciences or the importance and universality of chemistry in daily life.

1.1.1.1: Chemistry: The Central Science

Chemistry is sometimes referred to as “the central science” due to its interconnectedness with a vast array of other STEM disciplines (STEM stands for areas of study in the science, technology, engineering, and math fields). Chemistry and the language of chemists play vital roles in biology, medicine, materials science, forensics, environmental science, and many other fields (Figure 1.1.1.2). The basic principles of physics are essential for understanding many aspects of chemistry, and there is extensive overlap between many subdisciplines within the two fields, such as chemical physics and nuclear chemistry. Mathematics, computer science, and information theory provide important tools that help us calculate, interpret, describe, and generally make sense of the chemical world. Biology and chemistry converge in biochemistry, which is crucial to understanding the many complex factors and processes that keep living organisms (such as us) alive. Chemical engineering, materials science, and nanotechnology combine chemical principles and empirical findings to produce useful substances, ranging from gasoline to fabrics to electronics. Agriculture, food science, veterinary science, and brewing and wine making help provide sustenance in the form of food and drink to the world’s population. Medicine, pharmacology, biotechnology, and botany identify and produce substances that help keep us healthy. Environmental science, geology, oceanography, and atmospheric science incorporate many chemical ideas to help us better understand and protect our physical world. Chemical ideas are used to help understand the universe in astronomy and cosmology.

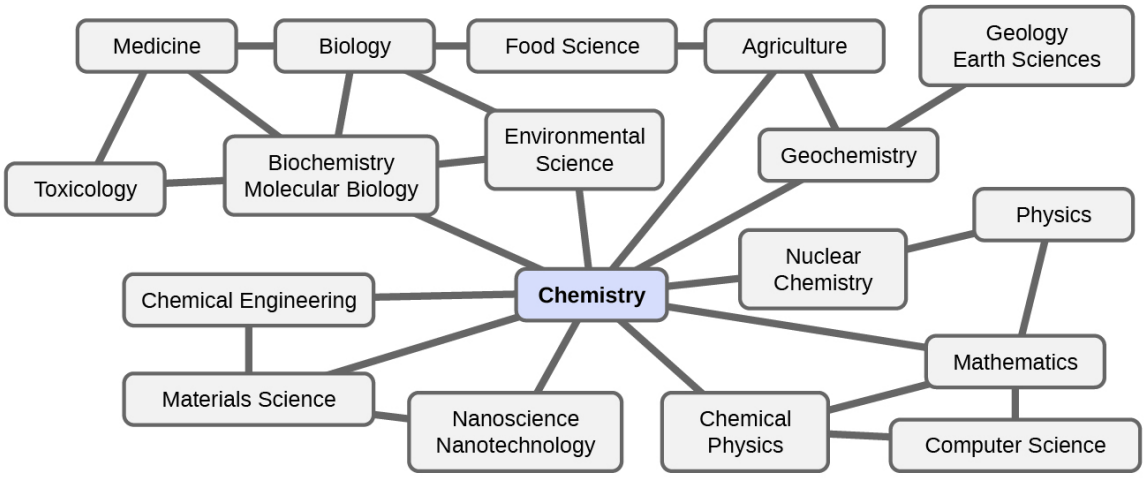


Figure 1.1.1.2: Knowledge of chemistry is central to understanding a wide range of scientific disciplines. This diagram shows just some of the interrelationships between chemistry and other fields.

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.

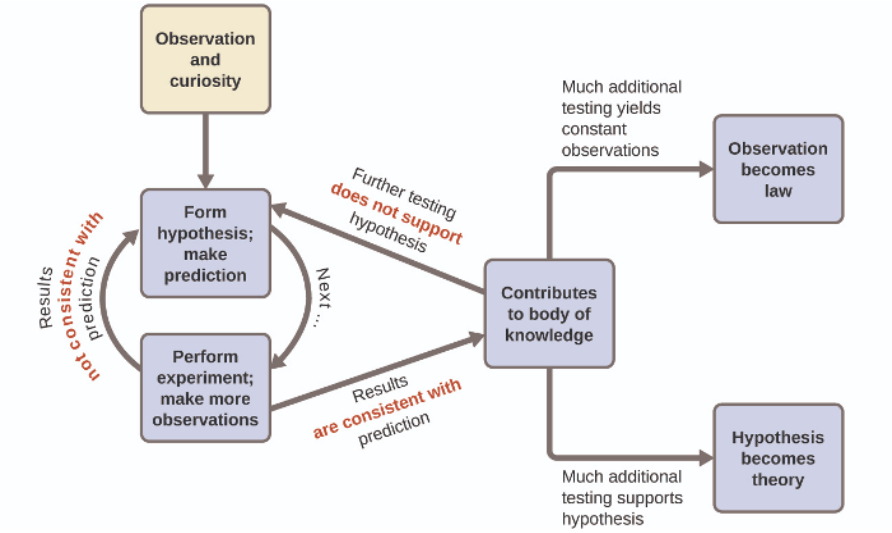
What are some changes in matter that are essential to daily life? Digesting and assimilating food, synthesizing polymers that are used to make clothing, containers, cookware, and credit cards, and refining crude oil into gasoline and other products are just a few examples. As you proceed through this course, you will discover many different examples of changes in the composition and structure of matter, how to classify these changes and how they occurred, their causes, the changes in energy that accompany them, 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.

1.1.1.2: 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. We test a hypothesis by experimentation, calculation, and/or comparison with the experiments of others and then refine it 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 1.1.1.3).



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.

Figure 1.1.1.3: 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.

1.1.1.3: 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, or changes such as density, solubility, and flammability.

The microscopic domain of chemistry is almost always visited in the imagination. *Micro* also comes from Greek and means “small.” Some aspects of the microscopic domains are visible through a microscope, such as a magnified image of graphite or bacteria. Viruses, for instance, are too small to be seen with the naked eye, but when we’re suffering from a cold, we’re reminded of how real they are.

However, most of the subjects in the microscopic domain of chemistry—such as atoms and molecules—are too small to be seen even with standard microscopes and often must 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. This domain includes the individual metal atoms in a wire, the ions that compose a salt crystal, the changes in individual molecules that result in a color change, the conversion of nutrient molecules into tissue and energy, and the evolution of heat as bonds that hold atoms together are created.

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 and drawings. We can also consider calculations as part of the symbolic domain. 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 makes 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 1.1.4) are macroscopic observations. But some properties of water fall into the microscopic domain—what we cannot observe with the naked eye. The description of water as comprised of 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.

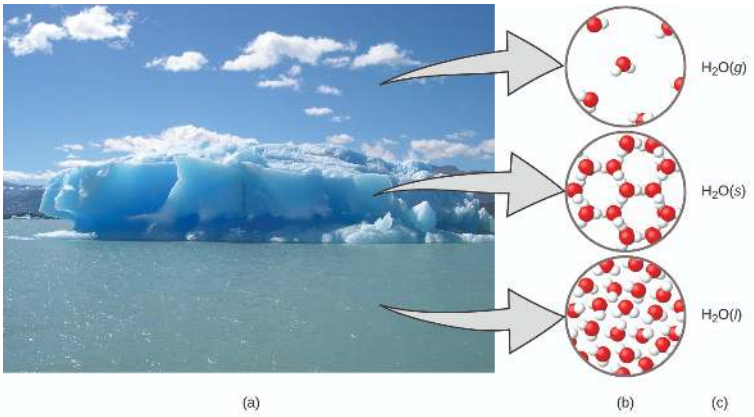


Figure 1.1.1.4: (a) Moisture in the air, icebergs, and the ocean represent water in the macroscopic domain. (b) At the molecular level (microscopic domain), gas molecules are far apart and disorganized, solid water molecules are close together and organized, and liquid molecules are close together and disorganized. (c) The formula H_2O symbolizes water, and (g), (s), and (l) symbolize its phases. Note that clouds are actually comprised of 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. (credit a: modification of work by "Gorkaazk"/Wikimedia Commons).

Figure A shows 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 subscript 2 O gas, the water molecules are disconnected and widely spaced. In the ice, which is the solid form of water, H subscript 2 O solid, 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 subscript 2 O liquid, the water molecules are very densely packed. The molecules are not bonded together.

1.1.1.4: Key Concepts and Summary

Chemistry deals with the composition, structure, and properties of matter, and the ways by which various forms of matter may be interconverted. Thus, it occupies a central place in the study and practice of science and technology. Chemists use the scientific method to perform experiments, pose hypotheses, and formulate laws and develop theories, so that they can better understand the behavior of the natural world. To do so, they operate in the macroscopic, microscopic, and symbolic domains. Chemists measure, analyze, purify, and synthesize a wide variety of substances that are important to our lives.

Glossary

chemistry

study of the composition, properties, and interactions of matter

hypothesis

tentative explanation of observations that acts as a guide for gathering and checking information

law

statement that summarizes a vast number of experimental observations, and describes or predicts some aspect of the natural world

macroscopic domain

realm of everyday things that are large enough to sense directly by human sight and touch

microscopic domain

realm of things that are much too small to be sensed directly

scientific method

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

symbolic domain

specialized language used to represent components of the macroscopic and microscopic domains, such as chemical symbols, chemical formulas, chemical equations, graphs, drawings, and calculations

theory

well-substantiated, comprehensive, testable explanation of a particular aspect of nature

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1.1.2: Phases and Classification of Matter

Learning Objectives

- Describe the basic properties of each physical state of matter: solid, liquid, and gas.
- Define and give examples of atoms and molecules.
- Classify matter as an element, compound, homogeneous mixture, or heterogeneous mixture with regard to its physical state and composition.
- Use symbolic, particulate, or macroscopic representations to describe or classify the different types of matter.
- Distinguish between mass and weight.
- Apply the law of conservation 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 stay collapsed rather than inflate when filled with gas.

Solids, liquids, and gases are the three states of matter commonly found on earth (Figure 1.1.2.1). A solid is rigid and possesses a definite shape. A liquid flows and takes the shape of a 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.

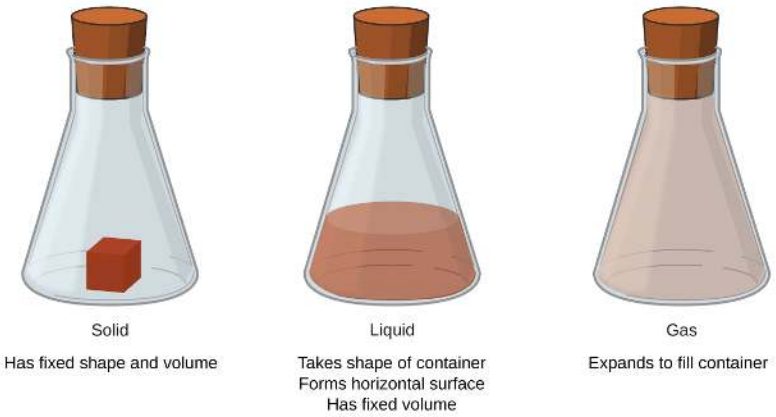


Figure 1.1.2.1: The three most common states or phases of matter are solid, liquid, and gas.

A beaker labeled solid contains a cube of red matter and says has fixed shape and volume. A beaker labeled liquid contains a brownish-red colored liquid. This beaker says takes shape of container, forms horizontal surfaces, has fixed volume. The beaker labeled gas is filled with a light brown gas. This beaker says expands to fill container.

A fourth state of matter, plasma, occurs naturally in the interiors of stars. A plasma is a gaseous state of matter that contains appreciable numbers of electrically charged particles (Figure 1.1.2.2). 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 1.1.2.2: A plasma torch can be used to cut metal. (credit: “Hypertherm”/Wikimedia Commons)

A cutting torch is being used to cut a piece of metal. Bright, white colored plasma can be seen near the tip of the torch, where it is contacting the metal.



***Video* 1.1.2.1** *: 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. Watch this video to learn more about plasma and the places you encounter it.*

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 goes to the moon. But her weight on the moon is only one-sixth her earth-bound weight because the moon’s gravity is only one-sixth that of the earth’s. She may feel “weightless” during her trip when she experiences negligible external forces (gravitational or any other), although she 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 1.1.2.4). 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.

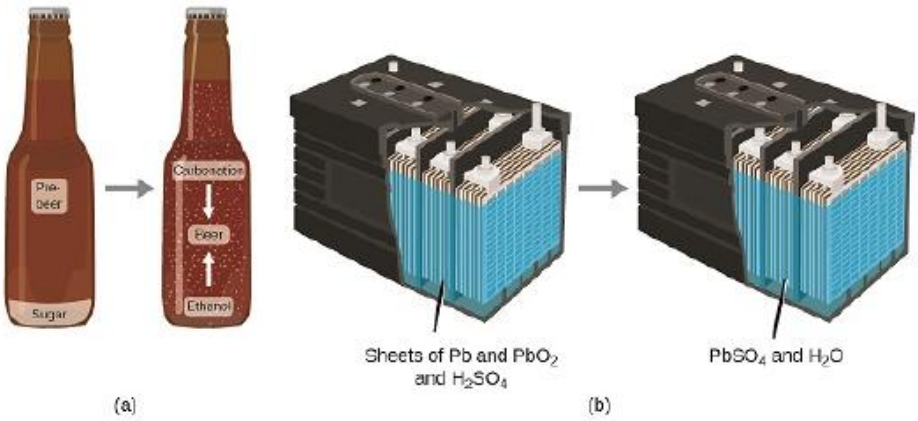


Figure 1.1.2.3: (a) The mass of beer precursor materials is the same as the mass of beer produced: Sugar has become alcohol and carbonation. (b) The mass of the lead, lead oxide plates, and sulfuric acid that goes into the production of electricity is exactly equal to the mass of lead sulfate and water that is formed.

Diagram A shows a beer bottle containing pre-beer and sugar. An arrow points from this bottle to a second bottle. This second bottle contains the same volume of liquid, however, the sugar has been converted into ethanol and carbonation as beer was made. Diagram B shows a car battery that contains sheets of P B and P B O subscript 2 along with H subscript 2 S O subscript 4. After the battery is used, it contains an equal mass of P B S O subscript 4 and H subscript 2 O.

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.

1.1.2.1: Atoms and Molecules

An atom is the smallest particle of an element that has the properties of that element and can enter into a chemical combination. Consider the element gold, for example. Imagine cutting a gold nugget in half, then cutting one of the halves in half, and repeating this process until a piece of gold remained that was so small that it could not be cut in half (regardless of how tiny your knife may be). This minimally sized piece of gold is an atom (from the Greek *atomos*, meaning “indivisible”) (Figure 1.2.4). This atom would no longer be gold if it were divided any further.

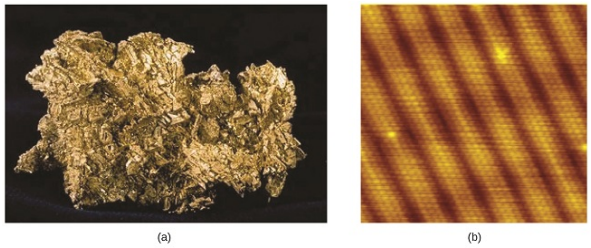


Figure 1.1.2.4: (a) This photograph shows a gold nugget. (b) A scanning-tunneling microscope (STM) can generate views of the surfaces of solids, such as this image of a gold crystal. Each sphere represents one gold atom. (credit a: modification of work by United States Geological Survey; credit b: modification of work by “Erwinrossen”/Wikimedia Commons)

Figure A shows a gold nugget as it would appear to the naked eye. The gold nugget is very irregular, with many sharp edges. It appears gold in color. The microscope image of a gold crystal shows many similarly sized gold stripes that are separated by dark areas. Looking closely, one can see that the gold stripes are made of many, tiny, circular atoms.

The first suggestion that matter is composed of atoms is attributed to the Greek philosophers Leucippus and Democritus, who developed their ideas in the 5th century BCE. However, it was not until the early nineteenth century that John Dalton (1766–1844), a British schoolteacher with a keen interest in science, supported this hypothesis with quantitative measurements. Since that time, repeated experiments have confirmed many aspects of this hypothesis, and it has become one of the central theories of chemistry.

Other aspects of Dalton's atomic theory are still used but with minor revisions (details of Dalton's theory are provided in the chapter on atoms and molecules).

An atom is so small that its size is difficult to imagine. One of the smallest things we can see with our unaided eye is a single thread of a spider web: These strands are about 1/10,000 of a centimeter (0.0001 cm) in diameter. Although the cross-section of one strand is almost impossible to see without a microscope, it is huge on an atomic scale. A single carbon atom in the web has a diameter of about 0.000000015 centimeter, and it would take about 7000 carbon atoms to span the diameter of the strand. To put this in perspective, if a carbon atom were the size of a dime, the cross-section of one strand would be larger than a football field, which would require about 150 million carbon atom "dimes" to cover it. (Figure 1.1.2.5) shows increasingly close microscopic and atomic-level views of ordinary cotton.

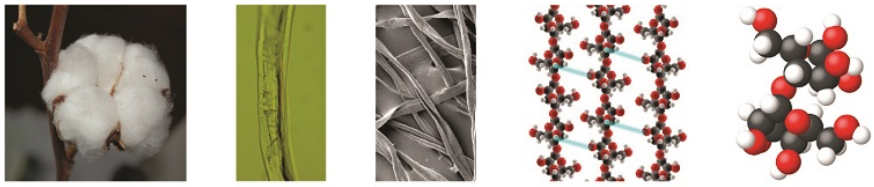


Figure 1.1.2.5: These images provide an increasingly closer view: (a) a cotton boll, (b) a single cotton fiber viewed under an optical microscope (magnified 40 times), (c) an image of a cotton fiber obtained with an electron microscope (much higher magnification than with the optical microscope); and (d and e) atomic-level models of the fiber (spheres of different colors represent atoms of different elements). (credit c: modification of work by "Featheredtar"/Wikimedia Commons)

Figure A shows a puffy white cotton boll growing on a brown twig. Figure B shows a magnified cotton strand. The strand appears transparent but contains dark areas within its interior. Figure C shows the surface of several crisscrossing and overlapping cotton fibers. Its surface is rough along the edges but smooth near the center of each strand. Figure D shows three strands of molecules connected into three vertical chains. Each strand contains about five molecules. Figure E shows that the cotton molecule contains about a dozen atoms. The black carbon atoms form rings that are connected by red oxygen atoms. Many of the carbon atoms are also bonded to hydrogen atoms, shown as white balls, or other oxygen atoms.

An atom is so light that its mass is also difficult to imagine. A billion lead atoms (1,000,000,000 atoms) weigh about 3×10^{-13} grams, a mass that is far too light to be weighed on even the world's most sensitive balances. It would require over 300,000,000,000,000 lead atoms (300 trillion, or 3×10^{14}) to be weighed, and they would weigh only 0.0000001 gram.

It is rare to find collections of individual atoms. Only a few elements, such as the gases helium, neon, and argon, consist of a collection of individual atoms that move about independently of one another. Other elements, such as the gases hydrogen, nitrogen, oxygen, and chlorine, are composed of units that consist of pairs of atoms (Figure 1.1.2.6). One form of the element phosphorus consists of units composed of four phosphorus atoms. The element sulfur exists in various forms, one of which consists of units composed of eight sulfur atoms. These units are called molecules. A molecule consists of two or more atoms joined by strong forces called chemical bonds. The atoms in a molecule move around as a unit, much like the cans of soda in a six-pack or a bunch of keys joined together on a single key ring. A molecule may consist of two or more identical atoms, as in the molecules found in the elements hydrogen, oxygen, and sulfur, or it may consist of two or more different atoms, as in the molecules found in water. Each water molecule is a unit that contains two hydrogen atoms and one oxygen atom. Each glucose molecule is a unit that contains 6 carbon atoms, 12 hydrogen atoms, and 6 oxygen atoms. Like atoms, molecules are incredibly small and light. If an ordinary glass of water were enlarged to the size of the earth, the water molecules inside it would be about the size of golf balls.

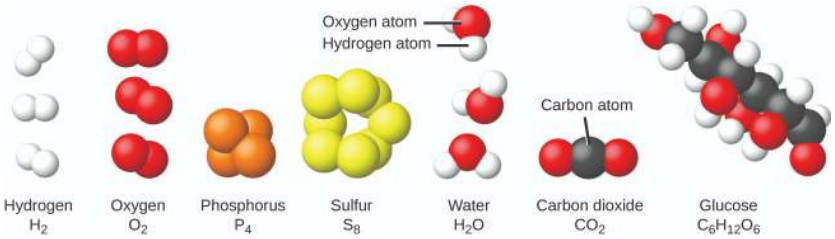


Figure 1.1.2.6: The elements hydrogen, oxygen, phosphorus, and sulfur form molecules consisting of two or more atoms of the same element. The compounds water, carbon dioxide, and glucose consist of combinations of atoms of different elements.

The hydrogen molecule, H subscript 2, is shown as two small, white balls bonded together. The oxygen molecule O subscript 2, is shown as two red balls bonded together. The phosphorous molecule, P subscript 4, is shown as four orange balls bonded tightly together. The sulfur molecule, S subscript 8, is shown as 8 yellow balls linked together. Water molecules, H subscript 2 O, consist of one red oxygen atom bonded to two smaller white hydrogen atoms. The hydrogen atoms are at an angle on the oxygen molecule. Carbon dioxide, C O subscript 2, consists of one carbon atom and two oxygen atoms. One oxygen atom is bonded to the carbon's right side and the other oxygen is bonded to the carbon's left side. Glucose, C subscript 6 H subscript 12 O subscript 6, contains a chain of carbon atoms that have attached oxygen or hydrogen atoms.

1.1.2.2: Classifying Matter

We can classify matter 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.

We can divide pure substances 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 (Figure 1.1.2.7). 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).

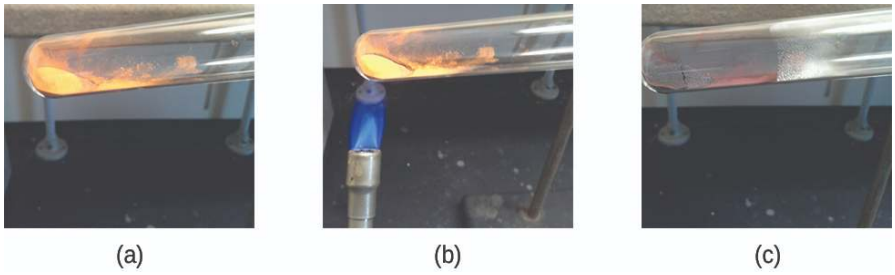


Figure 1.1.2.7: (a)The compound mercury(II) oxide, (b)when heated, (c) decomposes into silvery droplets of liquid mercury and invisible oxygen gas. (credit: modification of work by Paul Flowers)

This figure shows a series of three photos labeled a, b, and c. Photo a shows the bottom of a test tube that is filled with an orange-red substance. A slight amount of a silver substance is also visible. Photo b shows the substance in the test tube being heated over a flame. Photo c shows a test tube that is not longer being heated. The orange-red substance is almost completely gone, and small, silver droplets of a substance are left.

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 1.1.2.1*a*). Its composition can vary because we can make it 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 1.1.2.1*b*). 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.



Figure 1.1.2.7: (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. (credit a “left”: modification of work by John Mayer; credit a “right”: modification of work by Umberto Salvagnin; credit b “left: modification of work by Jeff Bedford)

Diagram A shows a glass containing a red liquid with a layer of yellow oil floating on the surface of the red liquid. A zoom in box is magnifying a portion of the red liquid that contains some of the yellow oil. The zoomed in image shows that oil is forming round droplets within the red liquid. Diagram B shows a photo of Gatorade G 2. A zoom in box is magnifying a portion of the Gatorade, which is uniformly red.

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 by which we can 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 1.2.8).

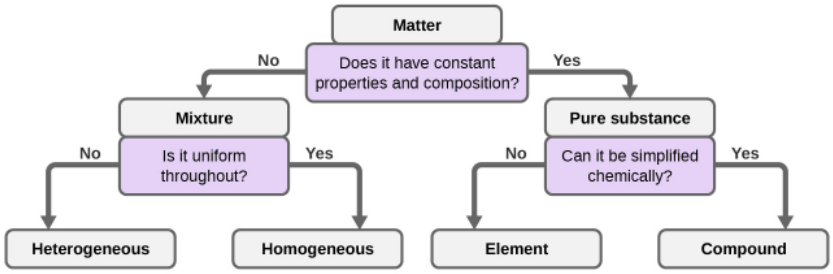


Figure 1.1.2.8: Depending on its properties, a given substance can be classified as a homogeneous mixture, a heterogeneous mixture, a compound, or an element.

This flow chart begins with matter at the top and the question: does the matter have constant properties and composition? If no, then it is a mixture. This leads to the next question: is it uniform throughout? If no, it is heterogeneous. If yes, it is homogenous. If the matter does have constant properties and composition, it is a pure substance. This leads to the next question: can it be simplified chemically? If no, it is an element. If yes, then it is a compound.

Eleven elements make up about 99% of the earth’s crust and atmosphere (Table 1.1.2.1). 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.

Table 1.1.2.1: Elemental Composition of Earth

Element	Symbol	Percent Mass	Element	Symbol	Percent Mass

Element	Symbol	Percent 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

1.1.2.3: Decomposition of Water / Production of Hydrogen

Water consists of the elements hydrogen and oxygen combined in a 2 to 1 ratio. Water can be broken down into hydrogen and oxygen gases by the addition of energy. One way to do this is with a battery or power supply, as shown in (Figure 1.1.2.9).

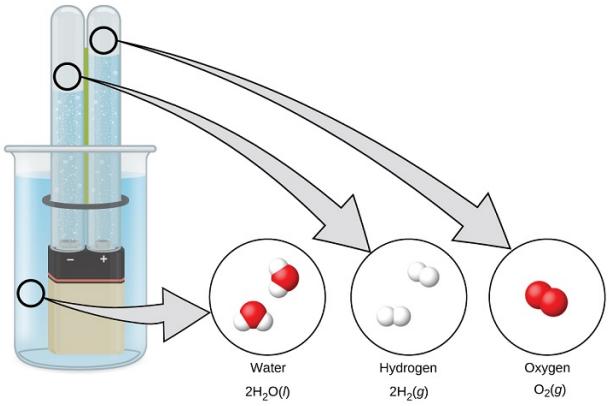


Figure 1.1.2.9: The decomposition of water is shown at the macroscopic, microscopic, and symbolic levels. The battery provides an electric current (microscopic) that decomposes water. At the macroscopic level, the liquid separates into the gases hydrogen (on the left) and oxygen (on the right). Symbolically, this change is presented by showing how liquid H_2O separates into H_2 and O_2 gases.

A rectangular battery is immersed in a beaker filled with liquid. Each of the battery terminals are covered by an overturned test tube. The test tubes each contain a bubbling liquid. Zoom in areas indicate that the liquid in the beaker is water, 2 H subscript 2 O liquid. The bubbles in the test tube over the negative terminal are hydrogen gas, 2 H subscript 2 gas. The bubbles in the test tube over the positive terminal are oxygen gas, O subscript 2 gas.

The breakdown of water involves a rearrangement of the atoms in water molecules into different molecules, each composed of two hydrogen atoms and two oxygen atoms, respectively. Two water molecules form one oxygen molecule and two hydrogen molecules. The representation for what occurs, $2\,H_2O(l) \rightarrow 2\,H_2(g) + O_2(g)$, will be explored in more depth in later chapters.

The two gases produced have distinctly different properties. Oxygen is not flammable but is required for combustion of a fuel, and hydrogen is highly flammable and a potent energy source. How might this knowledge be applied in our world? One application involves research into more fuel-efficient transportation. Fuel-cell vehicles (FCV) run on hydrogen instead of gasoline (Figure 1.1.2.10). They are more efficient than vehicles with internal combustion engines, are nonpolluting, and reduce greenhouse gas emissions, making us less dependent on fossil fuels. FCVs are not yet economically viable, however, and current hydrogen production depends on natural gas. If we can develop a process to economically decompose water, or produce hydrogen in another environmentally sound way, FCVs may be the way of the future.

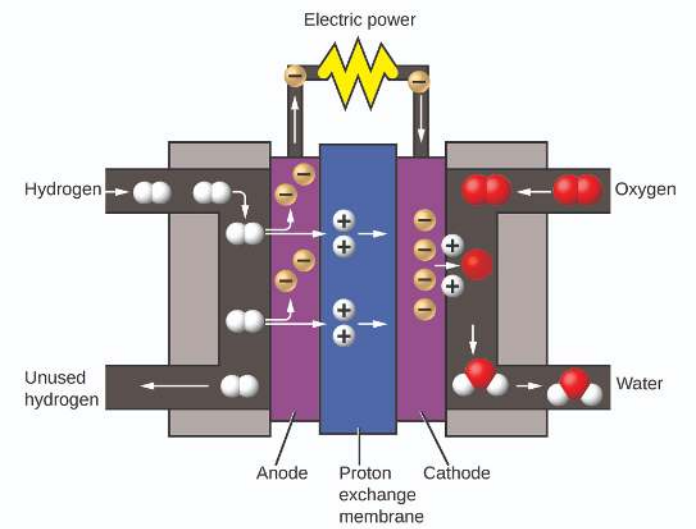


Figure 1.1.2.10: A fuel cell generates electrical energy from hydrogen and oxygen via an electrochemical process and produces only water as the waste product.

The fuel cell consists of a proton exchange membrane sandwiched between an anode and a cathode. Hydrogen gas enters the battery near the anode. Oxygen gas enters the battery near the cathode. The entering hydrogen gas is broken up into single white spheres that each have a positive charge. These are protons. The protons repel negatively-charged electrons within the anode. These electrons travel through a circuit, providing electricity to anything attached to the battery. The protons continue through the proton exchange membrane and through the cathode to reach the oxygen gas molecules at the opposite end of the battery. There, the oxygen atoms split up into single red spheres. Each oxygen atom takes on two of the incoming protons to form a water molecule.

1.1.2.4: Chemistry of Cell Phones

Imagine how different your life would be without cell phones (Figure 1.1.2.11) and other smart devices. Cell phones are made from numerous chemical substances, which are extracted, refined, purified, and assembled using an extensive and in-depth understanding of chemical principles. About 30% of the elements that are found in nature are found within a typical smart phone. The case/body/frame consists of a combination of sturdy, durable polymers comprised primarily of carbon, hydrogen, oxygen, and nitrogen [acrylonitrile butadiene styrene (ABS) and polycarbonate thermoplastics], and light, strong, structural metals, such as aluminum, magnesium, and iron. The display screen is made from a specially toughened glass (silica glass strengthened by the addition of aluminum, sodium, and potassium) and coated with a material to make it conductive (such as indium tin oxide). The circuit board uses a semiconductor material (usually silicon); commonly used metals like copper, tin, silver, and gold; and more unfamiliar elements such as yttrium, praseodymium, and gadolinium. The battery relies upon lithium ions and a variety of other materials, including iron, cobalt, copper, polyethylene oxide, and polyacrylonitrile.



Figure 1.1.2.11: Almost one-third of naturally occurring elements are used to make a modern cell phone. (credit: modification of work by John Taylor)

A cell phone is labeled to show what its components are made of. The case components are made of polymers such as A B S and or metals such as aluminum, iron, and magnesium. The processor components are made of silicon, common metals such as copper, tin and gold, and uncommon elements such as yttrium and gadolinium. The screen components are made of silicon oxide, also known as glass. The glass is strengthened by the addition of aluminum, sodium, and potassium. The battery components contain lithium combined with other metals such as cobalt, iron, and copper.

Summary

Matter is anything that occupies space and has mass. The basic building block of matter is the atom, the smallest unit of an element that can enter into combinations with atoms of the same or other elements. In many substances, atoms are combined into molecules. On earth, matter commonly exists in three states: solids, of fixed shape and volume; liquids, of variable shape but fixed volume; and gases, of variable shape and volume. Under high-temperature conditions, matter also can exist as a plasma. Most matter is a mixture: It is composed of two or more types of matter that can be present in varying amounts and can be separated by physical means. Heterogeneous mixtures vary in composition from point to point; homogeneous mixtures have the same composition from point to point. Pure substances consist of only one type of matter. A pure substance can be an element, which consists of only one type of atom and cannot be broken down by a chemical change, or a compound, which consists of two or more types of atoms.

Glossary

atom
: smallest particle of an element that can enter into a chemical combination

compound
: pure substance that can be decomposed into two or more elements

element
: substance that is composed of a single type of atom; a substance that cannot be decomposed by a chemical change

gas
: state in which matter has neither definite volume nor shape

heterogeneous mixture
: combination of substances with a composition that varies from point to point

homogeneous mixture
: (also, solution) combination of substances with a composition that is uniform throughout

liquid
: state of matter that has a definite volume but indefinite shape

law of conservation of matter
: when matter converts from one type to another or changes form, there is no detectable change in the total amount of matter present

mass
: fundamental property indicating amount of matter

matter
: anything that occupies space and has mass

mixture
: matter that can be separated into its components by physical means

molecule
: bonded collection of two or more atoms of the same or different elements

plasma
: gaseous state of matter containing a large number of electrically charged atoms and/or molecules

pure substance
: homogeneous substance that has a constant composition

solid

state of matter that is rigid, has a definite shape, and has a fairly constant volume

weight

force that gravity exerts on an object

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1.1.3: Physical and Chemical Properties

Learning Objectives

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

The characteristics that enable us to distinguish one substance from another are called properties. A physical property is a characteristic of matter that is not associated with a change in its chemical composition. Familiar examples of physical properties include density, color, hardness, melting and boiling points, and electrical conductivity. We can observe some physical properties, such as density and color, without changing the physical state of the matter observed. Other physical properties, such as the melting temperature of iron or the freezing temperature of water, can only be observed as matter undergoes a physical change. A physical change is a change in the state or properties of matter without any accompanying change in its chemical composition (the identities of the substances contained in the matter). We observe a physical change when wax melts, when sugar dissolves in coffee, and when steam condenses into liquid water (Figure 1.1.3.1). Other examples of physical changes include magnetizing and demagnetizing metals (as is done with common antitheft security tags) and grinding solids into powders (which can sometimes yield noticeable changes in color). In each of these examples, there is a change in the physical state, form, or properties of the substance, but no change in its chemical composition.



Figure 1.1.3.1: (a) Wax undergoes a physical change when solid wax is heated and forms liquid wax. (b) Steam condensing inside a cooking pot is a physical change, as water vapor is changed into liquid water. (credit a: modification of work by "95jb14"/Wikimedia Commons; credit b: modification of work by "mjneuby"/Flickr).

The change of one type of matter into another type (or the inability to change) is a chemical property. Examples of chemical properties include flammability, toxicity, acidity, reactivity (many types), and heat of combustion. Iron, for example, combines with oxygen in the presence of water to form rust; chromium does not oxidize (Figure 1.1.3.2). Nitroglycerin is very dangerous because it explodes easily; neon poses almost no hazard because it is very unreactive.

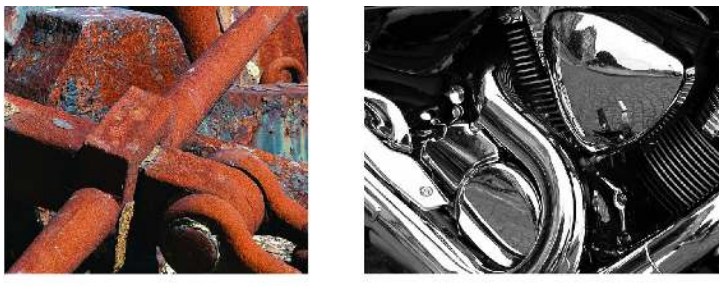


Figure 1.1.3.2: (a) One of the chemical properties of iron is that it rusts; (b) one of the chemical properties of chromium is that it does not. (credit a: modification of work by Tony Hisgett; credit b: modification of work by "Atoma"/Wikimedia Commons)

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

To identify a chemical property, we look for a chemical change. A chemical change always produces one or more types of matter that differ from the matter present before the change. The formation of rust is a chemical change because rust is a different kind of matter than the iron, oxygen, and water present before the rust formed. The explosion of nitroglycerin is a chemical change because the gases produced are very different kinds of matter from the original substance. Other examples of chemical changes include reactions that are performed in a lab (such as copper reacting with nitric acid), all forms of combustion (burning), and food being cooked, digested, or rotting (Figure 1.1.3.3).

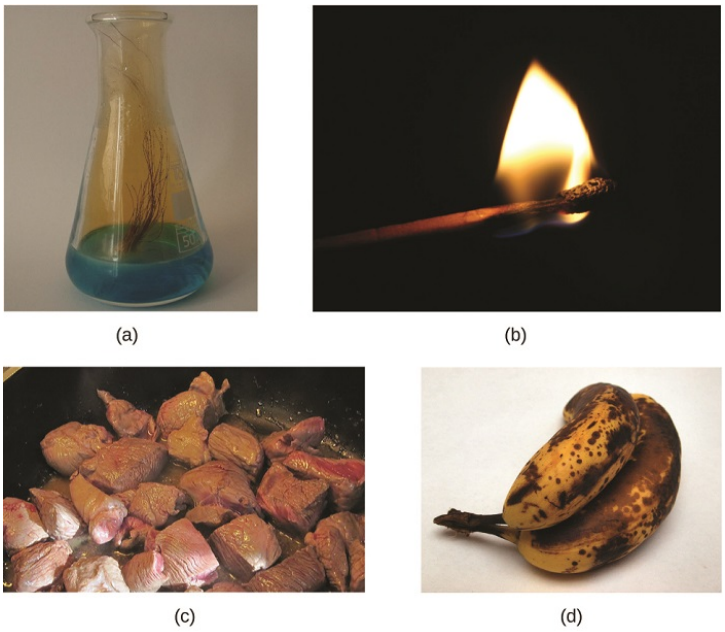


Figure 1.1.3.3: (a) Copper and nitric acid undergo a chemical change to form copper nitrate and brown, gaseous nitrogen dioxide. (b) During the combustion of a match, cellulose in the match and oxygen from the air undergo a chemical change to form carbon dioxide and water vapor. (c) Cooking red meat causes a number of chemical changes, including the oxidation of iron in myoglobin that results in the familiar red-to-brown color change. (d) A banana turning brown is a chemical change as new, darker (and less tasty) substances form. (credit b: modification of work by Jeff Turner; credit c: modification of work by Gloria Cabada-Leman; credit d: modification of work by Roberto Verzo)

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

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

1.1.3.1: Hazard Diamond

You may have seen the symbol shown in Figure 1.1.3.4on containers of chemicals in a laboratory or workplace. Sometimes called a “fire diamond” or “hazard diamond,” this chemical hazard diamond provides valuable information that briefly summarizes the various dangers of which to be aware when working with a particular substance.

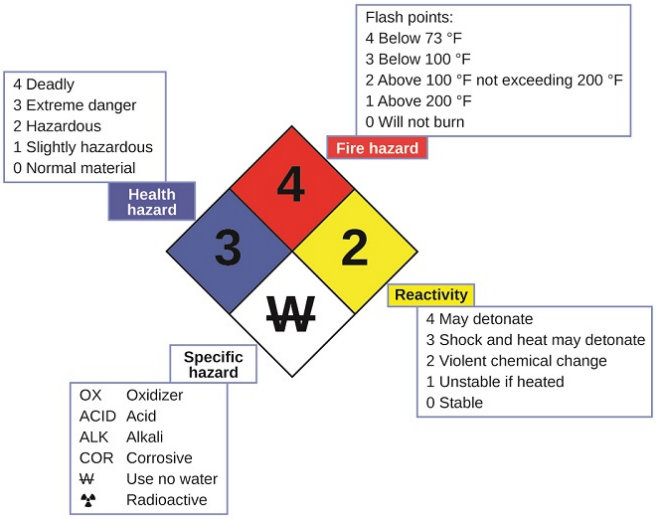


Figure 1.1.3.4: The National Fire Protection Agency (NFPA) hazard diamond summarizes the major hazards of a chemical substance.

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

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

The periodic table is a table of elements that places elements with similar properties close together (Figure 1.1.3.5). You will learn more about the periodic table as you continue your study of chemistry.

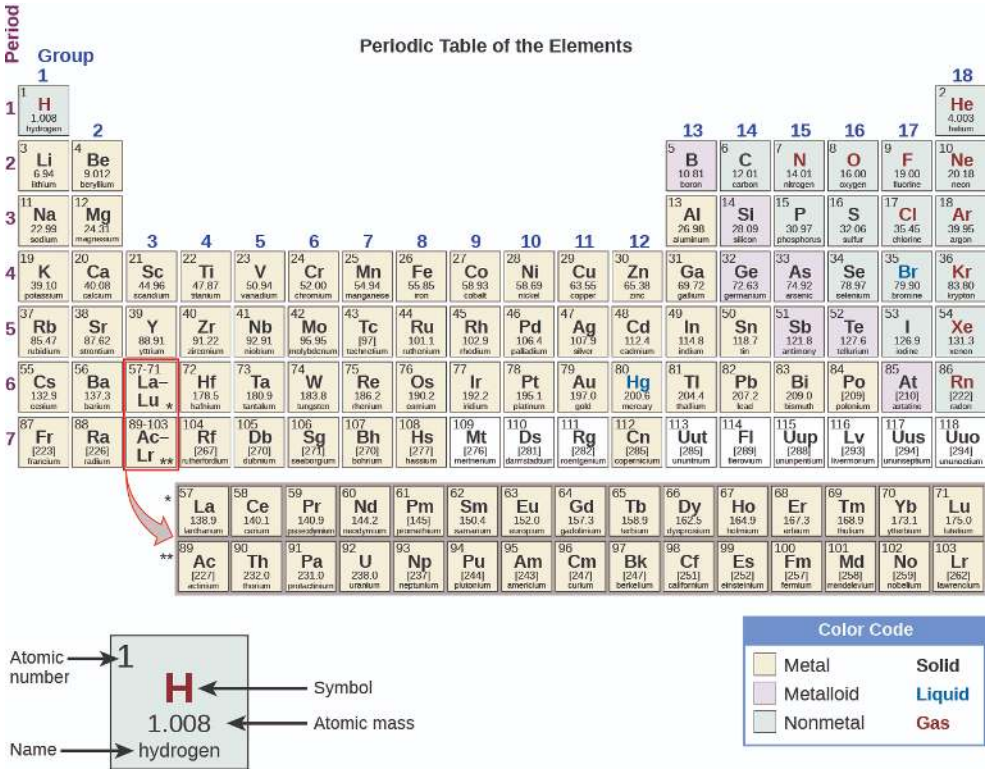


Figure 1.1.3.5: The periodic table shows how elements may be grouped according to certain similar properties. Note the background color denotes whether an element is a metal, metalloid, or nonmetal, whereas the element symbol color indicates whether it is a solid, liquid, or gas.

Summary

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

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

Glossary

chemical change

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

chemical property

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

extensive property

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

intensive property

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

physical change

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

physical property

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

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1.1.4: Measurements

Learning Objectives

- Explain the process of measurement and describe the three basic parts of a quantity.
- Describe the properties and units of length, mass, volume, density, temperature, and time.
- Recognize the common unit prefixes and use them to describe the magnitude of a measurement.
- Describe and calculate the density of a substance.
- Perform basic unit calculations and conversions in the metric and other unit systems.

Measurements provide the macroscopic information that is the basis of most of the hypotheses, theories, and laws that describe 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. 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, pounds, and centimeters, are standards of comparison for measurements. When we buy a 2-liter bottle of a soft drink, we expect that the volume of the drink was measured, so it is two times larger than the volume that everyone agrees to be 1 liter. The meat used to prepare a 0.25-pound hamburger is measured so it weighs one-fourth as much as 1 pound. 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.

We usually report the results of scientific measurements in SI units, an updated version of the metric system, using the units listed in Table 1.1.4.1. Other units can be derived from these base units. 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*). SI units have been used by the United States National Institute of Standards and Technology (NIST) since 1964.

Table 1.1.4.1: 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

Sometimes we use units that are fractions or multiples of a base unit. Ice cream is sold in quarts (a familiar, non-SI base unit), pints (0.5 quart), or gallons (4 quarts). We also use fractions or multiples of units in the SI system, 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 1.1.4.2

NG, equals 4 times ten to the negative 9, or 0.000000004 g. The prefix micro has the greek letter mu as its symbol and a factor of 10 to the negative sixth power. Therefore, 1 microliter, or mu L, is equal to one times ten to the negative 6 or 0.000001 L. The

prefix milli has a lowercase M as its symbol and a factor of 10 to the negative third power. Therefore, 2 millimoles, or M mol, are equal to two times ten to the negative 3 or 0.002 mol. The prefix centi has a lowercase C as its symbol and a factor of 10 to the negative second power. Therefore, 7 centimeters, or C M, are equal to seven times ten to the negative 2 meters or 0.07 M O L. The prefix deci has a lowercase D as its symbol and a factor of 10 to the negative first power. Therefore, 1 deciliter, or lowercase D uppercase L, are equal to one times ten to the negative 1 meters or 0.1 L. The prefix kilo has a lowercase K as its symbol and a factor of 10 to the third power. Therefore, 1 kilometer, or K M, is equal to one times ten to the third meters or 1000 M. The prefix mega has an uppercase M as its symbol and a factor of 10 to the sixth power. Therefore, 3 megahertz, or M H Z, are equal to three times 10 to the sixth hertz, or 3000000 H Z. The prefix giga has an uppercase G as its symbol and a factor of 10 to the ninth power. Therefore, 8 gigayears, or G Y R, are equal to eight times 10 to the ninth years, or 800000000 G Y R. The prefix tera has an uppercase T as its symbol and a factor of 10 to the twelfth power. Therefore, 5 terawatts, or T W, are equal to five times 10 to the twelfth watts, or 5000000000000 W." data-quail-id="64" data-mt-width="1076">

Table 1.1.4.2: 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 Gyr)
tera	T	10^{12}	5 terawatts (TW) = 5×10^{12} W (5,000,000,000,000 W)

1.1.4.1: SI Base Units

The initial units of the metric system, which eventually evolved into the SI system, were established in France during the French Revolution. The original standards for the meter and the kilogram were adopted there in 1799 and eventually by other countries. This section introduces four of the SI base units commonly used in chemistry. Other SI units will be introduced in subsequent chapters.

1.1.4.1.1: 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 1.1.4.1); 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).

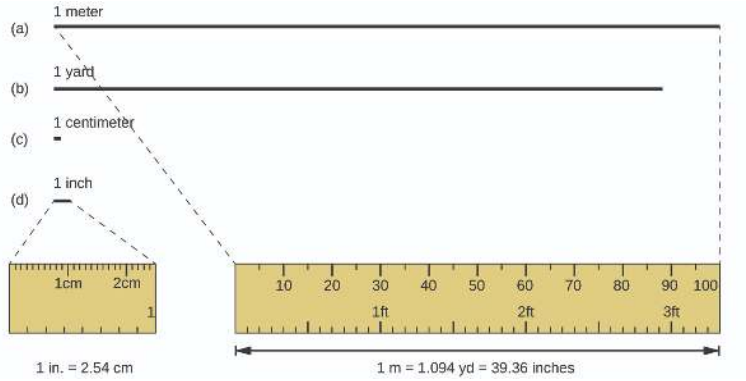


Figure 1.1.4.1: The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd.

A ruler is shown with various lengths of black line shown above it to compare the relative lengths of 1 inch, meter, centimeter, and yard.

1.1.4.1.2: Mass

The standard unit of mass in the SI system is the kilogram (kg). A kilogram was originally defined as the mass of a liter of water (a cube of water with an edge length of exactly 0.1 meter). It is now defined by a certain cylinder of platinum-iridium alloy, which is kept in France (Figure 1.4.2). Any object with the same mass as this cylinder is said to have a mass of 1 kilogram. 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 1.1.4.2: This replica prototype kilogram is housed at the National Institute of Standards and Technology (NIST) in Maryland. (credit: National Institutes of Standards and Technology).

1.1.4.1.3: 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.

1.1.4.1.4: 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.

1.1.4.2: 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.

1.1.4.2.1: 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 1.1.4.3). 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.

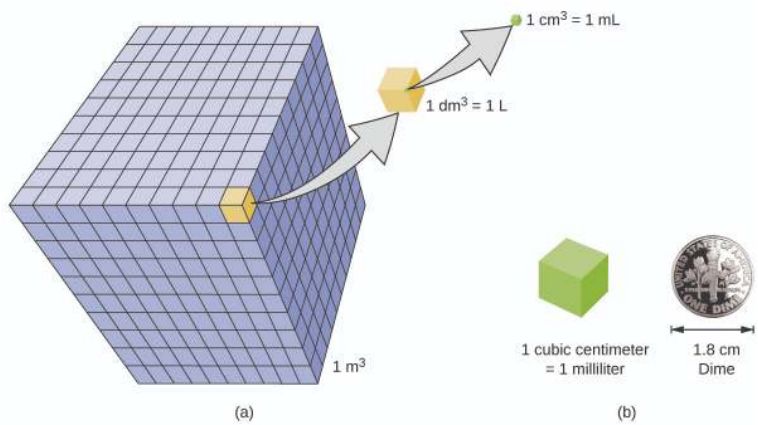


Figure 1.1.4.3: (a) The relative volumes are shown for cubes of 1 m^3, 1 dm^3 (1 L), and 1 cm^3 (1 mL) (not to scale). (b) The diameter of a dime is compared relative to the edge length of a 1-cm^3 (1-mL) cube.

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 1.06 quarts. A cubic centimeter (cm^3) is the volume of a cube with an edge length of exactly one centimeter. The abbreviation **cc** (for **c**ubic **c**entimeter) is often used by health professionals. A cubic centimeter is also called a milliliter (mL) and is 1/1000 of a liter.

1.1.4.2.2: 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 1.1.4.3shows the densities of some common substances.

Table 1.1.4.3: Densities of Common Substances

Solids	Liquids	Gases (at 25 °C and 1 atm)
ice (at 0 °C) 0.92 g/cm^3	water 1.0 g/cm^3	dry air 1.20 g/L
oak (wood) 0.60–0.90 g/cm^3	ethanol 0.79 g/cm^3	oxygen 1.31 g/L
iron 7.9 g/cm^3	acetone 0.79 g/cm^3	nitrogen 1.14 g/L
copper 9.0 g/cm^3	glycerin 1.26 g/cm^3	carbon dioxide 1.80 g/L
lead 11.3 g/cm^3	olive oil 0.92 g/cm^3	helium 0.16 g/L
silver 10.5 g/cm^3	gasoline 0.70–0.77 g/cm^3	neon 0.83 g/L
gold 19.3 g/cm^3	mercury 13.6 g/cm^3	radon 9.1 g/L

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.

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

Example 1.1.4.1

Calculation of Density Gold—in bricks, bars, and coins—has been a form of currency for centuries. In order to swindle 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.

$$\text{volume of lead cube} = 2.00\ \text{cm} \times 2.00\ \text{cm} \times 2.00\ \text{cm} = 8.00\ \text{cm}^3$$

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{90.7\ \text{g}}{8.00\ \text{cm}^3} = \frac{11.3\ \text{g}}{1.00\ \text{cm}^3} = 11.3\ \text{g/cm}^3$$

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

Exercise 1.1.4.1

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?

Answer a

0.599 cm^3;

Answer b

8.91 g/cm^3

Example 1.1.4.2: Using Displacement of Water to Determine Density

This PhET simulation illustrates another way to determine density, using displacement of water. Determine the density of the red and yellow blocks.

Solution

When you open the density simulation and select Same Mass, you can choose from several 5.00-kg colored blocks that you can drop into a tank containing 100.00 L water. The yellow block floats (it is less dense than water), and the water level rises to 105.00 L. While floating, the yellow block displaces 5.00 L water, an amount equal to the weight of the block. The red block sinks (it is more dense than water, which has density = 1.00 kg/L), and the water level rises to 101.25 L.

The red block therefore displaces 1.25 L water, an amount equal to the volume of the block. The density of the red block is:

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{5.00\ \text{kg}}{1.25\ \text{L}} = 4.00\ \text{kg/L}$$

Note that since the yellow block is not completely submerged, you cannot determine its density from this information. But if you hold the yellow block on the bottom of the tank, the water level rises to 110.00 L, which means that it now displaces 10.00 L water, and its density can be found:

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{5.00\ \text{kg}}{10.00\ \text{L}} = 0.500\ \text{kg/L}$$

? Exercise 1.1.4.1

Remove all of the blocks from the water and add the green block to the tank of water, placing it approximately in the middle of the tank. Determine the density of the green block.

Answer

2.00 kg/L

Summary

Measurements provide quantitative information that is critical in studying and practicing chemistry. Each measurement has an amount, a unit for comparison, and an uncertainty. Measurements can be represented in either decimal or scientific notation. Scientists primarily use the SI (International System) or metric systems. We use base SI units such as meters, seconds, and kilograms, as well as derived units, such as liters (for volume) and g/cm^3 (for density). In many cases, we find it convenient to use unit prefixes that yield fractional and multiple units, such as microseconds (10^{-6} seconds) and megahertz (10^6 hertz), respectively.

1.1.4.3: Key Equations

- $\text{density} = \dfrac{\text{mass}}{\text{volume}}$

Glossary

Celsius (°C)
unit of temperature; water freezes at 0 °C and boils at 100 °C on this scale

cubic centimeter (cm^3 or cc)
volume of a cube with an edge length of exactly 1 cm

cubic meter (m^3)
SI unit of volume

density
ratio of mass to volume for a substance or object

kelvin (K)
SI unit of temperature; 273.15 K = 0 ºC

kilogram (kg)
standard SI unit of mass; 1 kg = approximately 2.2 pounds

length
measure of one dimension of an object

liter (L)
(also, cubic decimeter) unit of volume; 1 L = 1,000 cm^3

meter (m)
standard metric and SI unit of length; 1 m = approximately 1.094 yards

milliliter (mL)
1/1,000 of a liter; equal to 1 cm^3

second (s)
SI unit of time

SI units (International System of Units)

standards fixed by international agreement in the International System of Units (*Le Système International d'Unités*)

unit

standard of comparison for measurements

volume

amount of space occupied by an object

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1.1.5: Measurement Uncertainty, Accuracy, and Precision

Learning Objectives

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

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

1.1.5.1: 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.

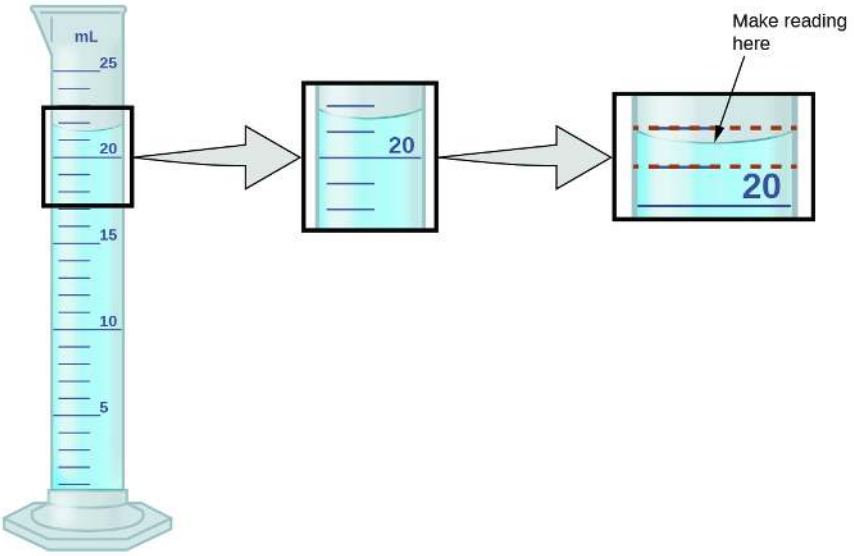


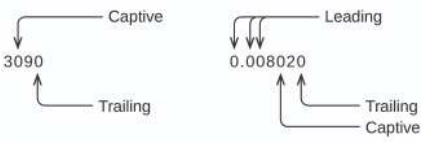
Figure 1.1.5.1: To measure the volume of liquid in this graduated cylinder, you must mentally subdivide the distance between the 21 and 22 mL marks into tenths of a milliliter, and then make a reading (estimate) at the bottom of the meniscus.

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

Refer to the illustration in Figure 1.1.5.1 The bottom of the meniscus in this case clearly lies between the 21 and 22 markings, meaning the liquid volume is *certainly* greater than 21 mL but less than 22 mL. The meniscus appears to be a bit closer to the 22-mL mark than to the 21-mL mark, and so a reasonable estimate of the liquid's volume would be 21.6 mL. In the number 21.6, then, the digits 2 and 1 are certain, but the 6 is an estimate. Some people might estimate the meniscus position to be equally distant from each of the markings and estimate the tenth-place digit as 5, while others may think it to be even closer to the 22-mL mark and estimate this digit to be 7. Note that it would be pointless to attempt to estimate a digit for the hundredths place, given that the tenths-place digit is uncertain. In general, numerical scales such as the one on this graduated cylinder will permit measurements to one-tenth of the smallest scale division. The scale in this case has 1-mL divisions, and so volumes may be measured to the nearest 0.1 mL.

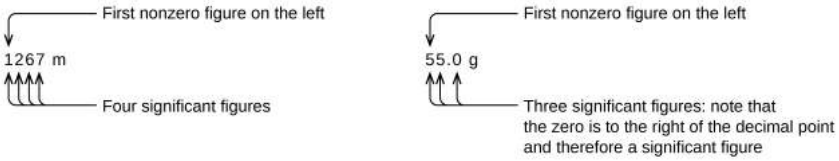
This concept holds true for all measurements, even if you do not actively make an estimate. If you place a quarter on a standard electronic balance, you may obtain a reading of 6.72 g. The digits 6 and 7 are certain, and the 2 indicates that the mass of the quarter is likely between 6.71 and 6.73 grams.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

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



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

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



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

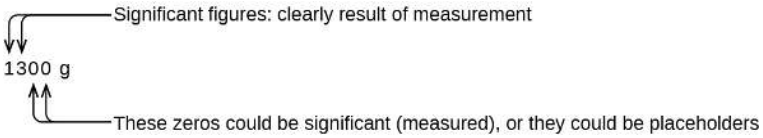
Captive zeros result from measurement and are therefore always significant. Leading zeros, however, are never significant—they merely tell us where the decimal point is located.



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

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

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



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

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

1.1.5.2: 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. We must take the uncertainty in our measurements into account to avoid misrepresenting the uncertainty in calculated results. One way to do this is to report the result of a calculation with the correct number of significant figures, which is determined by the following three rules for rounding numbers:

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

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

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

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

Example 1.1.5.1: Rounding Numbers

Round the following to the indicated number of significant figures:

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

Solution

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

Exercise 1.1.5.1

Round the following to the indicated number of significant figures:

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

Answer a

0.42

Answer b

0.00387

Answer c

421.2

Answer d

28,684

Example 1.1.5.2: Addition and Subtraction with Significant Figures Rule:

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

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

Solution

(a)

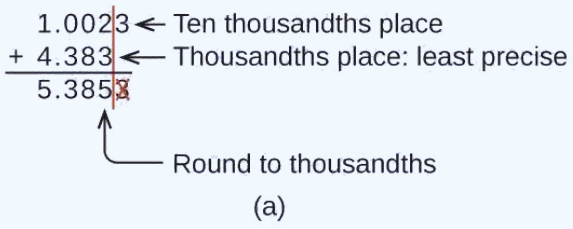
$$\begin{array}{r} 1.0023\ \text{g} \\ +\ 4.383\ \text{g} \\ \hline 5.3853\ \text{g} \end{array}$$

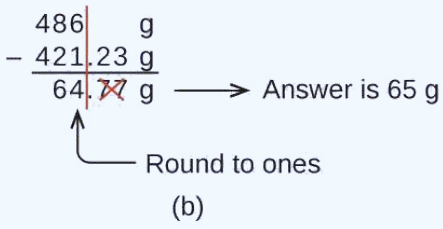
Answer is 5.385 g (round to the thousandths place; three decimal places)

(b)

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

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





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Exercise 1.1.5.2

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

Answer a

2.64 mL

Answer b

0.658 m

Example 1.1.5.3: Multiplication and Division with Significant Figures

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

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

Solution

(a)

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

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

(b)

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

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

Exercise 1.1.5.3

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

Answer a

0.747 cm^2

Answer b

0.9884 m/s

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

Example 1.1.5.4: Calculation with Significant Figures

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

Solution

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

Exercise 1.1.5.4: Determination of Density Using Water Displacement

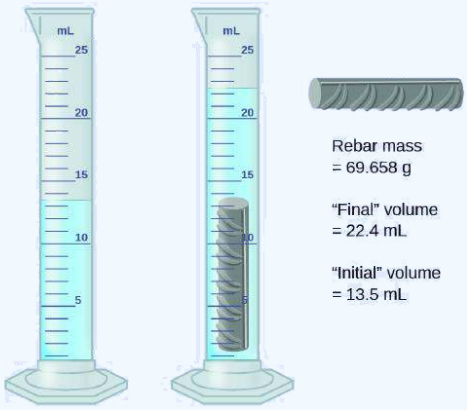
What is the density of a liquid with a mass of 31.1415 g and a volume of 30.13 cm^3?

Answer

1.034 g/mL

Example 1.1.5.4

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



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

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

Solution

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

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

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

The density is the mass-to-volume ratio:

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

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

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

Exercise 1.1.5.4

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



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

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

Answer a

19 g/cm^3

Answer b

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

1.1.5.3: Accuracy and Precision

Scientists typically make repeated measurements of a quantity to ensure the quality of their findings and to know both the precision and the accuracy of their results. Measurements are said to be precise if they yield very similar results when repeated in the same manner. A measurement is considered accurate if it yields a result that is very close to the true or accepted value. Precise values agree with each other; accurate values agree with a true value. These characterizations can be extended to other contexts, such as the results of an archery competition (Figure 1.1.5.2).

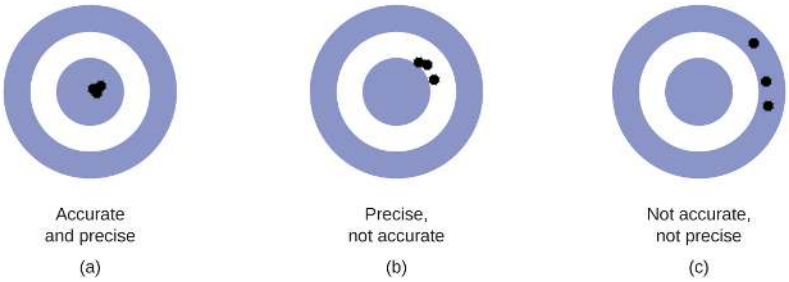


Figure 1.1.5.2: (a) These arrows are close to both the bull's eye and one another, so they are both accurate and precise. (b) These arrows are close to one another but not on target, so they are precise but not accurate. (c) These arrows are neither on target nor close to one another, so they are neither accurate nor precise.

Suppose a quality control chemist at a pharmaceutical company is tasked with checking the accuracy and precision of three different machines that are meant to dispense 10 ounces (296 mL) of cough syrup into storage bottles. She proceeds to use each machine to fill five bottles and then carefully determines the actual volume dispensed, obtaining the results tabulated in Table 1.1.5.2

Table 1.1.5.2: Volume (mL) of Cough Medicine Delivered by 10-oz (296 mL) Dispensers

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

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

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

Summary

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

Glossary

uncertainty
: estimate of amount by which measurement differs from true value

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

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

precision
: how closely a measurement matches the same measurement when repeated

exact number
: number derived by counting or by definition

accuracy
: how closely a measurement aligns with a correct value

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1.1.6: Mathematical Treatment of Measurement Results

Learning Objectives

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

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

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

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

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

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

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

The time can then be computed as:

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

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

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

1.1.6.1: Conversion Factors and Dimensional Analysis

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

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

Several other commonly used conversion factors are given in Table 1.1.6.1.

Table 1.1.6.1: Common Conversion Factors

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

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

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

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

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

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

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

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

Example 1.1.6.1: Using a Unit Conversion Factor

The mass of a competition Frisbee is 125 g. Convert its mass to ounces using the unit conversion factor derived from the relationship 1 oz = 28.349 g (Table 1.1.6.1).

Solution

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

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

We write the unit conversion factor in its two forms:

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

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

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

? Exercise 1.1.6.1

Convert a volume of 9.345 qt to liters.

Answer

8.844 L

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

✓ Example 1.1.6.2: Computing Quantities from Measurement Results

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

Solution

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

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

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

1. *Convert quarts to liters.*

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

2. *Convert liters to milliliters.*

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

Then,

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

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

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

? Exercise 1.1.6.2

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

Answer

2.956×10^{-2} L

✓ Example 1.1.6.3: Computing Quantities from Measurement Results

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

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

Solution

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

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

and then convert volume from liters to gallons:

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

Then,

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

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

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

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

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

? Exercise 1.1.6.3

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

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

Answer a

51 mpg

Answer b

$62

1.1.6.2: Conversion of Temperature Units

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

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

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

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

where

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

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

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

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

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

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

The equation relating the temperature scales is then:

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

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

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

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

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

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

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

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

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

The 273.15 in these equations has been determined experimentally, so it is not exact. Figure 1.1.6.1 shows the relationship among the three temperature scales. Recall that we do not use the degree sign with temperatures on the kelvin scale.

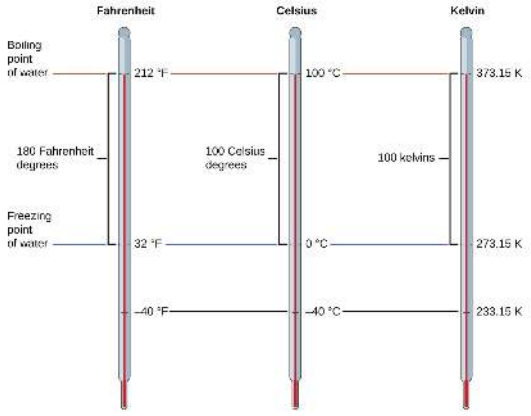


Figure 1.1.6.1: The Fahrenheit, Celsius, and kelvin temperature scales are compared.

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

Example 1.1.6.4: Conversion from Celsius

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

Solution

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

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

Exercise 1.1.6.4

Convert 80.92 °C to K and °F.

Answer

354.07 K, 177.7 °F

Example 1.1.6.5: Conversion from Fahrenheit

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

Solution

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

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

Exercise 1.1.6.5

Convert 50 °F to °C and K.

Answer

10 °C, 280 K

Summary

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

1.1.6.3: Key Equations

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

Glossary

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

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

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

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1.1.7: How to Solve Chemistry Problems

In CHEM 1510 and 1520 we spend a lot of time solving qualitative and quantitative problems in chemistry. It is helpful to have a consistent approach to solving problems.

1. Read the question carefully and highlight what information you are given and what information you are asked to find.
2. Make a list of what information you have and identify which items you need to use. Make a list of what you need to find.
3. If this is a quantitative problem look carefully at the units of the information you have and the units of what you need to find. The units will tell you what to do!
4. Plan your approach to solve the problem. Make a prediction about the answer using your chemistry knowledge.
5. Identify the equation or concept you need to use to solve the problem. If this is a quantitative problem perform any unit conversions needed.
6. Solve the problem. If this is a quantitative problem make sure you follow significant figures through the problem and express final answer with correct significant figures and units.
7. Check your answer. Compare your result with your prediction and ask yourself if it makes chemical sense.

What do I **KNOW**?

What do I **WANT**?

HOW can I solve for it?

PREDICT?

SOLVE the problem!

CHECK your answer!

Example 1.1.7.1

An aqueous solution has a density of 1.15 g/cm^3. How much would 32.00 mL of this solution weigh in mg?

Solution

What do I **KNOW**? Given: density solution 1.15 g/cm^3; volume solution 32.00 mL

What do I **WANT**? Need to find: mass in mg

HOW can I solve for it? Look at units and plan:

volume in mL, need density to have same units then can solve for mass in g, and convert to mg

equation to use: $\text{density} = \frac{\text{mass}}{\text{volume}}$ $\quad \text{d} = \frac{\text{m}}{\text{V}}$

Prediction: mass will be over 32 g (and less than 40g) since density just over 1

Solve:

convert density to g/mL

recall - conversion factors have infinite sig figs

$1.15 \frac{g}{cm^3} x \frac{1 cm^3}{1 mL}$ = 1.15 g/mL

calculate mass in grams

$1.15 \frac{g}{mL} x (32.00 mL)$= 36.8 g

convert mass to mg

$$36.8g(\frac{1000mg}{1g}) = 36800mg$$

express with correct significant figures and units

Need 3 sig figs in final answer since density given with 3 sig figs and multiplying & dividing, so use scienfitic notation

$36800mg = 3.68x10^4mg$

Check - does it make chemical sense? **Yes**, 36.8 g > 32 g which makes sense based on the density value given.

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1.1.E: Essential Ideas of Chemistry (Exercises)

1.1.E.1: Chemistry in Context

Exercise 1.1.E.1

Explain how you could experimentally determine whether the outside temperature is higher or lower than 0 °C (32 °F) without using a thermometer.

Answer

Place a glass of water outside. It will freeze if the temperature is below 0 °C.

Exercise 1.1.E.2

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.

Answer

(a) law (states a consistently observed phenomenon, can be used for prediction); (b) theory (a widely accepted explanation of the behavior of matter); (c) hypothesis (a tentative explanation, can be investigated by experimentation).

Exercise 1.1.E.3

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. A certain molecule contains one H atom and one Cl atom.

b. Copper wire has a density of about 8 g/cm^3.

c. The bottle contains 15 grams of Ni powder.

d. A sulfur molecule is composed of eight sulfur atoms.

Answer

(a) symbolic, microscopic; (b) macroscopic; (c) symbolic, macroscopic; (d) microscopic.

Exercise 1.1.E.4

The amount of heat required to melt 2 lbs of ice is twice the amount of heat required to melt 1 lb of ice. Is this observation a macroscopic or microscopic description of chemical behavior? Explain your answer.

Answer

Macroscopic. The heat required is determined from macroscopic properties.

1.1.E.2: Phases and Classification of Matter

Exercise 1.1.E.5

What properties distinguish solids from liquids? Liquids from gases? Solids from gases?

Answer

Liquids can change their shape (flow); solids can't. Gases can undergo large volume changes as pressure changes; liquids do not. Gases flow and change volume; solids do not.

Exercise 1.1.E.6a

How does a homogeneous mixture differ from a pure substance? How are they similar?

Answer

The mixture can have a variety of compositions; a pure substance has a definite composition. Both have the same composition from point to point.

Exercise 1.1.E.6b

How does a heterogeneous mixture differ from a homogeneous mixture? How are they similar?

Answer

A heterogeneous mixture has different composition at different points. A homogeneous mixture has constant composition throughout.

Exercise 1.1.E.7

How do molecules of elements and molecules of compounds differ? In what ways are they similar?

Answer

Molecules of elements contain only one type of atom; molecules of compounds contain two or more types of atoms. They are similar in that both are comprised of two or more atoms chemically bonded together.

Exercise 1.1.E.8

Many of the items you purchase are mixtures of pure compounds. Select a commercial product and prepare a list of the ingredients that are pure compounds.

Answer

You answers will vary depending on what commercial product you chose. Sample answer: Gatorade is a mixture. It contains water, sugar, dextrose, citric acid, salt, sodium chloride, monopotassium phosphate, and sucrose acetate isobutyrate.

Exercise 1.1.E.9

1. Classify each of the following as an element, a compound, or a mixture:
   a. iron
   b. oxygen
   c. mercury oxide
   d. pancake syrup
   e. carbon dioxide
   f. a substance composed of molecules each of which contains one hydrogen atom and one chlorine atom

g. baking soda
h. baking powder

Answer

(a) element; (b) element; (c) compound; (d) mixture, (e) compound; (f) compound; (g) compound; (h) mixture.

Exercise 1.1.E.10

How are the molecules in oxygen gas, the molecules in hydrogen gas, and water molecules similar? How do they differ?

Answer

In each case, a molecule consists of two or more combined atoms. They differ in that the types of atoms change from one substance to the next.

Exercise 1.1.E.11

When elemental iron corrodes it combines with oxygen in the air to ultimately form red brown iron(III) oxide which we call 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?

Answer

(a) Increased as it would have combined with oxygen in the air thus increasing the amount of matter and therefore the mass.
(b) 0.900 g

Exercise 1.1.E.12

1. Yeast converts glucose to ethanol and carbon dioxide during anaerobic fermentation as depicted in the simple chemical equation here:

$$\text{glucose} \rightarrow \text{ethanol} + \text{carbon dioxide} \tag{1.1.E.1}$$

   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?

Answer

(a) 200.0 g; (b) The mass of the container and contents would decrease as carbon dioxide is a gaseous product and would leave the container. (c) 102.3 g.

1.1.E.3: Physical and Chemical Properties

Exercise 1.1.E.13

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

Answer

(a) physical; (b) chemical; (c) chemical; (d) physical; (e) physical.

Exercise 1.1.E.14

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?

Answer

physical

Exercise 1.1.E.15

Explain the difference between extensive properties and intensive properties.

Answer

The value of an extensive property depends upon the amount of matter being considered, whereas the value of an intensive property is the same regardless of the amount of matter being considered.

Exercise 1.1.E.16

The density (d) of a substance is an intensive property that is defined as the ratio of its mass (m) to its volume (V).

$$\text{density} = \frac{\text{mass}}{\text{volume}} \quad \text{d} = \frac{\text{m}}{\text{V}}$$

Considering that mass and volume are both extensive properties, explain why their ratio, density, is intensive.

Answer

Being extensive properties, both mass and volume are directly proportional to the amount of substance under study. Dividing one extensive property by another will in effect “cancel” this dependence on amount, yielding a ratio that is independent of amount (an intensive property).

1.1.E.4: 1.4: Measurements

Exercise 1.1.E.17

Indicate the SI base units or derived units that are appropriate for the following measurements:

a. the mass of the moon

b. the distance from Vancouver to Toronto

c. the speed of sound

d. the density of air

e. the temperature at which alcohol boils

f. the area of the province of BC

g. the volume of a COVID-19 vaccine

Answer

(a) kilograms; (b) meters; (c) kilometers/second; (d) kilograms/cubic meter; (e) kelvin; (f) square meters; (g) cubic meters

Exercise 1.1.E.18

Give the name of the prefix and the quantity indicated by the following symbols that are used with SI base units.

1. (a) c
2. (b) d
3. (c) G
4. (d) k
5. (e) m
6. (f) n
7. (g) p
8. (h) T

Answer

(a) centi-, $\times 10^{-2}$; (b) deci-, $\times 10^{-1}$; (c) Giga-, $\times 10^{9}$; (d) kilo-, $\times 10^{3}$; (e) milli-, $\times 10^{-3}$; (f) nano-, $\times 10^{-9}$; (g) pico-, $\times 10^{-12}$; (h) tera-, $\times 10^{12}$

Exercise 1.1.E.19

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.

Answer

10.5 g/mL

Pure silver has a density of 10.5 g/mL, so it is a likely substance that the jewelry is made of.

1.1.E.5: Measurement Uncertainty, Accuracy, and Precision

Exercise 1.1.E.20

Express each of the following numbers in exponential notation with correct significant figures:

1. (a) 704
2. (b) 0.03344
3. (c) 547.9
4. (d) 22086
5. (e) 1000.00
6. (f) 0.0000000651
7. (g) 0.007157

Answer

Exercise 1.1.E.21

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

(a) the number of seconds in an hour

(b) the number of pages in this book

(c) the number of grams in your weight

(d) the number of grams in 3 kilograms

(e) the volume of water you drink in one day

(f) the distance from Vancouver to Calgary

Answer

(a) exact; (b) exact; (c) uncertain; (d) exact; (e) uncertain; (f) uncertain

Exercise 1.1.E.22

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

(a) 53 cm

(b) 2.05×10^8 m

(c) 86,002 J

(d) 9.740×10^4 m/s

(e) 10.0613 m^3

(f) 0.17 g/mL

(g) 0.88400 s

Answer

(a) two; (b) three; (c) five; (d) four; (e) six; (f) two; (g) five

Exercise 1.1.E.23

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

Answer

(a) 0.44; (b) 9.0; (c) 27; (d) 140; (e) 1.5×10^{-3}; (f) 0.44

Exercise 1.1.E.24

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) $\dfrac{28.0}{13.483}$

(d) 8119×0.000023

(e) 14.98 + 27,340 + 84.7593

(f) 42.7 + 0.259

Answer

(a) 2.15×10^5; (b) 4.2×10^6; (c) 2.08; (d) 0.19; (e) 27,440; (f) 43.0

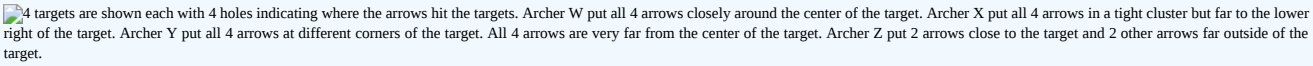
Exercise 1.1.E. 25

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?


4 targets are shown each with 4 holes indicating where the arrows hit the targets. Archer W put all 4 arrows closely around the center of the target. Archer X put all 4 arrows in a tight cluster but far to the lower right of the target. Archer Y put all 4 arrows at different corners of the target. All 4 arrows are very far from the center of the target. Archer Z put 2 arrows close to the target and 2 other arrows far outside of the target.

Answer

(a) Archer X; (b) Archer W; (c) Archer Y

1.1.E.6: Mathematical Treatment of Measurement Results

Exercise 1.1.E. 26

Write conversion factors (as ratios) for the number of:

a. yards in 1 meter
b. liters in 1 liquid quart
c. pounds in 1 kilogram

Answer

(a) $\frac{1.0936\ \text{yd}}{1\ \text{m}}$; (b) $\frac{0.94635\ \text{L}}{1\ \text{qt}}$; (c) $\frac{2.2046\ \text{lb}}{1\ \text{kg}}$

Exercise 1.1.E. 27

Soccer is played with a round ball having a circumference between 27 and 28 in. and a weight between 14 and 16 oz. What are these specifications in units of centimeters and grams?

Answer

68–71 cm; 400–450 g

Exercise 1.1.E. 28

How many milliliters of a soft drink are contained in a 12.0-oz can?

Answer

355 mL

Exercise 1.1.E. 29

Many medical laboratory tests are run using 5.0 μL blood serum. What is this volume in milliliters?

Answer

5.0×10^{-3} mL

Exercise 1.1.E.30

Use scientific (exponential) notation to express the following quantities in terms of the SI base units in [link]:

(a) 0.13 g

(b) 232 Gg

(c) 5.23 pm

(d) 86.3 mg

(e) 37.6 cm

(f) 54 µm

(g) 1 Ts

(h) 27 ps

(i) 0.15 mK

Answer

(a) 1.3×10^{-4} kg; (b) 2.32×10^{8} kg; (c) 5.23×10^{-12} m; (d) 8.63×10^{-5} kg; (e) 3.76×10^{-1} m; (f) 5.4×10^{-5} m; (g) 1×10^{12} s; (h) 2.7×10^{-11} s; (i) 1.5×10^{-4} K

Exercise 1.1.E.31

Make the conversion indicated in each of the following:

(a) the length of a soccer field, 120 m (three significant figures), to feet

(b) the height of Mt. Kilimanjaro, at 19,565 ft the highest mountain in Africa, to kilometers

(c) the area of an 8.5 t 11-inch sheet of paper in cm^2

(d) the displacement volume of an automobile engine, 161 $in.^3$, to liters

(e) the estimated mass of the atmosphere, 5.6 t 10^{15} tons, to kilograms

(f) the mass of a bushel of rye, 32.0 lb, to kilograms

(g) the mass of a 5.00-grain aspirin tablet to milligrams (1 grain = 0.00229 oz)

Answer

(a) 394 ft
(b) 5.9634 km
(c) 6.0×10^{2}
(d) 2.64 L
(e) 5.1×10^{18} kg
(f) 14.5 kg
(g) 324 mg

Exercise 1.1.E.32

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?

Answer

Yes, the acid's volume is 123 mL.

Exercise 1.1.E.33

Calculate the density of aluminum if 27.6 cm^3 has a mass of 74.6 g.

Answer

2.70 g/cm^3

Exercise 1.1.E.34

Calculate these masses.

(a) What is the mass of 6.00 cm^3 of mercury, density = 13.5939 g/cm^3?

(b) What is the mass of 25.0 mL octane, density = 0.702 g/cm^3?

Answer

(a) 81.6 g; (b) 17.6 g

Exercise 1.1.E.35

Calculate these volumes.

(a) What is the volume of 25 g iodine, density = 4.93 g/cm^3?

(b) What is the volume of 3.28 g gaseous hydrogen, density = 0.089 g/L?

Answer

(a) 5.1 mL; (b) 37 L

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1.1.S: Essential ideas of Chemistry (Study Guide)

1.1: The Study of Chemistry

An understanding of chemistry is essential for understanding much of the natural world and is central to many other disciplines. Chemistry is the study of matter and the changes material substances undergo. It is essential for understanding much of the natural world and central to many other scientific disciplines, including astronomy, geology, paleontology, biology, and medicine.

The Molecular Perspective of Chemistry

- **Matter** – physical material of the universe, has mass and takes up space
- **Atoms** – the building blocks of matter
- **Molecules** – groups of combined atoms

Why Study Chemistry?

- important in understanding our world
- chemistry is the central science
- many various subjects have some kind of relation to chemistry

1.2: Classification of Matter

Matter can be classified according to physical and chemical properties. Matter is anything that occupies space and has mass. The three states of matter are solid, liquid, and gas. A physical change involves the conversion of a substance from one state of matter to another, without changing its chemical composition. Most matter consists of mixtures of pure substances, which can be homogeneous (uniform in composition) or heterogeneous (different regions possess different compositions & properties.

States of Matter

- states of matter: liquid, solid, and gas

Pure Substances and Mixtures

- **pure substance** – matter that has a fixed composition and distinct properties
- substances can be classified as **elements** or **compounds**
- **elements** – composed of only one atom
- **compounds** – two ore more elements
- **mixtures** – combination of two or more substances
- **heterogeneous** – mixtures that are not uniform throughout
- **homogeneous** – mixtures that are uniform throughout; also called solutions

Separation of Mixtures

- components in a mixture retain their own properties
- mixtures can be separated by using the different properties of each substance
- types of separation: filtration, distillation, chromatography

Elements

- over 90% of earth’s crust consists of oxygen, silicon, aluminum, iron, and calcium
- human body consists of 90% of oxygen, carbon, and hydrogen

Compounds

- **law of constant composition (law of definite proportions)** – elemental composition of a pure compound is always the same

1.3: Properties of Matter

All matter has physical and chemical properties. Physical properties are characteristics that scientists can measure without changing the composition of the sample under study, such as mass, color, and volume (the amount of space occupied by a sample). Chemical properties describe the characteristic ability of a substance to react to form new substances; they include its flammability and susceptibility to corrosion.

- **physical properties** – properties measured by not changing the identity and composition of the substance
- **chemical properties** – the way a substance may change or react to form other substances
- **intensive properties** – identify substances
- **extensive properties** – amount of substance

Physical and Chemical Changes

- physical change results in a change in appearance but not composition
- changes of state are physical changes
- chemical changes (chemical reactions) results in a chemically different substance

1.4: Units of Measurement

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

SI Units

- seven base units

SI Units

Prefix	Abbreviation	Meaning
Mega-	M	10^{6}
Kilo-	K	10^{3}
Deci-	D	10^{-1}
Centi-	C	10^{-2}
Milli-	m	10^{-3}
Micro-	μ[a]	10^{-6}
Nano-	n	10^{-9}
Pico-	p	10^{-12}
Femto-	f	10^{-15}

Length and Mass

- SI base unit for length is the meter (m)
- Mass is a measure of the amount of material in an object

Temperature

- Celsius and Kelvin scales are used commonly in science
- Both have equal sized units
- K = °C + 273.15
- °C = (5/9)(°F –32)
- °F = (9/5)(°C) + 32

Derived SI Units

Volume

- SI unit is cubic meter
- Equipment to measure volume accurately : syringes, burets, and pipets

Density

- density = mass/volume

1.5: Uncertainty in Measurement

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

1.5.1 Precision and Accuracy

- **precision** – the closeness of individual measurements to one another
- **accuracy** – the correctness of individual measurements

Significant Figures

- Nonzero digits are always significant
- Zeros between nonzero digits are always significant
- Zeros at the beginning of a number are never significant
- Zeros that fall both at the end of a number and after the decimal point are always significant
- When a number ends in zeros but contains no decimal point, the zeros may or may not be significant
- Scientific notation can be used to get the correct significant numbers

Significant Figures in Calculations

- Addition/Subtraction: the number of *decimal places* is determined by the number that has the fewest *decimal places* in the calculation
- Multiplication/Division: the number of *significant figures* is determined by the number that has the fewest *significant figures* in the calculation

1.6: Dimensional Analysis

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

- aid in problem solving
- conversion factor – fraction where the numerator and denominator are the same quantity

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SECTION OVERVIEW

1.2: Atoms, Molecules, and Ions

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.

1.2.1: Prelude to Atoms

1.2.2: Early Ideas in Atomic Theory

1.2.3: Evolution of Atomic Theory

1.2.4: Atomic Structure and Symbolism

1.2.5: Chemical Formulas

1.2.6: The Periodic Table

1.2.7: Molecular and Ionic Compounds

1.2.8: Chemical Nomenclature

1.2.E: Atoms, Molecules, and Ions (Exercises)

1.2.S: Atoms, Molecules, and Ions (Study Guide)

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1.2.1: Prelude to Atoms

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.

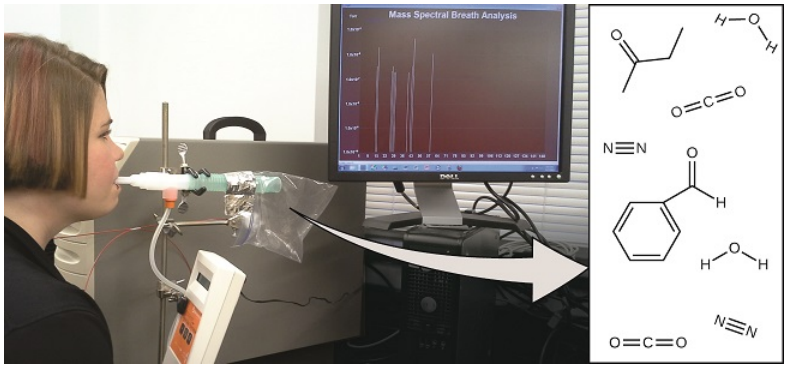


Figure 1.2.1.1: Analysis of molecules in an exhaled breath can provide valuable information, leading to early diagnosis of diseases or detection of environmental exposure to harmful substances. (credit: modification of work by Paul Flowers)

A person is shown blowing into a tube connected to a plastic bag. There is a computer screen displaying data that reads "Mass Spectral Breath Analysis." An arrow from the plastic bag points to an illustration of different molecular compounds contained in the person's exhalation

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.

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1.2.2: Early Ideas in Atomic Theory

Learning Objectives

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

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

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

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

1.2.2.1: Atomic Theory through the Nineteenth Century

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

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

1. Matter is composed of exceedingly small particles called atoms. An atom is the smallest unit of an element that can participate in a chemical change.
2. An element consists of only one type of atom, which has a mass that is characteristic of the element and is the same for all atoms of that element (Figure 1.2.2.1). A macroscopic sample of an element contains an incredibly large number of atoms, all of which have identical chemical properties.

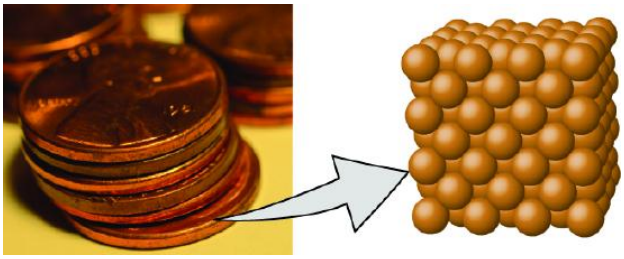


Figure 1.2.2.1: A pre-1982 copper penny (left) contains approximately 3×10^{22} copper atoms (several dozen are represented as brown spheres at the right), each of which has the same chemical properties. (credit: modification of work by "slgckgc"/Flickr)

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

3. Atoms of one element differ in properties from atoms of all other elements.
4. A compound consists of atoms of two or more elements combined in a small, whole-number ratio. In a given compound, the numbers of atoms of each of its elements are always present in the same ratio (Figure 1.2.2.2).

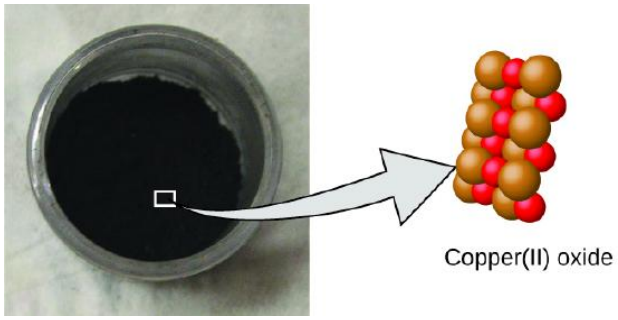


Figure 1.2.2.2: Copper(II) oxide, a powdery, black compound, results from the combination of two types of atoms—copper (brown spheres) and oxygen (red spheres)—in a 1:1 ratio. (credit: modification of work by "Chemicalinterest"/Wikimedia Commons)

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

5. *Atoms are neither created nor destroyed during a chemical change, but are instead rearranged to yield substances that are different from those present before the change (Figure* 1.2.2.3*).*

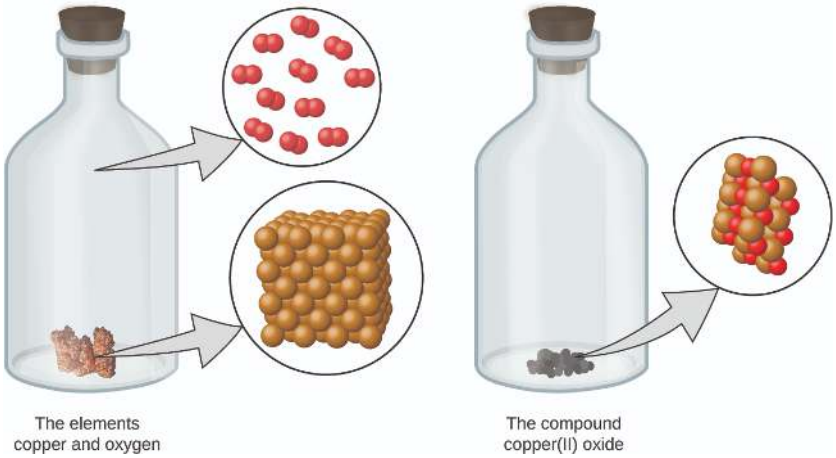


Figure 1.2.2.3: When the elements copper (a shiny, red-brown solid, shown here as brown spheres) and oxygen (a clear and colorless gas, shown here as red spheres) react, their atoms rearrange to form a compound containing copper and oxygen (a powdery, black solid). (credit copper: modification of work by Copper [images-of-elements.com]).

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

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

Example 1.2.2.1: Testing Dalton's Atomic Theory

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



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

Solution

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

? Exercise 1.2.2.1

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



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

Answer

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

Dalton knew of the experiments of French chemist Joseph Proust, who demonstrated that *all samples of a pure compound contain the same elements in the same proportion by mass*. This statement is known as the law of definite proportions or the law of constant composition. The suggestion that the numbers of atoms of the elements in a given compound always exist in the same ratio is consistent with these observations. For example, when different samples of isooctane (a component of gasoline and one of the standards used in the octane rating system) are analyzed, they are found to have a carbon-to-hydrogen mass ratio of 5.33:1, as shown in Table 1.2.2.1.

Table 1.2.2.1: Constant Composition of Isooctane

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

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

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

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

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

This can be explained by atomic theory if the copper-to-chlorine ratio in the brown compound is 1 copper atom to 2 chlorine atoms, and the ratio in the green compound is 1 copper atom to 1 chlorine atom. The ratio of chlorine atoms (and thus the ratio of their masses) is therefore 2 to 1 (Figure 1.2.2.4).

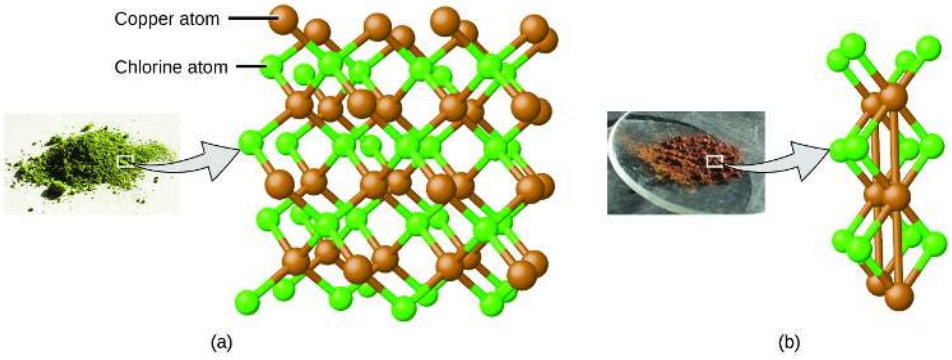


Figure 1.2.2.4: Compared to the copper chlorine compound in (a), where copper is represented by brown spheres and chlorine by green spheres, the copper chlorine compound in (b) has twice as many chlorine atoms per copper atom. (credit a: modification of work by "Benjah-bmm27"/Wikimedia Commons; credit b: modification of work by "Walkerma"/Wikimedia Commons)

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

Example 1.2.2.2: Laws of Definite and Multiple Proportions

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

Solution

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

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

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

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

The ratio of these ratios is:

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

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

Exercise 1.2.2.1

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

Answer

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

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

The ratio of these ratios is

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

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

Summary

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

Glossary

Dalton's atomic theory
set of postulates that established the fundamental properties of atoms

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

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

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

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

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1.2.3: Evolution of Atomic Theory

Learning Objectives

- Outline milestones in the development of modern atomic theory
- Summarize and interpret the results of the experiments of Thomson, Millikan, and Rutherford
- Describe the three subatomic particles that compose atoms
- Introduce the term isotopes

In the two centuries since Dalton developed his ideas, scientists have made significant progress in furthering our understanding of atomic theory. Much of this came from the results of several seminal experiments that revealed the details of the internal structure of atoms. Here, we will discuss some of those key developments, with an emphasis on application of the scientific method, as well as understanding how the experimental evidence was analyzed. While the historical persons and dates behind these experiments can be quite interesting, it is most important to understand the concepts resulting from their work.

1.2.3.1: Atomic Theory after the Nineteenth Century

If matter were composed of atoms, what were atoms composed of? Were they the smallest particles, or was there something smaller? In the late 1800s, a number of scientists interested in questions like these investigated the electrical discharges that could be produced in low-pressure gases, with the most significant discovery made by English physicist J. J. Thomson using a cathode ray tube. This apparatus consisted of a sealed glass tube from which almost all the air had been removed; the tube contained two metal electrodes. When high voltage was applied across the electrodes, a visible beam called a cathode ray appeared between them. This beam was deflected toward the positive charge and away from the negative charge, and was produced in the same way with identical properties when different metals were used for the electrodes. In similar experiments, the ray was simultaneously deflected by an applied magnetic field, and measurements of the extent of deflection and the magnetic field strength allowed Thomson to calculate the charge-to-mass ratio of the cathode ray particles. The results of these measurements indicated that these particles were much lighter than atoms (Figure 1.2.3.1).

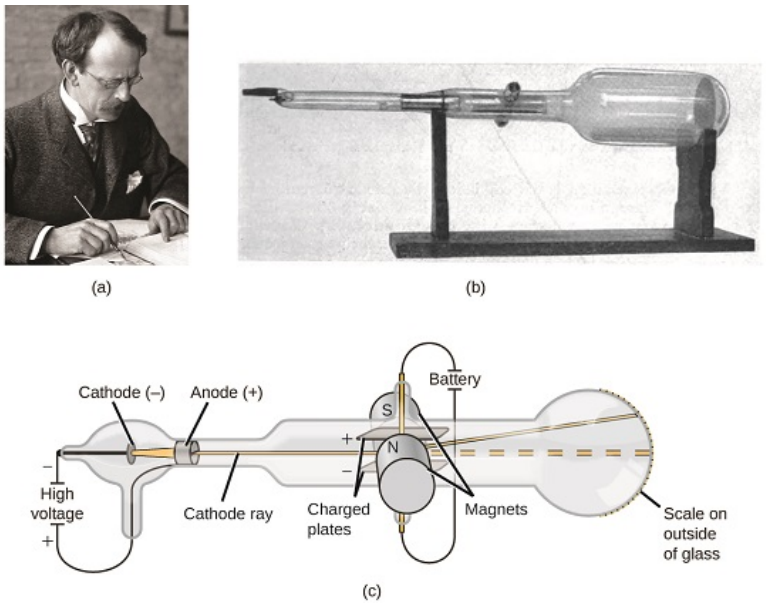
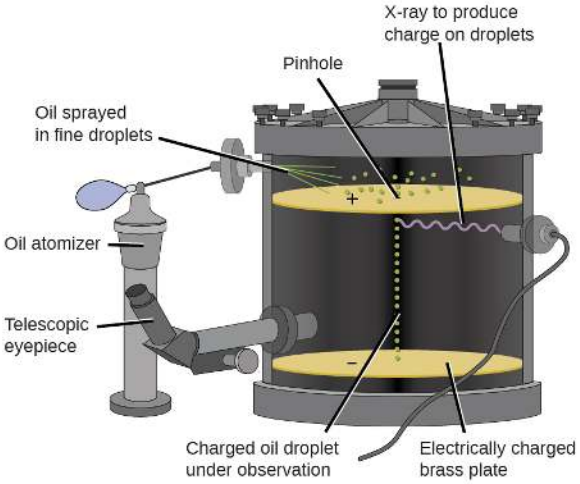


Figure 1.2.3.1: (a) J. J. Thomson produced a visible beam in a cathode ray tube. (b) This is an early cathode ray tube, invented in 1897 by Ferdinand Braun. (c) In the cathode ray, the beam (shown in yellow) comes from the cathode and is accelerated past the anode toward a fluorescent scale at the end of the tube. Simultaneous deflections by applied electric and magnetic fields permitted Thomson to calculate the mass-to-charge ratio of the particles composing the cathode ray. (credit a: modification of work by Nobel Foundation; credit b: modification of work by Eugen Nesper; credit c: modification of work by "Kurzon"/Wikimedia Commons).

Based on his observations, here is what Thomson proposed and why: The particles are attracted by positive (+) charges and repelled by negative (−) charges, so they must be negatively charged (like charges repel and unlike charges attract); they are less massive than atoms and indistinguishable, regardless of the source material, so they must be fundamental, subatomic constituents of all atoms. Although controversial at the time, Thomson's idea was gradually accepted, and his cathode ray particle is what we

now call an electron, a negatively charged, subatomic particle with a mass more than one thousand-times less that of an atom. The term “electron” was coined in 1891 by Irish physicist George Stoney, from “*electr*ic i*on*.”

In 1909, more information about the electron was uncovered by American physicist Robert A. Millikan via his “oil drop” experiments. Millikan created microscopic oil droplets, which could be electrically charged by friction as they formed or by using X-rays. These droplets initially fell due to gravity, but their downward progress could be slowed or even reversed by an electric field lower in the apparatus. By adjusting the electric field strength and making careful measurements and appropriate calculations, Millikan was able to determine the charge on individual drops (Figure 1.2.3.2).



Oil drop	Charge in coulombs (C)
A	4.8×10^{-19} C
B	3.2×10^{-19} C
C	6.4×10^{-19} C
D	1.6×10^{-19} C
E	4.8×10^{-19} C

Figure 1.2.3.2: Millikan’s experiment measured the charge of individual oil drops. The tabulated data are examples of a few possible values.

Looking at the charge data that Millikan gathered, you may have recognized that the charge of an oil droplet is always a multiple of a specific charge, 1.6×10^{-19} C. Millikan concluded that this value must therefore be a fundamental charge—the charge of a single electron—with his measured charges due to an excess of one electron (1 times 1.6×10^{-19} C), two electrons (2 times 1.6×10^{-19} C), three electrons (3 times 1.6×10^{-19} C), and so on, on a given oil droplet. Since the charge of an electron was now known due to Millikan’s research, and the charge-to-mass ratio was already known due to Thomson’s research (1.759×10^{11} C/kg), it only required a simple calculation to determine the mass of the electron as well.

$$\text{Mass of electron} = 1.602 \times 10^{-19} \ \cancel{\text{C}} \times \frac{1 \text{ kg}}{1.759 \times 10^{11} \ \cancel{\text{C}}} = 9.107 \times 10^{-31} \text{ kg} \tag{2.3.1}$$

Scientists had now established that the atom was not indivisible as Dalton had believed, and due to the work of Thomson, Millikan, and others, the charge and mass of the negative, subatomic particles—the electrons—were known. However, the positively charged part of an atom was not yet well understood. In 1904, Thomson proposed the “plum pudding” model of atoms, which described a positively charged mass with an equal amount of negative charge in the form of electrons embedded in it, since all atoms are electrically neutral. A competing model had been proposed in 1903 by Hantaro Nagaoka, who postulated a Saturn-like atom, consisting of a positively charged sphere surrounded by a halo of electrons (Figure 1.2.3.3).

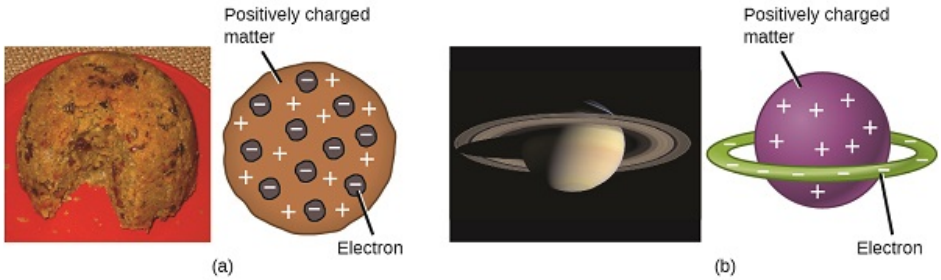


Figure 1.2.3.3: (a) Thomson suggested that atoms resembled plum pudding, an English dessert consisting of moist cake with embedded raisins (“plums”). (b) Nagaoka proposed that atoms resembled the planet Saturn, with a ring of electrons surrounding a positive “planet.” (credit a: modification of work by “Man vyi”/Wikimedia Commons; credit b: modification of work by “NASA”/Wikimedia Commons).

The next major development in understanding the atom came from Ernest Rutherford, a physicist from New Zealand who largely spent his scientific career in Canada and England. He performed a series of experiments using a beam of high-speed, positively charged alpha particles (α particles) that were produced by the radioactive decay of radium; α particles consist of two protons and two neutrons (you will learn more about radioactive decay in the chapter on nuclear chemistry). Rutherford and his colleagues Hans Geiger (later famous for the Geiger counter) and Ernest Marsden aimed a beam of α particles, the source of which was embedded in a lead block to absorb most of the radiation, at a very thin piece of gold foil and examined the resultant scattering of the α particles using a luminescent screen that glowed briefly where hit by an α particle.

What did they discover? Most particles passed right through the foil without being deflected at all. However, some were diverted slightly, and a very small number were deflected almost straight back toward the source (Figure 1.2.3.4). Rutherford described finding these results: "It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you"[1] (p. 68).

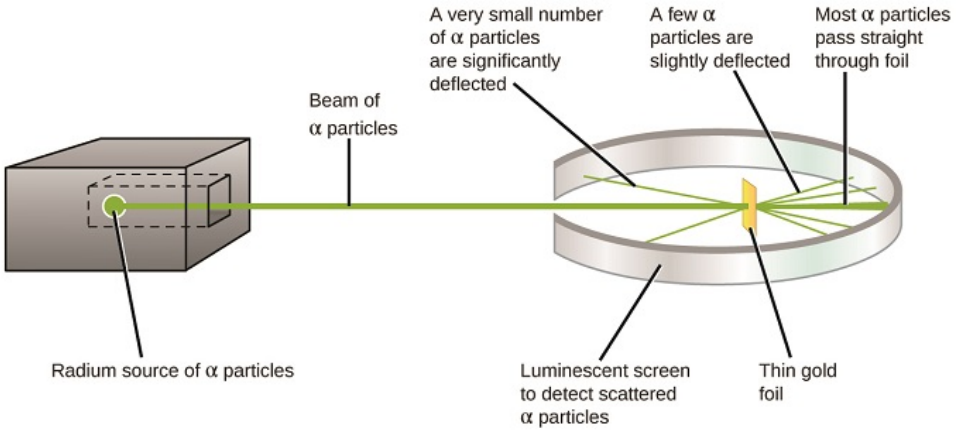


Figure 1.2.3.4: Geiger and Rutherford fired α particles at a piece of gold foil and detected where those particles went, as shown in this schematic diagram of their experiment. Most of the particles passed straight through the foil, but a few were deflected slightly and a very small number were significantly deflected.

Here is what Rutherford deduced: Because most of the fast-moving α particles passed through the gold atoms undeflected, they must have traveled through essentially empty space inside the atom. Alpha particles are positively charged, so deflections arose when they encountered another positive charge (like charges repel each other). Since like charges repel one another, the few positively charged α particles that changed paths abruptly must have hit, or closely approached, another body that also had a highly concentrated, positive charge. Since the deflections occurred a small fraction of the time, this charge only occupied a small amount of the space in the gold foil. Analyzing a series of such experiments in detail, Rutherford drew two conclusions:

1. The volume occupied by an atom must consist of a large amount of empty space.
2. A small, relatively heavy, positively charged body, the nucleus, must be at the center of each atom.

This analysis led Rutherford to propose a model in which an atom consists of a very small, positively charged nucleus, in which most of the mass of the atom is concentrated, surrounded by the negatively charged electrons, so that the atom is electrically neutral (Figure 1.2.3.5).

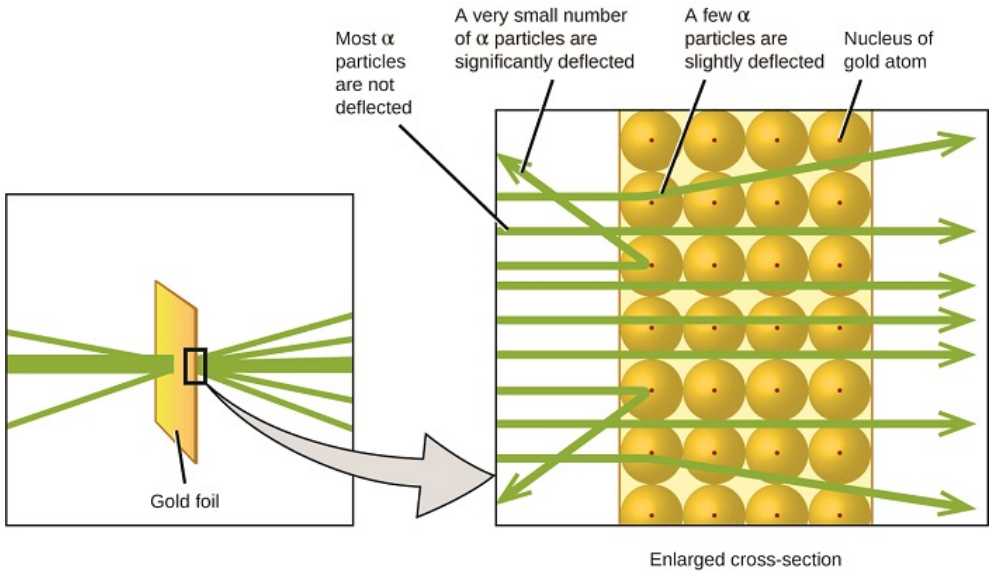


Figure 1.2.3.5: The α particles are deflected only when they collide with or pass close to the much heavier, positively charged gold nucleus. Because the nucleus is very small compared to the size of an atom, very few α particles are deflected. Most pass through the relatively large region occupied by electrons, which are too light to deflect the rapidly moving particles.

After many more experiments, Rutherford also discovered that the nuclei of other elements contain the hydrogen nucleus as a "building block," and he named this more fundamental particle the proton, the positively charged, subatomic particle found in the nucleus. With one addition, which you will learn next, this nuclear model of the atom, proposed over a century ago, is still used today.

Another important finding was the discovery of isotopes. During the early 1900s, scientists identified several substances that appeared to be new elements, isolating them from radioactive ores. For example, a "new element" produced by the radioactive decay of thorium was initially given the name mesothorium. However, a more detailed analysis showed that mesothorium was chemically identical to radium (another decay product), despite having a different atomic mass. This result, along with similar findings for other elements, led the English chemist Frederick Soddy to realize that an element could have types of atoms with different masses that were chemically indistinguishable. These different types are called isotopes—atoms of the same element that differ in mass. Soddy was awarded the Nobel Prize in Chemistry in 1921 for this discovery.

One puzzle remained: The nucleus was known to contain almost all of the mass of an atom, with the number of protons only providing half, or less, of that mass. Different proposals were made to explain what constituted the remaining mass, including the existence of neutral particles in the nucleus. As you might expect, detecting uncharged particles is very challenging, and it was not until 1932 that James Chadwick found evidence of neutrons, uncharged, subatomic particles with a mass approximately the same as that of protons. The existence of the neutron also explained isotopes: They differ in mass because they have different numbers of neutrons, but they are chemically identical because they have the same number of protons. This will be explained in more detail later in this chapter.

Summary

Although no one has actually seen the inside of an atom, experiments have demonstrated much about atomic structure. Thomson's cathode ray tube showed that atoms contain small, negatively charged particles called electrons. Millikan discovered that there is a fundamental electric charge—the charge of an electron. Rutherford's gold foil experiment showed that atoms have a small, dense, positively charged nucleus; the positively charged particles within the nucleus are called protons. Chadwick discovered that the nucleus also contains neutral particles called neutrons. Soddy demonstrated that atoms of the same element can differ in mass; these are called isotopes.

Footnotes

1. Ernest Rutherford, “The Development of the Theory of Atomic Structure,” ed. J. A. Ratcliffe, in *Background to Modern Science*, eds. Joseph Needham and Walter Pagel, (Cambridge, UK: Cambridge University Press, 1938), 61–74. Accessed September 22, 2014, https://ia600508.us.archive.org/3/it...e032734mbp.pdf.

Glossary

alpha particle (α particle)
positively charged particle consisting of two protons and two neutrons

electron
negatively charged, subatomic particle of relatively low mass located outside the nucleus

isotopes
atoms that contain the same number of protons but different numbers of neutrons

neutron
uncharged, subatomic particle located in the nucleus

proton
positively charged, subatomic particle located in the nucleus

nucleus
massive, positively charged center of an atom made up of protons and neutrons

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1.2.4: Atomic Structure and Symbolism

Learning Objectives

- Write and interpret symbols that depict the atomic number, mass number, and charge of an atom or ion
- Define the atomic mass unit and average atomic mass
- Calculate average atomic mass and isotopic abundance

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 1.2.4.1).



Figure 1.2.4.1: If an atom could be expanded to the size of a football stadium, the nucleus would be the size of a single blueberry. (credit middle: modification of work by "babyknight"/Wikimedia Commons; credit right: modification of work by Paxson Woelber).

The diagram on the left shows a picture of an atom with a nucleus. The central figure shows a photograph of an American football stadium. The figure on the right shows a photograph of a handful of blueberries.

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 = 1.602×10^{-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 1.2.4.1 (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 the 12.00 amu of an actual carbon-12 atom. This "missing" mass is known as the mass defect, and you will learn about it in the chapter on nuclear chemistry.)

Table 1.2.4.1: 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}

Name	Location	Charge (C)	Unit Charge	Mass (amu)	Mass (g)
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.

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

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

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

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

Example 1.2.4.1: 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 1.2.4.2).

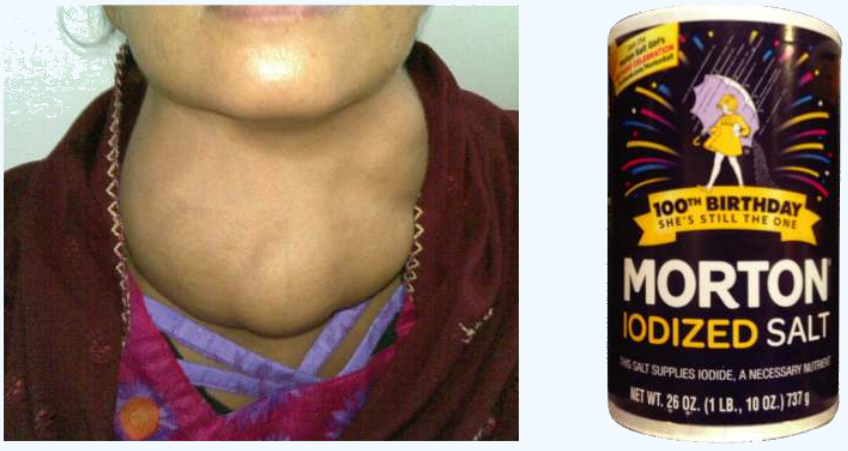


Figure 1.2.4.2: (a) Insufficient iodine in the diet can cause an enlargement of the thyroid gland called a goiter. (b) The addition of small amounts of iodine to salt, which prevents the formation of goiters, has helped eliminate this concern in the US where salt consumption is high. (credit a: modification of work by “Almazi”/Wikimedia Commons; credit b: modification of work by Mike Mozart)

Figure A shows a photo of a person who has a very swollen thyroid in his or her neck. Figure B shows a photo of a canister of Morton iodized salt.

The addition of small amounts of iodine to table salt (iodized salt) has essentially eliminated this health concern in the United States, but as much as 40% of the world’s population is still at risk of iodine deficiency. The iodine atoms are added as anions,

and each has a 1− charge and a mass number of 127. Determine the numbers of protons, neutrons, and electrons in one of these iodine anions.

Solution

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

? Exercise 1.2.4.1

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

Answer

78 protons; 117 neutrons; charge is 4+

1.2.4.1: Chemical Symbols

A chemical symbol is an abbreviation that we use to indicate an element or an atom of an element. For example, the symbol for mercury is Hg (Figure 1.2.4.3). We use the same symbol to indicate one atom of mercury (microscopic domain) or to label a container of many atoms of the element mercury (macroscopic domain).



Figure 1.2.4.3: The symbol Hg represents the element mercury regardless of the amount; it could represent one atom of mercury or a large amount of mercury. from Wikipedia (user: Materialscientist).

The symbols for several common elements and their atoms are listed in Table 1.2.4.2 Some symbols are derived from the common name of the element; others are abbreviations of the name in another language. Symbols have one or two letters, for example, H for hydrogen and Cl for chlorine. To avoid confusion with other notations, only the first letter of a symbol is capitalized. For example, Co is the symbol for the element cobalt, but CO is the notation for the compound carbon monoxide, which contains atoms of the elements carbon (C) and oxygen (O). All known elements and their symbols are in the periodic table.

Table 1.2.4.2: 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

Element	Symbol	Element	Symbol
cobalt	Co	potassium	K (from *kalium*)
copper	Cu (from *cuprum*)	silicon	Si
fluorine	F	silver	Ag (from *argentum*)
gold	Au (from *aurum*)	sodium	Na (from *natrium*)
helium	He	sulfur	S
hydrogen	H	tin	Sn (from *stannum*)
iodine	I	zinc	Zn

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

1.2.4.2: 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 1.2.4.4). The atomic number is sometimes written as a subscript preceding the symbol, but since this number defines the element's identity, as does its symbol, it is often omitted. For example, magnesium exists as a mixture of three isotopes, each with an atomic number of 12 and with mass numbers of 24, 25, and 26, respectively. These isotopes can be identified as ^{24}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.

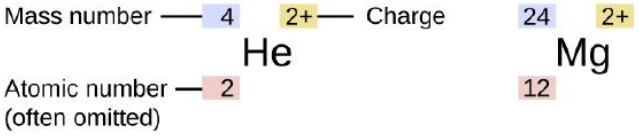


Figure 1.2.4.4: The symbol for an atom indicates the element via its usual two-letter symbol, the mass number as a left superscript, the atomic number as a left subscript (sometimes omitted), and the charge as a right superscript.

This diagram shows the symbol for helium, "H e." The number to the upper left of the symbol is the mass number, which is 4. The number to the upper right of the symbol is the charge which is positive 2. The number to the lower left of the symbol is the atomic number, which is 2. This number is often omitted. Also shown is "M g" which stands for magnesium It has a mass number of 24, a charge of positive 2, and an atomic number of 12.

Information about the naturally occurring isotopes of elements with atomic numbers 1 through 10 is given in Table 1.2.4.2 Note that in addition to standard names and symbols, the isotopes of hydrogen are often referred to using common names and accompanying symbols. Hydrogen-2, symbolized ^{2}H, is also called deuterium and sometimes symbolized D. Hydrogen-3, symbolized ^{3}H, is also called tritium and sometimes symbolized T.

Table 1.2.4.2: Nuclear Compositions of Atoms of the Very Light Elements

Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
hydrogen	$^{1}_{1}$H (protium)	1	1	0	1.0078	99.989

Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
	$^{2}_{1}\mathrm{H}$ (deuterium)	1	1	1	2.0141	0.0115
	$^{3}_{1}\mathrm{H}$ (tritium)	1	1	2	3.01605	— (trace)
helium	$^{3}_{2}\mathrm{He}$	2	2	1	3.01603	0.00013
	$^{4}_{2}\mathrm{He}$	2	2	2	4.0026	100
lithium	$^{6}_{3}\mathrm{Li}$	3	3	3	6.0151	7.59
	$^{7}_{3}\mathrm{Li}$	3	3	4	7.0160	92.41
beryllium	$^{9}_{4}\mathrm{Be}$	4	4	5	9.0122	100
boron	$^{10}_{5}\mathrm{B}$	5	5	5	10.0129	19.9
	$^{11}_{5}\mathrm{B}$	5	5	6	11.0093	80.1
carbon	$^{12}_{6}\mathrm{C}$	6	6	6	12.0000	98.89
	$^{13}_{6}\mathrm{C}$	6	6	7	13.0034	1.11
	$^{14}_{6}\mathrm{C}$	6	6	8	14.0032	— (trace)
nitrogen	$^{14}_{7}\mathrm{N}$	7	7	7	14.0031	99.63
	$^{15}_{7}\mathrm{N}$	7	7	8	15.0001	0.37
oxygen	$^{16}_{8}\mathrm{O}$	8	8	8	15.9949	99.757
	$^{17}_{8}\mathrm{O}$	8	8	9	16.9991	0.038
	$^{18}_{8}\mathrm{O}$	8	8	10	17.9992	0.205
fluorine	$^{19}_{9}\mathrm{F}$	9	9	10	18.9984	100
neon	$^{20}_{10}\mathrm{Ne}$	10	10	10	19.9924	90.48
	$^{21}_{10}\mathrm{Ne}$	10	10	11	20.9938	0.27
	$^{22}_{10}\mathrm{Ne}$	10	10	12	21.9914	9.25

1.2.4.3: 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:

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

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

Example 1.2.4.2: 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

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

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

Exercise 1.2.4.2

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.

Answer

24.31 amu

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

Example 1.2.4.3: Calculation of Percent Abundance

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

Solution

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

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

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

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

Substituting this into the average mass equation, we have:

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

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

Exercise 1.2.4.3

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

Answer

69.15% Cu-63 and 30.85% Cu-65

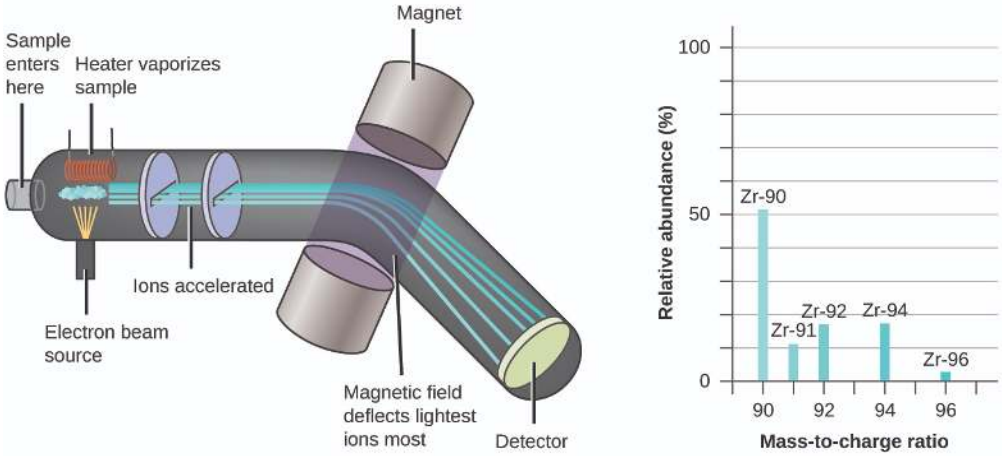


Figure 1.2.4.5: Analysis of zirconium in a mass spectrometer produces a mass spectrum with peaks showing the different isotopes of Zr.

The left diagram shows how a mass spectrometer works. The graph to the right of the spectrometer shows a mass spectrum of zirconium. The relative abundance, as a percentage from 0 to 100, is graphed on the y axis, and the mass to charge ratio is graphed on the x axis. The sample contains five different isomers of zirconium.

The occurrence and natural abundances of isotopes can be experimentally determined using an instrument called a mass spectrometer. Mass spectrometry (MS) is widely used in chemistry, forensics, medicine, environmental science, and many other fields to analyze and help identify the substances in a sample of material. In a typical mass spectrometer (Figure 1.2.4.5), the sample is vaporized and exposed to a high-energy electron beam that causes the sample's atoms (or molecules) to become electrically charged, typically by losing one or more electrons. These cations then pass through a (variable) electric or magnetic field that deflects each cation's path to an extent that depends on both its mass and charge (similar to how the path of a large steel ball bearing rolling past a magnet is deflected to a lesser extent that that of a small steel BB). The ions are detected, and a plot of the relative number of ions generated versus their mass-to-charge ratios (a *mass spectrum*) is made. The height of each vertical feature or peak in a mass spectrum is proportional to the fraction of cations with the specified mass-to-charge ratio. Since its initial use during the development of modern atomic theory, MS has evolved to become a powerful tool for chemical analysis in a wide range of applications.



***Video* 1.2.4.1** *: Watch this video from the Royal Society for Chemistry for a brief description of the rudiments of mass spectrometry.*

Summary

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

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

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

1.2.4.4: Key Equations

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

Glossary

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

atomic mass
average mass of atoms of an element, expressed in amu

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

atomic number (Z)
number of protons in the nucleus of an atom

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

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

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

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

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

mass number (A)

sum of the numbers of neutrons and protons in the nucleus of an atom

unified atomic mass unit (u)

alternative unit equivalent to the atomic mass unit

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

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1.2.5: Chemical Formulas

Learning Objectives

- Symbolize the composition of molecules using molecular formulas and empirical formulas
- Represent the bonding arrangement of atoms within molecules using structural 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 1.2.5.1). 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.

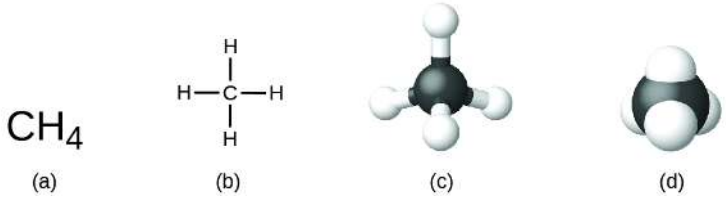


Figure 1.2.5.1: A methane molecule can be represented as (a) a molecular formula, (b) a structural formula, (c) a ball-and-stick model, and (d) a space-filling model. Carbon and hydrogen atoms are represented by black and white spheres, respectively.

Figure A shows C H subscript 4. Figure B shows a carbon atom that is bonded to four hydrogen atoms at right angles: one above, one to the left, one to the right, and one below. Figure C shows a 3-D, ball-and-stick model of the carbon atom bonded to four hydrogen atoms. Figure D shows a space-filling model of a carbon atom with hydrogen atoms partially embedded into the surface of the carbon atom.

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 1.2.5.2).

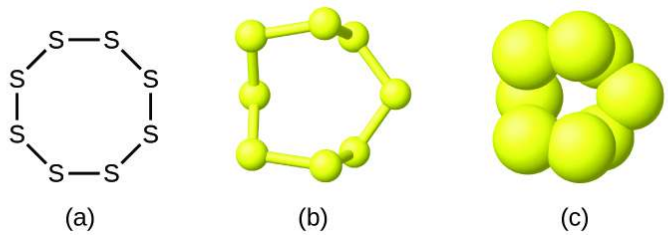


Figure 1.2.5.2: A molecule of sulfur is composed of eight sulfur atoms and is therefore written as S_8. It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres.

Figure A shows eight sulfur atoms, symbolized with the letter S, that are bonded to each other to form an octagon. Figure B shows a 3-D, ball-and-stick model of the arrangement of the sulfur atoms. The shape is clearly not octagonal as it is represented in the structural formula. Figure C is a space-filling model that shows each sulfur atom is partially embedded into the sulfur atom it bonds with.

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 1.2.5.3).

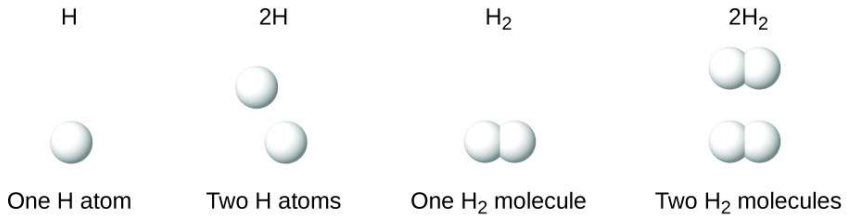


Figure 1.2.5.3: The symbols H, 2H, H_2, and $2H_2$ represent very different entities.

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 2 H subscript 2 shows two sets of bonded, white spheres. It is labeled 2 H subscript 2 molecules.

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 1.2.5.4).

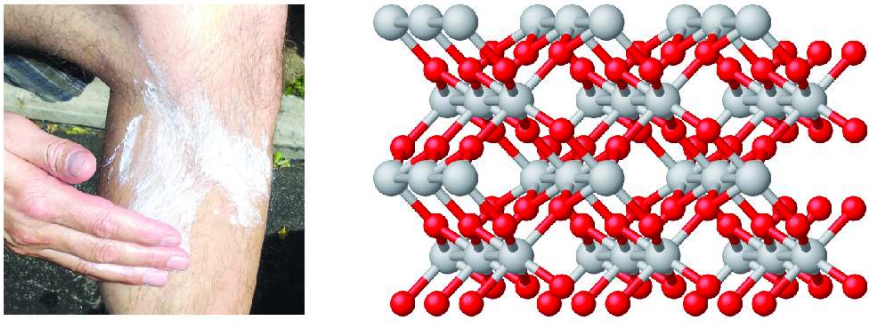


Figure 1.2.5.4: (a) The white compound titanium dioxide provides effective protection from the sun. (b) A crystal of titanium dioxide, TiO_2, contains titanium and oxygen in a ratio of 1 to 2. The titanium atoms are gray and the oxygen atoms are red. (credit a: modification of work by “osseous”/Flickr).

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 1.2.5.5).

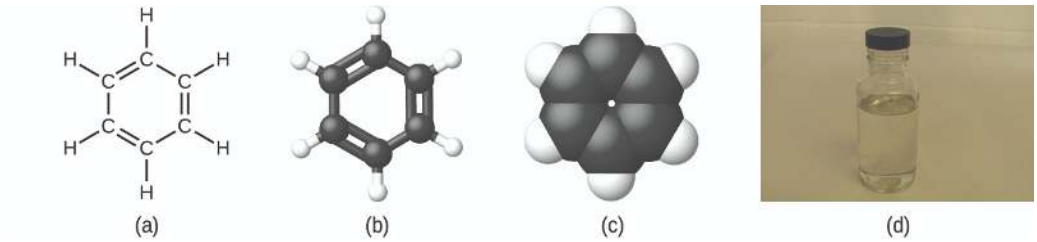


Figure 1.2.5.5: Benzene, C_6H_6, is produced during oil refining and has many industrial uses. A benzene molecule can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. (d) Benzene is a clear liquid. (credit d: modification of work by Sahar Atwa).

Figure A shows that benzene is composed of six carbons shaped like a hexagon. Every other bond between the carbon atoms is a double bond. Each carbon also has a single bonded hydrogen atom. Figure B shows a 3-D, ball-and-stick drawing of benzene. The six carbon atoms are black spheres while the six hydrogen atoms are smaller, white spheres. Figure C is a space-filling model of benzene which shows that most of the interior space is occupied by the carbon atoms. The hydrogen atoms are embedded in the outside surface of the carbon atoms. Figure d shows a small vial filled with benzene which appears to be clear.

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 1.2.5.6) 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.

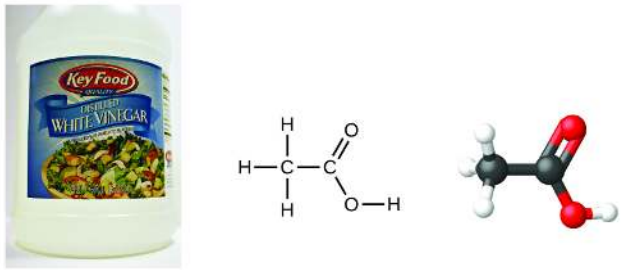


Figure 1.2.5.6: (a) Vinegar contains acetic acid, $C_2H_4O_2$, which has an empirical formula of CH_2O. It can be represented as (b) a structural formula and (c) as a ball-and-stick model. (credit a: modification of work by "HomeSpot HQ"/Flickr)

Figure A shows a jug of distilled, white vinegar. Figure B shows a structural formula for acetic acid which contains two carbon atoms connected by a single bond. The left carbon atom forms single bonds with three hydrogen atoms. The right carbon atom forms a double bond with an oxygen atom. The right carbon atom also forms a single bond with an oxygen atom. This oxygen forms a single bond with a hydrogen atom. Figure C shows a 3-D ball-and-stick model of acetic acid.

✔ Example 1.2.5.1: Empirical and Molecular Formulas

Molecules of glucose (blood sugar) contain 6 carbon atoms, 12 hydrogen atoms, and 6 oxygen atoms. What are the molecular and empirical formulas of glucose?

Solution

The molecular formula is $C_6H_{12}O_6$ because one molecule actually contains 6 C, 12 H, and 6 O atoms. The simplest whole-number ratio of C to H to O atoms in glucose is 1:2:1, so the empirical formula is CH_2O.

? Exercise 1.2.5.1

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

Answer

Molecular formula, $C_8H_{16}O_4$; empirical formula, C_2H_4O

It is important to be aware that it may be possible for the same atoms to be arranged in different ways: Compounds with the same molecular formula may have different atom-to-atom bonding and therefore different structures. For example, could there be another compound with the same formula as acetic acid, $C_2H_4O_2$? And if so, what would be the structure of its molecules?

If you predict that another compound with the formula $C_2H_4O_2$ could exist, then you demonstrated good chemical insight and are correct. Two C atoms, four H atoms, and two O atoms can also be arranged to form methyl formate, which is used in manufacturing, as an insecticide, and for quick-drying finishes. Methyl formate molecules have one of the oxygen atoms between the two carbon atoms, differing from the arrangement in acetic acid molecules. Acetic acid and methyl formate are examples of isomers—compounds with the same chemical formula but different molecular structures (Figure 1.2.5.7). Note that this small difference in the arrangement of the atoms has a major effect on their respective chemical properties. You would certainly not want to use a solution of methyl formate as a substitute for a solution of acetic acid (vinegar) when you make salad dressing.

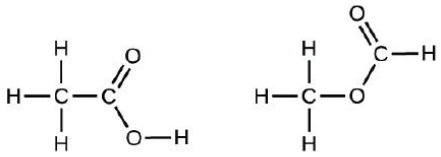


Figure 1.2.5.7: Molecules of (a) acetic acid and methyl formate (b) are structural isomers; they have the same formula ($C_2H_4O_2$) but different structures (and therefore different chemical properties).

Figure A shows a structural diagram of acetic acid, C subscript 2 H subscript 4 O subscript 2. Acetic acid contains two carbon atoms connected by a single bond. The left carbon atom forms single bonds with three hydrogen atoms. The carbon on the right forms a double bond with an oxygen atom. The right carbon atom also forms a single bond to an oxygen atom which forms a single bond with a hydrogen atom. Figure B shows a structural diagram of methyl formate, C subscript 2 H subscript 4 O subscript 2. This molecule contains a carbon atom which forms single bonds with three hydrogen atoms, and a single bond with an oxygen atom. The oxygen atom forms a single bond with another carbon atom which forms a double bond with another oxygen atom and a single bond with a hydrogen atom.

Many types of isomers exist (Figure 1.2.5.8). Acetic acid and methyl formate are structural isomers, compounds in which the molecules differ in how the atoms are connected to each other. There are also various types of spatial isomers, in which the relative orientations of the atoms in space can be different. For example, the compound carvone (found in caraway seeds, spearmint, and mandarin orange peels) consists of two isomers that are mirror images of each other. *S*-(+)-carvone smells like caraway, and *R*-(−)-carvone smells like spearmint.

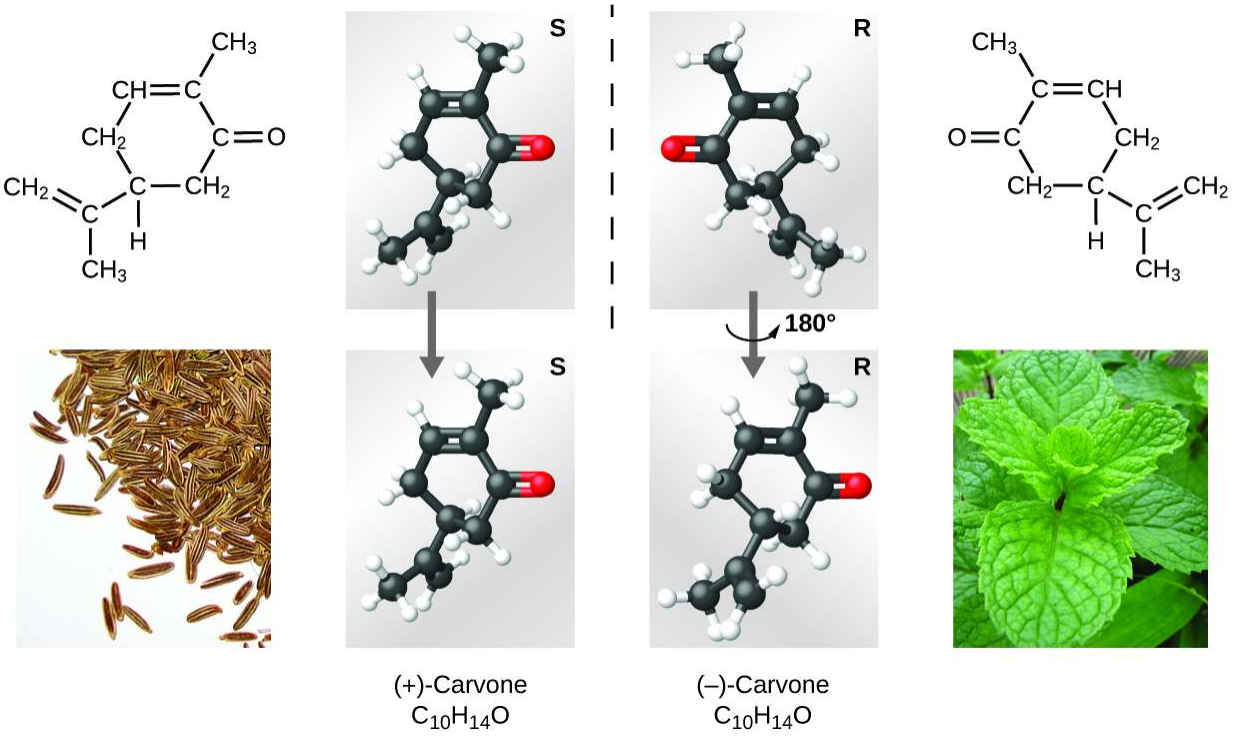


Figure 1.2.5.8: Molecules of carvone are spatial isomers; they only differ in the relative orientations of the atoms in space. (credit bottom left: modification of work by “Miansari66”/Wikimedia Commons; credit bottom right: modification of work by Forest & Kim Starr)

Summary

A molecular formula uses chemical symbols and subscripts to indicate the exact numbers of different atoms in a molecule or compound. An empirical formula gives the simplest, whole-number ratio of atoms in a compound. A structural formula indicates the bonding arrangement of the atoms in the molecule. Ball-and-stick and space-filling models show the geometric arrangement of atoms in a molecule. Isomers are compounds with the same molecular formula but different arrangements of atoms.

Glossary

empirical formula
formula showing the composition of a compound given as the simplest whole-number ratio of atoms

isomers
compounds with the same chemical formula but different structures

molecular formula
formula indicating the composition of a molecule of a compound and giving the actual number of atoms of each element in a molecule of the compound.

spatial isomers
compounds in which the relative orientations of the atoms in space differ

structural isomer
one of two substances that have the same molecular formula but different physical and chemical properties because their atoms are bonded differently

structural formula
shows the atoms in a molecule and how they are connected

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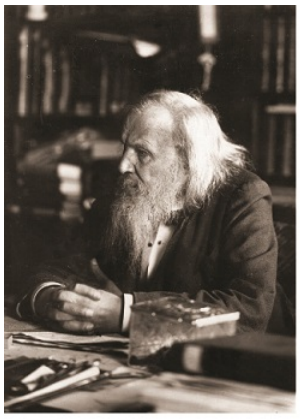
1.2.6: The Periodic Table

Learning Objectives

- State the periodic law and explain the organization of elements in the periodic table
- Predict the general properties of elements based on their location within the periodic table
- Identify metals, nonmetals, and metalloids by their properties and/or location on 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 1.2.6.1).



Reihen	Gruppe I. — R²O	Gruppe II. — RO	Gruppe III. — R²O³	Gruppe IV. RH⁴ RO²	Gruppe V. RH³ R²O⁵	Gruppe VI. RH² RO³	Gruppe VII. RH R²O⁷	Gruppe VIII. — RO⁴
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=86	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	—	— — — —

(a) (b)

Figure 1.2.6.1: (a) Dimitri Mendeleev is widely credited with creating (b) the first periodic table of the elements. (credit a: modification of work by Serge Lachinov; credit b: modification of work by “Den fjättrade ankan”/Wikimedia Commons)

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. In the first group (—, R superscript plus sign 0) is the following information: H = 1, L i = 7, N a = 23, K = 39, (C u = 63), R b = 85, (A g = 108), C a = 183, (—),—, (A u = 199) —. Note that each of these entries corresponds to one of the twelve periods respectively. The second group (—, R 0) contains the following information: (not entry for period 1) B o = 9, 4, M g = 24, C a = 40, Z n = 65, S r = 87, C d = 112, B a = 187, —, —, H g = 200, —. Note the ach of these entries corresponds to one of the twelve periods respectively. Group three (—, R superscript one 0 superscript nine) contains the information: (no entry for period 1), B = 11, A l = 27, 8. — = 44, — = 68, ? Y t = 88, I n = 113, ? D I = 138, —, ? E r = 178, T l = 204, —. Note that each of these entries corresponds to one of the twelve periods respectively. Group four (RH superscript four, R0 superscript eight) contains the following information: (no entry for period 1), C = 12, B i = 28, T i = 48, — = 72, Z r = 90, S n = 118, ? C o = 140, ? L a = 180, P b = 207, T h = 231. Note that each of these entries corresponds to one of the twelve periods respectively. Group five (R H superscript two, R superscript two 0 superscript five) contains the following information: (no entry for period 1), N = 14, P = 31, V = 51, A s = 75, N b = 94, S b = 122, —, —, T a = 182, B l = 208, —. Note that each of these entries corresponds to one of the twelve periods respectively. Group six (R H superscript two, R 0 superscript three) contains the following information: (no entry for period 1), O = 16, S = 32, C r = 52, S o = 78, M o = 96, T o = 125, —, —, W = 184, —, U = 240. Note that each of these entries corresponds to one of the twelve periods respectively. Group seven (R H , R superscript plus sing, 0 superscript 7) contains the following information: (no entry for period 1), F = 19, C l = 35, 5, M n = 55, B r = 80, — = 100, J = 127, —, —, —, —, —. Note that each of these entries corresponds to one of the twelve periods respectively. Group 8 (—, R 0 superscript four) contains the following information: (no entry for periods 1, 2, 3), in period 4: F o = 56, C o = 59, N i = 59, C u = 63, no entry for period five, in period 6: R u = 104, R h = 104, P d = 106, A g = 108, no entries for periods 7, 8 , or 9, in period 10: O s = 195, I r = 197, P t = 198, A u = 199, no entries for periods 11 or 12.

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 1.2.6.2). 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.

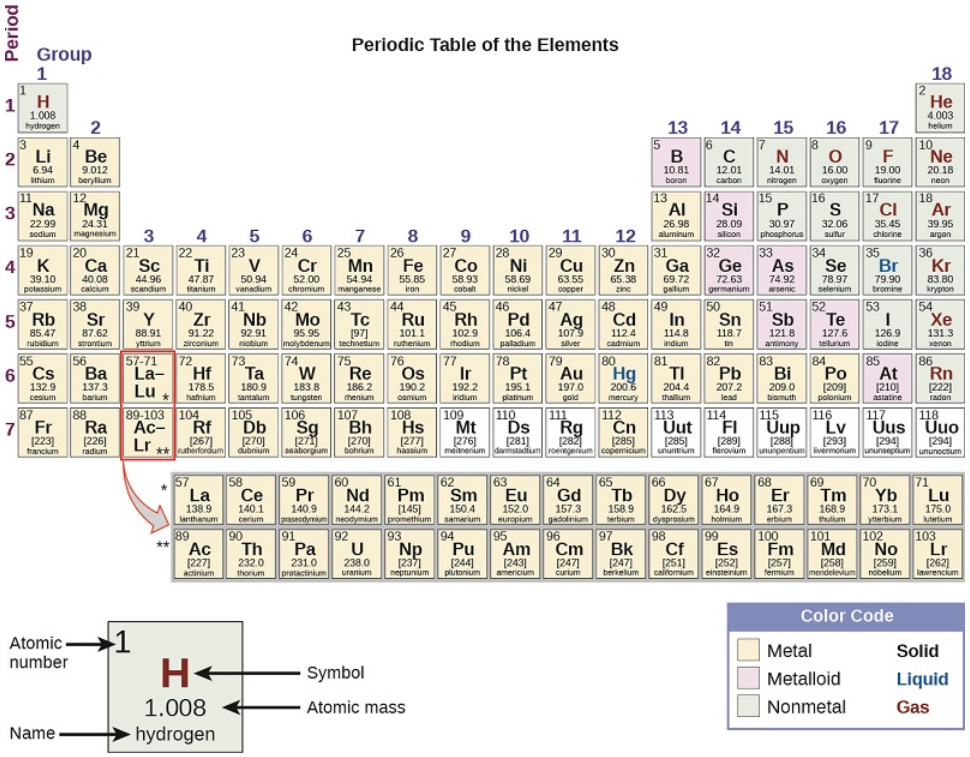


Figure 1.2.6.2: Elements in the periodic table are organized according to their properties.

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. Beginning at the top left of the table, or period 1, group 1, is a box containing “1; hydrogen; H; nonmetal; gas; and 1.008.” There is only one other element box in period 1, group 18, which contains “2; helium; H e; nonmetal; gas; and 4.003.” Period 2, group 1 contains “3; lithium; L i; metal; solid; and 6.94” Group 2 contains “4; beryllium; B e; metal; solid; and 9.012.” Groups 3 through 12 are skipped and group 13 contains “5; boron; B; metalloid; solid; 10.81.” Group 14 contains “6; carbon; C; nonmetal; solid; and 12.01.” Group 15 contains “7; nitrogen; N; nonmetal; gas; and 14.01.” Group 16 contains “8; oxygen; O; nonmetal; gas; and 16.00.” Group 17 contains “9; fluorine; F; nonmetal; gas; and 19.00.” Group 18 contains “10; neon; N e; nonmetal; gas; and 20.18.” Period 3, group 1 contains “11; sodium; N a; metal; solid; and 22.99.” Group 2 contains “12; magnesium; M g; metal; solid; and 24.31.” Groups 3 through 12 are skipped again in period 3 and group 13 contains “13; aluminum; A l; metal; solid; and 26.98.” Group 14 contains “14; silicon; S i; metalloid; solid; and 28.09.” Group 15 contains “15; phosphorous; P; nonmetal; solid; and 30.97.” Group 16 contains “16; sulfur; S; nonmetal; solid; and 32.06.” Group 17 contains “17; chlorine; C l; nonmetal; gas; and 35.45.” Group 18 contains “18; argon; A r; nonmetal; gas; and 39.95.” Period 4, group 1 contains “19; potassium; K; metal; solid; and 39.10.” Group 2 contains “20; calcium; C a; metal; solid; and 40.08.” Group 3 contains “21; scandium; S c; metal; solid; and 44.96.” Group 4 contains “22; titanium; T i; metal; solid; and 47.87.” Group 5 contains “23; vanadium; V; metal; solid; and 50.94.” Group 6 contains “24; chromium; C r; metal; solid; and 52.00.” Group 7 contains “25; manganese; M n; metal; solid; and 54.94.” Group 8 contains “26; iron; F e; metal; solid; and 55.85.” Group 9 contains “27; cobalt; C o; metal; solid; and 58.93.” Group 10 contains “28; nickel; N i; metal; solid; and 58.69.” Group 11 contains “29; copper; C u; metal; solid; and 63.55.” Group 12 contains “30; zinc; Z n; metal; solid; and 65.38.” Group 13 contains “31; gallium; G a; metal; solid; and 69.72.” Group 14 contains “32; germanium; G e; metalloid; solid; and 72.63.” Group 15 contains “33; arsenic; A s; metalloid; solid; and 74.92.” Group 16 contains “34; selenium; S e; nonmetal; solid; and 78.97.” Group 17 contains “35; bromine; B r; nonmetal; liquid; and 79.90.” Group 18 contains “36; krypton; K r; nonmetal; gas; and 83.80.” Period 5, group 1 contains “37; rubidium; R b; metal; solid; and 85.47.” Group 2 contains “38; strontium; S r; metal; solid; and 87.62.” Group 3 contains “39; yttrium; Y; metal; solid; and 88.91.” Group 4 contains “40; zirconium; Z r; metal; solid; and 91.22.” Group 5 contains “41; niobium; N b; metal; solid; and 92.91.” Group 6 contains “42; molybdenum; M o; metal; solid; and 95.95.” Group 7 contains “43; technetium; T c; metal; solid; and 97.” Group 8 contains “44; ruthenium; R u; metal; solid; and 101.1.” Group 9 contains “45; rhodium; R h; metal; solid; and 102.9.” Group 10 contains “46; palladium; P d; metal; solid; and 106.4.” Group 11 contains “47; silver; A g; metal; solid; and 107.9.” Group 12 contains “48; cadmium; C d; metal; solid; and 112.4.” Group 13 contains “49; indium; I n; metal; solid; and 114.8.” Group 14 contains “50; tin; S n; metal; solid; and 118.7.” Group 15 contains “51; antimony; S b; metalloid; solid; and 121.8.” Group 16 contains “52; tellurium; T e; metalloid; solid; and 127.6.” Group 17 contains “53; iodine; I; nonmetal; solid; and 126.9.” Group 18 contains “54; xenon; X e; nonmetal; gas; and 131.3.” Period 6, group 1 contains “55; cesium; C s; metal; solid; and 132.9.” Group 2 contains “56; barium; B a; metal; solid; and 137.3.” Group 3 breaks the pattern. The box has a large arrow pointing to a row of elements below the table with atomic numbers ranging from 57-71. In sequential order by atomic number, the first box in this row

contains “57; lanthanum; L a; metal; solid; and 138.9.” To its right, the next is “58; cerium; C e; metal; solid; and 140.1.” Next is “59; praseodymium; P r; metal; solid; and 140.9.” Next is “60; neodymium; N d; metal; solid; and 144.2.” Next is “61; promethium; P m; metal; solid; and 145.” Next is “62; samarium; S m; metal; solid; and 150.4.” Next is “63; europium; E u; metal; solid; and 152.0.” Next is “64; gadolinium; G d; metal; solid; and 157.3.” Next is “65; terbium; T b; metal; solid; and 158.9.” Next is “66; dysprosium; D y; metal; solid; and 162.5.” Next is “67; holmium; H o; metal; solid; and 164.9.” Next is “68; erbium; E r; metal; solid; and 167.3.” Next is “69; thulium; T m; metal; solid; and 168.9.” Next is “70; ytterbium; Y b; metal; solid; and 173.1.” The last in this special row is “71; lutetium; L u; metal; solid; and 175.0.” Continuing in period 6, group 4 contains “72; hafnium; H f; metal; solid; and 178.5.” Group 5 contains “73; tantalum; T a; metal; solid; and 180.9.” Group 6 contains “74; tungsten; W; metal; solid; and 183.8.” Group 7 contains “75; rhenium; R e; metal; solid; and 186.2.” Group 8 contains “76; osmium; O s; metal; solid; and 190.2.” Group 9 contains “77; iridium; I r; metal; solid; and 192.2.” Group 10 contains “78; platinum; P t; metal; solid; and 195.1.” Group 11 contains “79; gold; A u; metal; solid; and 197.0.” Group 12 contains “80; mercury; H g; metal; liquid; and 200.6.” Group 13 contains “81; thallium; T l; metal; solid; and 204.4.” Group 14 contains “82; lead; P b; metal; solid; and 207.2.” Group 15 contains “83; bismuth; B i; metal; solid; and 209.0.” Group 16 contains “84; polonium; P o; metal; solid; and 209.” Group 17 contains “85; astatine; A t; metalloid; solid; and 210.” Group 18 contains “86; radon; R n; nonmetal; gas; and 222.” Period 7, group 1 contains “87; francium; F r; metal; solid; and 223.” Group 2 contains “88; radium; R a; metal; solid; and 226.” Group 3 breaks the pattern much like what occurs in period 6. A large arrow points from the box in period 7, group 3 to a special row containing the elements with atomic numbers ranging from 89-103, just below the row which contains atomic numbers 57-71. In sequential order by atomic number, the first box in this row contains “89; actinium; A c; metal; solid; and 227.” To its right, the next is “90; thorium; T h; metal; solid; and 232.0.” Next is “91; protactinium; P a; metal; solid; and 231.0.” Next is “92; uranium; U; metal; solid; and 238.0.” Next is “93; neptunium; N p; metal; solid; and N p.” Next is “94; plutonium; P u; metal; solid; and 244.” Next is “95; americium; A m; metal; solid; and 243.” Next is “96; curium; C m; metal; solid; and 247.” Next is “97; berkelium; B k; metal; solid; and 247.” Next is “98; californium; C f; metal; solid; and 251.” Next is “99; einsteinium; E s; metal; solid; and 252.” Next is “100; fermium; F m; metal; solid; and 257.” Next is “101; mendelevium; M d; metal; solid; and 258.” Next is “102; nobelium; N o; metal; solid; and 259.” The last in this special row is “103; lawrencium; L r; metal; solid; and 262.” Continuing in period 7, group 4 contains “104; rutherfordium; R f; metal; solid; and 267.” Group 5 contains “105; dubnium; D b; metal; solid; and 270.” Group 6 contains “106; seaborgium; S g; metal; solid; and 271.” Group 7 contains “107; bohrium; B h; metal; solid; and 270.” Group 8 contains “108; hassium; H s; metal; solid; and 277.” Group 9 contains “109; meitnerium; M t; not indicated; solid; and 276.” Group 10 contains “110; darmstadtium; D s; not indicated; solid; and 281.” Group 11 contains “111; roentgenium; R g; not indicated; solid; and 282.” Group 12 contains “112; copernicium; C n; metal; liquid; and 285.” Group 13 contains “113; ununtrium; U u t; not indicated; solid; and 285.” Group 14 contains “114; flerovium; F l; not indicated; solid; and 289.” Group 15 contains “115; ununpentium; U u p; not indicated; solid; and 288.” Group 16 contains “116; livermorium; L v; not indicated; solid; and 293.” Group 17 contains “117; ununseptium; U u s; not indicated; solid; and 294.” Group 18 contains “118; ununoctium; U u o; not indicated; solid; and 294.”

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—shaded yellow); nonmetals (elements that appear dull, poor conductors of heat and electricity—shaded green); and metalloids (elements that conduct heat and electricity moderately well, and possess some properties of metals and some properties of nonmetals—shaded purple).

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 1.2.6.3). 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.

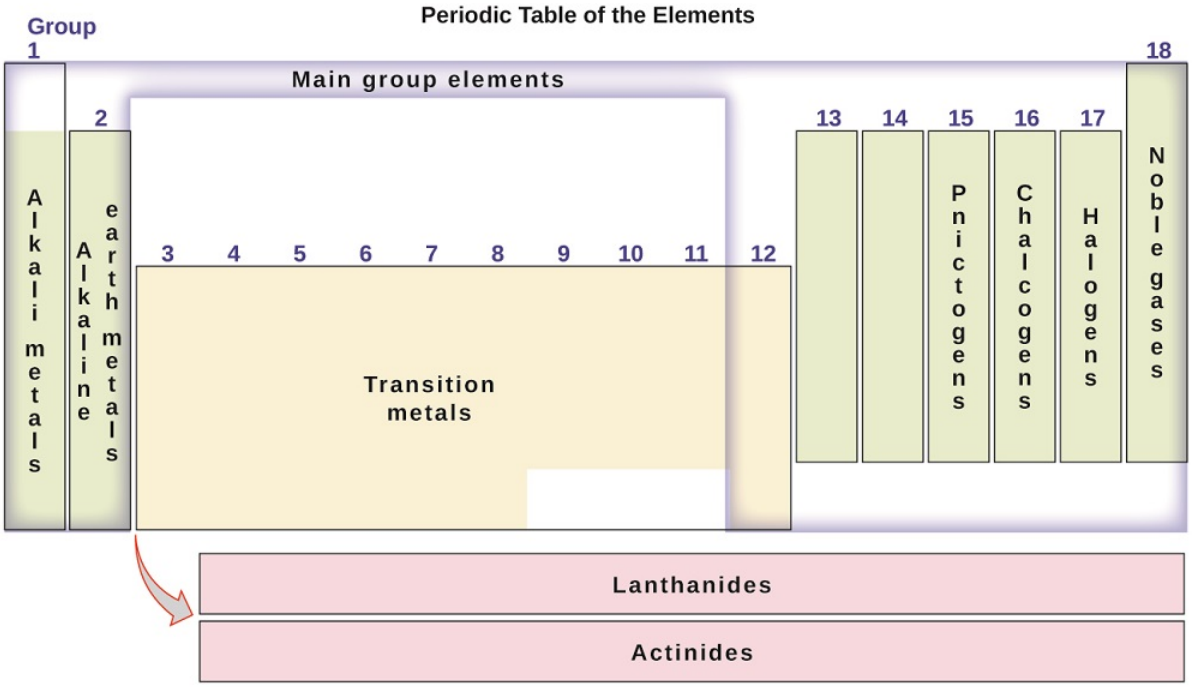


Figure 1.2.6.3: The periodic table organizes elements with similar properties into groups.

This diagram combines the groups and periods of the periodic table based on their similar properties. Group 1 contains the alkali metals, group 2 contains the earth alkaline metals, group 15 contains the pnictogens, group 16 contains the chalcogens, group 17 contains the halogens and group 18 contains the noble gases. The main group elements consist of groups 1, 2, and 12 through 18. Therefore, most of the transition metals, which are contained in groups 3 through 11, are not main group elements. The lanthanides and actinides are called out at the bottom of the periodic table.

✔ Example 1.2.6.1: 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
b. calcium
c. sodium
d. sulfur

Solution

The family names are as follows:

a. halogen
b. alkaline earth metal
c. alkali metal
d. chalcogen

? Exercise 1.2.6.1

Give the group name for each of the following elements:

a. krypton
b. selenium
c. barium
d. lithium

Answer a

noble gas

Answer b

chalcogen

Answer c

alkaline earth metal

Answer d

alkali metal

In studying the periodic table, you might have noticed something about the atomic masses of some of the elements. Element 43 (technetium), element 61 (promethium), and most of the elements with atomic number 84 (polonium) and higher have their atomic mass given in square brackets. This is done for elements that consist entirely of unstable, radioactive isotopes (you will learn more about radioactivity in the nuclear chemistry chapter). An average atomic weight cannot be determined for these elements because their radioisotopes may vary significantly in relative abundance, depending on the source, or may not even exist in nature. The number in square brackets is the atomic mass number (and approximate atomic mass) of the most stable isotope of that element.

Summary

The discovery of the periodic recurrence of similar properties among the elements led to the formulation of the periodic table, in which the elements are arranged in order of increasing atomic number in rows known as periods and columns known as groups. Elements in the same group of the periodic table have similar chemical properties. Elements can be classified as metals, metalloids, and nonmetals, or as a main-group elements, transition metals, and inner transition metals. Groups are numbered 1–18 from left to right. The elements in group 1 are known as the alkali metals; those in group 2 are the alkaline earth metals; those in 15 are the pnictogens; those in 16 are the chalcogens; those in 17 are the halogens; and those in 18 are the noble gases.

Glossary

actinide
inner transition metal in the bottom of the bottom two rows of the periodic table

alkali metal
element in group 1

alkaline earth metal
element in group 2

chalcogen
element in group 16

group
vertical column of the periodic table

halogen
element in group 17

inert gas
(also, noble gas) element in group 18

inner transition metal
(also, lanthanide or actinide) element in the bottom two rows; if in the first row, also called lanthanide, or if in the second row, also called actinide

lanthanide
inner transition metal in the top of the bottom two rows of the periodic table

main-group element
(also, representative element) element in columns 1, 2, and 12–18

metal
element that is shiny, malleable, good conductor of heat and electricity

metalloid
element that conducts heat and electricity moderately well, and possesses some properties of metals and some properties of nonmetals

noble gas
(also, inert gas) element in group 18

nonmetal
element that appears dull, poor conductor of heat and electricity

period
(also, series) horizontal row of the periodic table

periodic law
properties of the elements are periodic function of their atomic numbers.

periodic table
table of the elements that places elements with similar chemical properties close together

pnictogen
element in group 15

representative element
(also, main-group element) element in columns 1, 2, and 12–18

transition metal
element in columns 3–11

series
(also, period) horizontal row of the period table

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1.2.7: Molecular and Ionic Compounds

Learning Objectives

- Define ionic and molecular (covalent) compounds
- Predict the type of compound formed from elements based on their location within the periodic table
- Determine formulas for simple ionic 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 1.2.7.1).

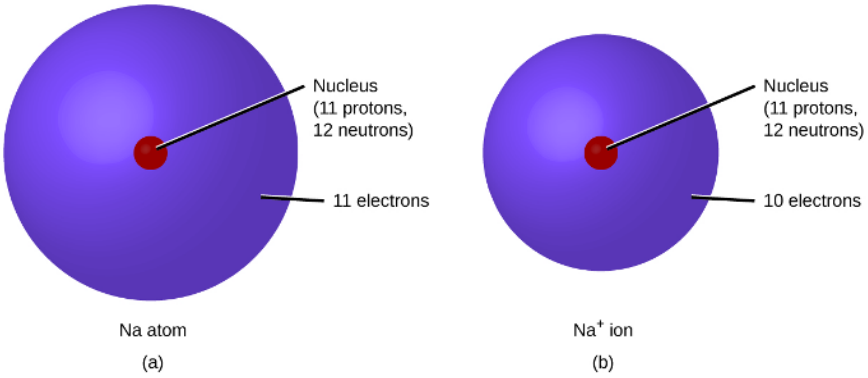


Figure 1.2.7.1: (a) A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. (b) A sodium cation (Na^+) has lost an electron, so it has one more proton (11) than electrons (10), giving it an overall positive charge, signified by a superscripted plus sign.

Figure A shows a sodium atom which has a nucleus containing 11 protons, 12 neutrons, and 11 electrons. Figure B shows a sodium ion. Its nucleus contains 11 protons, 12 neutrons, and 11 electrons.

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^-. (A discussion of the theory supporting the favored status of noble gas electron numbers reflected in these predictive rules for ion formation is provided in a later chapter of this text.)

Note the usefulness of the periodic table in predicting likely ion formation and charge (Figure 1.2.7.2). 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.

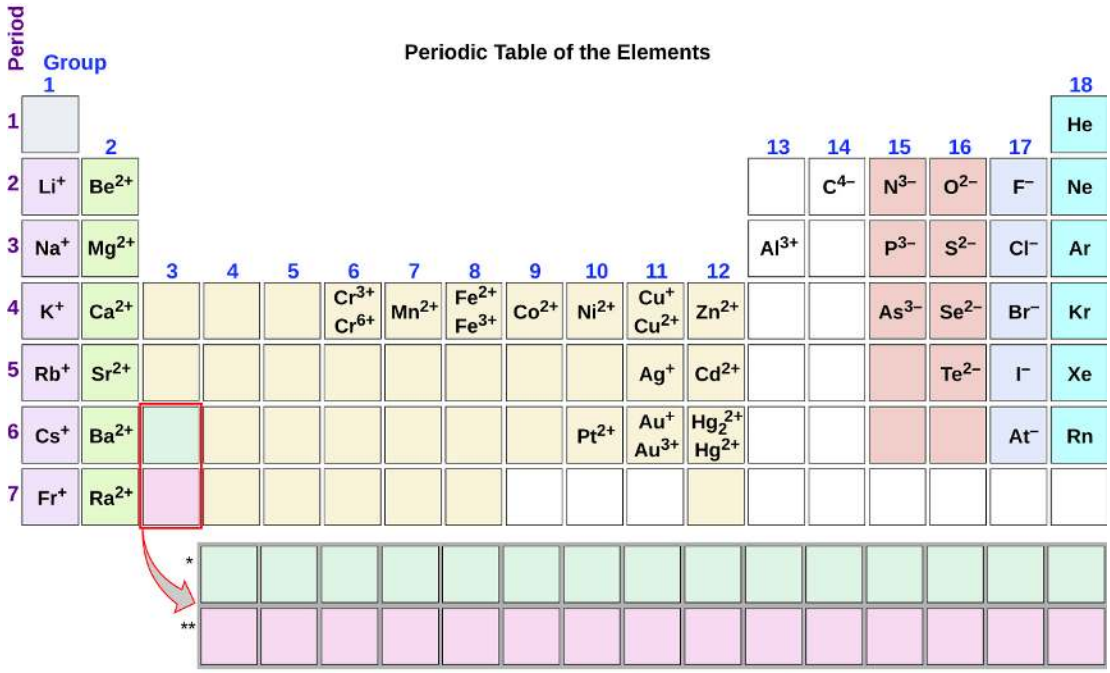


Figure 1.2.7.2: Some elements exhibit a regular pattern of ionic charge when they form ions.

This periodic table shows the charges of ions corresponding with the group number. Starting with a charge of positive one for group 1, positive 2 for group 2, and negative 4, 3, 2, and 1 for groups 14, 15, 16, and 17 respectively. Noble gases on the far right do not have any charges. Some of the ions of transition metals are shown, with multiple charges existing for certain metals.

✔ Example 1.2.7.1: 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+}.

? Exercise 1.2.7.1

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

Answer

Se^{2-}, the selenide ion

✔ Example 1.2.7.2: 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.

? Exercise 1.2.7.2

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.

Answer

Al will form a cation with a charge of 3+: Al^{3+}, an aluminum ion. Carbon will form an anion with a charge of 4−: C^{4-}, a carbide ion.

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 1.2.7.1. 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 1.2.7.1: Common Polyatomic Ions

Name	Formula	Related Acid	Formula
ammonium	NH_4^+		
hydronium	H_3O^+		
oxide	O^{2-}		
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	$HClO_3$

Name	Formula	Related Acid	Formula
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-}. This will be covered in more detail in the next module on nomenclature.

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.

1.2.7.1: 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 (Figure 1.2.7.3).

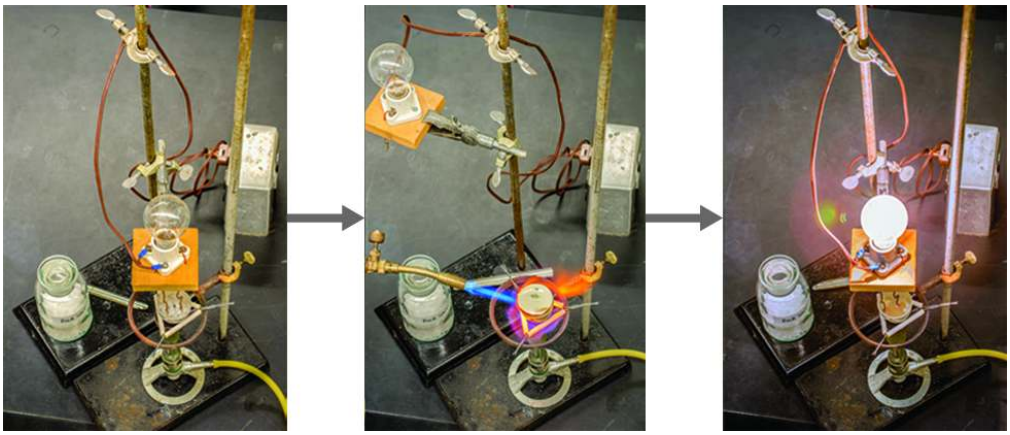


Figure 1.2.7.3: Sodium chloride melts at 801 °C and conducts electricity when molten. (credit: modification of work by Mark Blaser and Matt Evans)

This figure shows three photos connected by right-facing arrows. The first shows a light bulb as part of a complex lab equipment setup. The light bulb is not lit. The second photo shows a substances being heated or set on fire. The third shows the light bulb again which is lit.

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 1.2.7.3: Predicting the Formula of an Ionic Compound

The gemstone sapphire (Figure 1.2.7.4) 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 1.2.7.4: Although pure aluminum oxide is colorless, trace amounts of iron and titanium give blue sapphire its characteristic color. (credit: modification of work by Stanislav Doronenko)

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.

Exercise 1.2.7.3

Predict the formula of the ionic compound formed between the sodium cation, Na^+, and the sulfide anion, S^{2-}.

Answer

Na_2S

Many ionic compounds contain polyatomic ions (Table 1.2.7.1) 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 $\left(PO_4^{3-}\right)$ 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 1.2.7.4: 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 $H_2PO_4^-$. 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 $Ca(H_2PO_4)_2$.

Exercise 1.2.7.4

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.)

Answer

Li_2O_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, $C_2O_4^{2-}$.

1.2.7.2: 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 (gain or lose), 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 text. 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. Shades of gray exist between ionic and molecular compounds, and you'll learn more about those later.

Example 1.2.7.5: 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.

? Exercise 1.2.7.5

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

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

Answer a

molecular

Answer b

ionic

Answer c

molecular

Answer d

ionic

Summary

Metals (particularly those in groups 1 and 2) tend to lose the number of electrons that would leave them with the same number of electrons as in the preceding noble gas in the periodic table. By this means, a positively charged ion is formed. Similarly, nonmetals (especially those in groups 16 and 17, and, to a lesser extent, those in Group 15) can gain the number of electrons needed to provide atoms with the same number of electrons as in the next noble gas in the periodic table. Thus, nonmetals tend to form negative ions. Positively charged ions are called cations, and negatively charged ions are called anions. Ions can be either monatomic (containing only one atom) or polyatomic (containing more than one atom).

Compounds that contain ions are called ionic compounds. Ionic compounds generally form from metals and nonmetals. Compounds that do not contain ions, but instead consist of atoms bonded tightly together in molecules (uncharged groups of atoms that behave as a single unit), are called covalent compounds. Covalent compounds usually form from two or more nonmetals.

Glossary

covalent bond
attractive force between the nuclei of a molecule’s atoms and pairs of electrons between the atoms

covalent compound
(also, molecular compound) composed of molecules formed by atoms of two or more different elements

ionic bond
electrostatic forces of attraction between the oppositely charged ions of an ionic compound

ionic compound
compound composed of cations and anions combined in ratios, yielding an electrically neutral substance

molecular compound

(also, covalent compound) composed of molecules formed by atoms of two or more different elements

monatomic ion

ion composed of a single atom

polyatomic ion

ion composed of more than one atom

oxyanion

polyatomic anion composed of a central atom bonded to oxygen atoms

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1.2.8: Chemical Nomenclature

Learning Objectives

- Derive names for common types of inorganic compounds using a systematic approach.
- Describe how to name binary covalent compounds including acids and oxyacids.

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 text 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.

1.2.8.1: 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. We will begin with the nomenclature rules for ionic compounds.

1.2.8.2: 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 1.2.8.2

Table 1.2.8.1: 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

1.2.8.3: Compounds Containing Polyatomic Ions

Compounds containing polyatomic ions are named similarly to those containing only monatomic ions, except there is no need to change to an *–ide* ending, since the suffix is already present in the name of the anion. Examples are shown in Table 1.2.8.2

CL, ammonium chloride, C a S O subscript 4 calcium sulfate, and M g subscript 3 (P O subscript 4) subscript 2 magnesium phosphate." data-quail-id="54" data-mt-width="1246">

Table 1.2.8.2: Names of Some Polyatomic Ionic Compounds

$KC_2H_3O_2$, potassium acetate	$(NH_4)Cl$, ammonium chloride
$NaHCO_3$, sodium bicarbonate	$CaSO_4$, calcium sulfate
$Al_2(CO_3)_3$, aluminum carbonate	$Mg_3(PO_4)_2$, magnesium phosphate

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 1.2.8.3 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 1.2.8.3: Everyday Ionic Compounds

Ionic Compound	Name	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 in antacids)
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

1.2.8.4: Compounds Containing a Metal Ion with a Variable Charge

Most of the transition 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+, 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 1.2.8.4

Table 1.2.8.4: Names of Some Transition Metal Ionic Compounds

Transition Metal Ionic Compound	Name
$FeCl_3$	iron(III) chloride
Hg_2O	mercury(I) oxide
HgO	mercury(II) oxide
$Cu_3(PO_4)_2$	copper(II) phosphate

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.

Example 1.2.8.1: Naming Ionic Compounds

Name the following ionic compounds, which contain a metal that can have more than one ionic charge:

a. Fe_2S_3
b. CuSe
c. GaN
d. $CrCl_3$
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-}), 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. chromium(III) chloride
e. titanium(III) sulfate

Exercise 1.2.8.1

Write the formulas of the following ionic compounds:

a. chromium(III) phosphide
b. mercury(II) sulfide
c. manganese(II) phosphate
d. copper(I) oxide
e. chromium(VI) fluoride

Answer a

CrP

Answer b

HgS

Answer c

$Mn_3(PO_4)_2$

Answer d

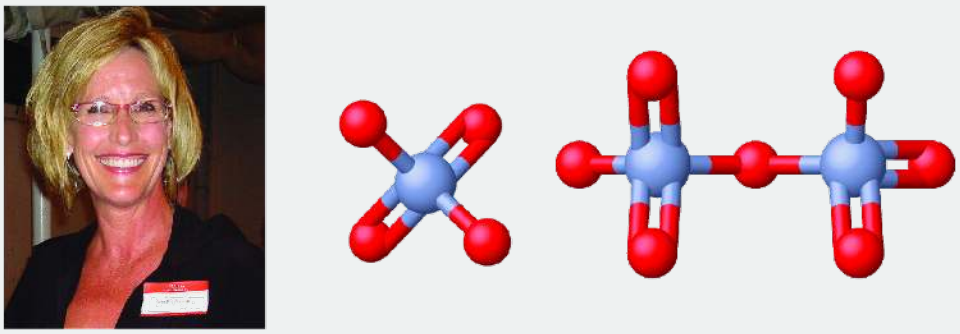
Cu_2O

Answer e

CrF_6

Erin Brokovich and Chromium Contamination

In the early 1990s, legal file clerk Erin Brockovich (Figure 1.2.8.2) discovered a high rate of serious illnesses in the small town of Hinckley, California. Her investigation eventually linked the illnesses to groundwater contaminated by Cr(VI) used by Pacific Gas & Electric (PG&E) to fight corrosion in a nearby natural gas pipeline. As dramatized in the film *Erin Brokovich* (for which Julia Roberts won an Oscar), Erin and lawyer Edward Masry sued PG&E for contaminating the water near Hinckley in 1993. The settlement they won in 1996—$333 million—was the largest amount ever awarded for a direct-action lawsuit in the US at that time.



(a) (b)

Figure **1.2.8.2**: (a) Erin Brockovich found that Cr(VI), used by PG&E, had contaminated the Hinckley, California, water supply. (b) The Cr(VI) ion is often present in water as the polyatomic ions chromate, CrO_4^{2-} (left), and dichromate, $Cr_2O_7^{2-}$ (right).

Chromium compounds are widely used in industry, such as for chrome plating, in dye-making, as preservatives, and to prevent corrosion in cooling tower water, as occurred near Hinckley. In the environment, chromium exists primarily in either the Cr(III) or Cr(VI) forms. Cr(III), an ingredient of many vitamin and nutritional supplements, forms compounds that are not very soluble in water, and it has low toxicity. Cr(VI), on the other hand, is much more toxic and forms compounds that are reasonably soluble in water. Exposure to small amounts of Cr(VI) can lead to damage of the respiratory, gastrointestinal, and immune systems, as well as the kidneys, liver, blood, and skin.

Despite cleanup efforts, Cr(VI) groundwater contamination remains a problem in Hinckley and other locations across the globe. A 2010 study by the Environmental Working Group found that of 35 US cities tested, 31 had higher levels of Cr(VI) in their tap water than the public health goal of 0.02 parts per billion set by the California Environmental Protection Agency.

1.2.8.5: Molecular (Covalent) 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.

1.2.8.6: 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 1.2.8.5

Table 1.2.8.5: Nomenclature Prefixes

Number	Prefix	Number	Prefix

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-

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 1.2.8.6

Table 1.2.8.6: 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 1.2.8.2: Naming Covalent Compounds

Name the following covalent compounds:

a. SF_6
b. N_2O_3
c. Cl_2O_7
d. P_4O_6

Solution

Because these compounds consist solely of nonmetals, we use prefixes to designate the number of atoms of each element:

a. sulfur hexafluoride
b. dinitrogen trioxide
c. dichlorine heptoxide
d. tetraphosphorus hexoxide

? Exercise 1.2.8.2

Write the formulas for the following compounds:

a. phosphorus pentachloride
b. dinitrogen monoxide
c. iodine heptafluoride
d. carbon tetrachloride

Answer a

PCl_5

Answer b

N_2O

Answer c

IF_7

Answer d

CCl_4

1.2.8.7: Binary Acids

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

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

For example, when the gas HCl (hydrogen chloride) is dissolved in water, the solution is called *hydrochloric acid*. Several other examples of this nomenclature are shown in Table 1.2.8.7.

Table 1.2.8.7: 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

1.2.8.8: Oxyacids

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

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

For example, consider H_2CO_3 (which you might be tempted to call "hydrogen carbonate"). To name this correctly, "hydrogen" is omitted; the *–ate* of carbonate is replace with *–ic*; and acid is added—so its name is carbonic acid. Other examples are given in Table 1.2.8.8 There are some exceptions to the general naming method (e.g., H_2SO_4 is called sulfuric acid, not sulfic acid, and H_2SO_3 is sulfurous, not sulfous, acid).

Table 1.2.8.8: Names of Common Oxyacids

Formula	Anion Name	Acid Name
$HC_2H_3O_2$	acetate	acetic acid
HNO_3	nitrate	nitric acid
HNO_2	nitrite	nitrous acid
$HClO_4$	perchlorate	perchloric acid
H_2CO_3	carbonate	carbonic acid
H_2SO_4	sulfate	sulfuric acid
H_2SO_3	sulfite	sulfurous acid
H_3PO_4	phosphate	phosphoric acid

Summary

Chemists use nomenclature rules to clearly name compounds. Ionic and molecular compounds are named using somewhat-different methods. Binary ionic compounds typically consist of a metal and a nonmetal. The name of the metal is written first, followed by the name of the nonmetal with its ending changed to *–ide*. For example, K_2O is called potassium oxide. If the metal can form ions with different charges, a Roman numeral in parentheses follows the name of the metal to specify its charge. Thus, $FeCl_2$ is iron(II) chloride and $FeCl_3$ is iron(III) chloride. Some compounds contain polyatomic ions; the names of common polyatomic ions should be memorized. Molecular compounds can form compounds with different ratios of their elements, so prefixes are used to specify the numbers of atoms of each element in a molecule of the compound. Examples include SF_6, sulfur hexafluoride, and N_2O_4, dinitrogen tetroxide. Acids are an important class of compounds containing hydrogen and having special nomenclature rules. Binary acids are named using the prefix *hydro-*, changing the *–ide* suffix to *–ic*, and adding "acid;" HCl is hydrochloric acid. Oxyacids are named by changing the ending of the anion (*-ate* to *–ic*, and *-ite* to *-ous*) and adding "acid;" H_2CO_3 is carbonic acid.

Glossary

binary acid

compound that contains hydrogen and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H^+ ions when dissolved in water)

binary compound

compound containing two different elements.

oxyacid

compound that contains hydrogen, oxygen, and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H^+ ions when dissolved in water)

nomenclature

system of rules for naming objects of interest

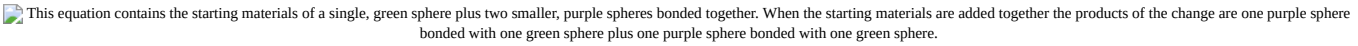
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1.2.E: Atoms, Molecules, and Ions (Exercises)

2.1: Early Ideas in Atomic Theory

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


This equation contains the starting materials of a single, green sphere plus two smaller, purple spheres bonded together. When the starting materials are added together the products of the change are one purple sphere bonded with one green sphere plus one purple sphere bonded with one green sphere.

The starting materials consist of one green sphere and two purple spheres. The products consist of two green spheres and two purple spheres. This violates Dalton's postulate that that atoms are not created during a chemical change, but are merely redistributed.

Which postulate of Dalton's theory is consistent with the following observation concerning the weights of reactants and products? When 100 grams of solid calcium carbonate is heated, 44 grams of carbon dioxide and 56 grams of calcium oxide are produced.

Identify the postulate of Dalton's theory that is violated by the following observations: 59.95% of one sample of titanium dioxide is titanium; 60.10% of a different sample of titanium dioxide is titanium.

This statement violates Dalton's fourth postulate: In a given compound, the numbers of atoms of each type (and thus also the percentage) always have the same ratio.

Samples of compound X, Y, and Z are analyzed, with results shown here.

Compound	Description	Mass of Carbon	Mass of Hydrogen
X	clear, colorless, liquid with strong odor	1.776 g	0.148 g
Y	clear, colorless, liquid with strong odor	1.974 g	0.329 g
Z	clear, colorless, liquid with strong odor	7.812 g	0.651 g

Do these data provide example(s) of the law of definite proportions, the law of multiple proportions, neither, or both? What do these data tell you about compounds X, Y, and Z?

2.2: Evolution of Atomic Theory

Exercises

1. The existence of isotopes violates one of the original ideas of Dalton's atomic theory. Which one?
2. How are electrons and protons similar? How are they different?
3. How are protons and neutrons similar? How are they different?
4. Predict and test the behavior of α particles fired at a "plum pudding" model atom.
    a. Predict the paths taken by α particles that are fired at atoms with a Thomson's plum pudding model structure. Explain why you expect the α particles to take these paths.
    b. If α particles of higher energy than those in (a) are fired at plum pudding atoms, predict how their paths will differ from the lower-energy α particle paths. Explain your reasoning.
    c. Now test your predictions from (a) and (b). Open the Rutherford Scattering simulation and select the "Plum Pudding Atom" tab. Set "Alpha Particles Energy" to "min," and select "show traces." Click on the gun to start firing α particles. Does this match your prediction from (a)? If not, explain why the actual path would be that shown in the simulation. Hit the pause button, or "Reset All." Set "Alpha Particles Energy" to "max," and start firing α particles. Does this match your prediction from (b)? If not, explain the effect of increased energy on the actual paths as shown in the simulation.
5. Predict and test the behavior of α particles fired at a Rutherford atom model.

a. (a) Predict the paths taken by α particles that are fired at atoms with a Rutherford atom model structure. Explain why you expect the α particles to take these paths.
b. (b) If α particles of higher energy than those in (a) are fired at Rutherford atoms, predict how their paths will differ from the lower-energy α particle paths. Explain your reasoning.
c. (c) Predict how the paths taken by the α particles will differ if they are fired at Rutherford atoms of elements other than gold. What factor do you expect to cause this difference in paths, and why?
d. (d) Now test your predictions from (a), (b), and (c). Open the Rutherford Scattering simulation and select the "Rutherford Atom" tab. Due to the scale of the simulation, it is best to start with a small nucleus, so select "20" for both protons and neutrons, "min" for energy, show traces, and then start firing α particles. Does this match your prediction from (a)? If not, explain why the actual path would be that shown in the simulation. Pause or reset, set energy to "max," and start firing α particles. Does this match your prediction from (b)? If not, explain the effect of increased energy on the actual path as shown in the simulation. Pause or reset, select "40" for both protons and neutrons, "min" for energy, show traces, and fire away. Does this match your prediction from (c)? If not, explain why the actual path would be that shown in the simulation. Repeat this with larger numbers of protons and neutrons. What generalization can you make regarding the type of atom and effect on the path of α particles? Be clear and specific.

Solutions

1 Dalton originally thought that all atoms of a particular element had identical properties, including mass. Thus, the concept of isotopes, in which an element has different masses, was a violation of the original idea. To account for the existence of isotopes, the second postulate of his atomic theory was modified to state that atoms of the same element must have identical chemical properties.

2 Both are subatomic particles that reside in an atom's nucleus. Both have approximately the same mass. Protons are positively charged, whereas neutrons are uncharged.

3 Both are subatomic particles that reside in an atom's nucleus. Both have approximately the same mass. Protons are positively charged, whereas neutrons are uncharged.

4. (a) The plum pudding model indicates that the positive charge is spread uniformly throughout the atom, so we expect the α particles to (perhaps) be slowed somewhat by the positive-positive repulsion, but to follow straight-line paths (i.e., not to be deflected) as they pass through the atoms. (b) Higher-energy α particles will be traveling faster (and perhaps slowed less) and will also follow straight-line paths through the atoms. (c) The α particles followed straight-line paths through the plum pudding atom. There was no apparent slowing of the α particles as they passed through the atoms.

5. (a) The Rutherford atom has a small, positively charged nucleus, so most α particles will pass through empty space far from the nucleus and be undeflected. Those α particles that pass near the nucleus will be deflected from their paths due to positive-positive repulsion. The more directly toward the nucleus the α particles are headed, the larger the deflection angle will be. (b) Higher-energy α particles that pass near the nucleus will still undergo deflection, but the faster they travel, the less the expected angle of deflection. (c) If the nucleus is smaller, the positive charge is smaller and the expected deflections are smaller—both in terms of how closely the α particles pass by the nucleus undeflected and the angle of deflection. If the nucleus is larger, the positive charge is larger and the expected deflections are larger—more α particles will be deflected, and the deflection angles will be larger. (d) The paths followed by the α particles match the predictions from (a), (b), and (c).

2.3: Atomic Structure and Symbolism

In what way are isotopes of a given element always different? In what way(s) are they always the same?

Write the symbol for each of the following ions:

1. (a) the ion with a 1+ charge, atomic number 55, and mass number 133
2. (b) the ion with 54 electrons, 53 protons, and 74 neutrons
3. (c) the ion with atomic number 15, mass number 31, and a 3− charge
4. (d) the ion with 24 electrons, 30 neutrons, and a 3+ charge

1.

(a) $^{133}Cs^{+}$; (b) $^{127}I^{-}$; (c) $^{31}P^{3-}$; (d) $^{57}Co^{3+}$

Write the symbol for each of the following ions:

1. (a) the ion with a 3+ charge, 28 electrons, and a mass number of 71

2. (b) the ion with 36 electrons, 35 protons, and 45 neutrons
3. (c) the ion with 86 electrons, 142 neutrons, and a 4+ charge
4. (d) the ion with a 2+ charge, atomic number 38, and mass number 87

Open the Build an Atom simulation and click on the Atom icon.

1. (a) Pick any one of the first 10 elements that you would like to build and state its symbol.
2. (b) Drag protons, neutrons, and electrons onto the atom template to make an atom of your element. State the numbers of protons, neutrons, and electrons in your atom, as well as the net charge and mass number.
3. (c) Click on “Net Charge” and “Mass Number,” check your answers to (b), and correct, if needed.
4. (d) Predict whether your atom will be stable or unstable. State your reasoning.
5. (e) Check the “Stable/Unstable” box. Was your answer to (d) correct? If not, first predict what you can do to make a stable atom of your element, and then do it and see if it works. Explain your reasoning.

(a) Carbon-12, ^{12}C; (b) This atom contains six protons and six neutrons. There are six electrons in a neutral ^{12}C atom. The net charge of such a neutral atom is zero, and the mass number is 12. (c) The preceding answers are correct. (d) The atom will be stable since C-12 is a stable isotope of carbon. (e) The preceding answer is correct. Other answers for this exercise are possible if a different element of isotope is chosen.

Open the Build an Atom simulation

(a) Drag protons, neutrons, and electrons onto the atom template to make a neutral atom of Oxygen-16 and give the isotope symbol for this atom.

(b) Now add two more electrons to make an ion and give the symbol for the ion you have created.

Open the Build an Atom simulation

(a) Drag protons, neutrons, and electrons onto the atom template to make a neutral atom of Lithium-6 and give the isotope symbol for this atom.

(b) Now remove one electron to make an ion and give the symbol for the ion you have created.

(a) Lithium-6 contains three protons, three neutrons, and three electrons. The isotope symbol is ^{6}Li or $^{6}_{3}Li$. (b) $^{6}Li^{+}$ or $^{6}_{3}Li^{+}$

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).

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−

(a) Iron, 26 protons, 24 electrons, and 32 neutrons; (b) iodine, 53 protons, 54 electrons, and 74 neutrons

Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes:

(a) $^{10}_{5}B$

(b) $^{199}_{80}Hg$

(c) $^{63}_{29}Cu$

(d) $^{13}_{6}C$

(e) $^{77}_{34}Se$

Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes:

(a) $^{7}_{3}\mathrm{Li}$

(b) $^{125}_{52}\mathrm{Te}$

(c) $^{109}_{47}\mathrm{Ag}$

(d) $^{15}_{7}\mathrm{N}$

(e) $^{31}_{15}\mathrm{P}$

(a) 3 protons, 3 electrons, 4 neutrons; (b) 52 protons, 52 electrons, 73 neutrons; (c) 47 protons, 47 electrons, 62 neutrons; (d) 7 protons, 7 electrons, 8 neutrons; (e) 15 protons, 15 electrons, 16 neutrons

Click on the site and select the “Mix Isotopes” tab, hide the “Percent Composition” and “Average Atomic Mass” boxes, and then select the element boron.

(a) Write the symbols of the isotopes of boron that are shown as naturally occurring in significant amounts.

(b) Predict the relative amounts (percentages) of these boron isotopes found in nature. Explain the reasoning behind your choice.

(c) Add isotopes to the black box to make a mixture that matches your prediction in (b). You may drag isotopes from their bins or click on “More” and then move the sliders to the appropriate amounts.

(d) Reveal the “Percent Composition” and “Average Atomic Mass” boxes. How well does your mixture match with your prediction? If necessary, adjust the isotope amounts to match your prediction.

(e) Select “Nature’s” mix of isotopes and compare it to your prediction. How well does your prediction compare with the naturally occurring mixture? Explain. If necessary, adjust your amounts to make them match “Nature’s” amounts as closely as possible.

Repeat Exercise using an element that has three naturally occurring isotopes.

Let us use neon as an example. Since there are three isotopes, there is no way to be sure to accurately predict the abundances to make the total of 20.18 amu average atomic mass. Let us guess that the abundances are 9% Ne-22, 91% Ne-20, and only a trace of Ne-21. The average mass would be 20.18 amu. Checking the nature’s mix of isotopes shows that the abundances are 90.48% Ne-20, 9.25% Ne-22, and 0.27% Ne-21, so our guessed amounts have to be slightly adjusted.

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.

Average atomic masses listed by IUPAC are based on a study of experimental results. Bromine has two isotopes ^{79}Br and ^{81}Br, whose masses (78.9183 and 80.9163 amu) and abundances (50.69% and 49.31%) were determined in earlier experiments. Calculate the average atomic mass of bromine based on these experiments.

79.904 amu

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.

The average atomic masses of some elements may vary, depending upon the sources of their ores. Naturally occurring boron consists of two isotopes with accurately known masses (^{10}B, 10.0129 amu and ^{11}B, 11.0931 amu). The actual atomic mass of boron can vary from 10.807 to 10.819, depending on whether the mineral source is from Turkey or the United States. Calculate the percent abundances leading to the two values of the average atomic masses of boron from these two countries.

Turkey source: 0.2649 (of 10.0129 amu isotope); US source: 0.2537 (of 10.0129 amu isotope)

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?

2.4: Chemical Formulas

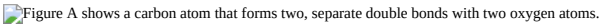
Explain why the symbol for an atom of the element oxygen and the formula for a molecule of oxygen differ.

The symbol for the element oxygen, O, represents both the element and one atom of oxygen. A molecule of oxygen, O_2, contains two oxygen atoms; the subscript 2 in the formula must be used to distinguish the diatomic molecule from two single oxygen atoms.

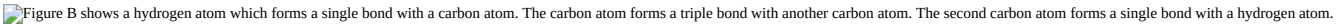
Explain why the symbol for the element sulfur and the formula for a molecule of sulfur differ.

Write the molecular and empirical formulas of the following compounds:

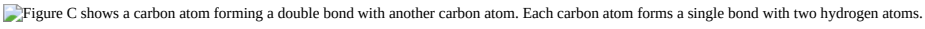
(a)


Figure A shows a carbon atom that forms two, separate double bonds with two oxygen atoms.

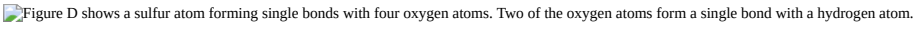
(b)


Figure B shows a hydrogen atom which forms a single bond with a carbon atom. The carbon atom forms a triple bond with another carbon atom. The second carbon atom forms a single bond with a hydrogen atom.

(c)


Figure C shows a carbon atom forming a double bond with another carbon atom. Each carbon atom forms a single bond with two hydrogen atoms.

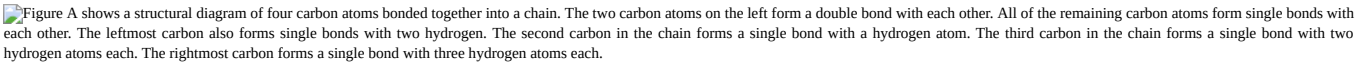
(d)


Figure D shows a sulfur atom forming single bonds with four oxygen atoms. Two of the oxygen atoms form a single bond with a hydrogen atom.

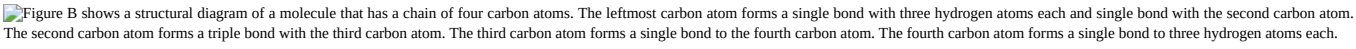
(a) molecular CO_2, empirical CO_2; (b) molecular C_2H_2, empirical CH; (c) molecular C_2H_4, empirical CH_2; (d) molecular H_2SO_4, empirical H_2SO_4

Write the molecular and empirical formulas of the following compounds:

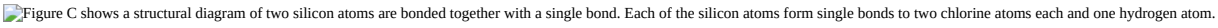
(a)


Figure A shows a structural diagram of four carbon atoms bonded together into a chain. The two carbon atoms on the left form a double bond with each other. All of the remaining carbon atoms form single bonds with each other. The leftmost carbon also forms single bonds with two hydrogen. The second carbon in the chain forms a single bond with a hydrogen atom. The third carbon in the chain forms a single bond with two hydrogen atoms each. The rightmost carbon forms a single bond with three hydrogen atoms each.

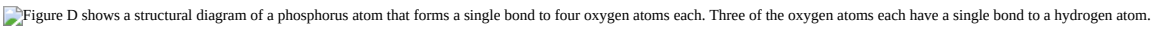
(b)


Figure B shows a structural diagram of a molecule that has a chain of four carbon atoms. The leftmost carbon atom forms a single bond with three hydrogen atoms each and single bond with the second carbon atom. The second carbon atom forms a triple bond with the third carbon atom. The third carbon atom forms a single bond to the fourth carbon atom. The fourth carbon atom forms a single bond to three hydrogen atoms each.

(c)


Figure C shows a structural diagram of two silicon atoms are bonded together with a single bond. Each of the silicon atoms form single bonds to two chlorine atoms each and one hydrogen atom.

(d)


Figure D shows a structural diagram of a phosphorus atom that forms a single bond to four oxygen atoms each. Three of the oxygen atoms each have a single bond to a hydrogen atom.

Determine the empirical formulas for the following compounds:

1. (a) caffeine, $C_8H_{10}N_4O_2$
2. (b) fructose, $C_{12}H_{22}O_{11}$
3. (c) hydrogen peroxide, H_2O_2
4. (d) glucose, $C_6H_{12}O_6$
5. (e) ascorbic acid (vitamin C), $C_6H_8O_6$

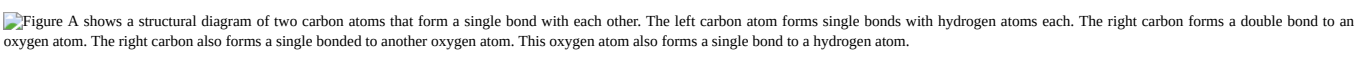
(a) $C_4H_5N_2O$; (b) $C_{12}H_{22}O_{11}$; (c) HO; (d) CH_2O; (e) $C_3H_4O_3$

Determine the empirical formulas for the following compounds:

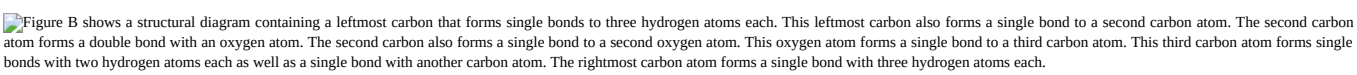
1. (a) acetic acid, $C_2H_4O_2$
2. (b) citric acid, $C_6H_8O_7$
3. (c) hydrazine, N_2H_4
4. (d) nicotine, $C_{10}H_{14}N_2$
5. (e) butane, C_4H_{10}

Write the empirical formulas for the following compounds:

(a)


Figure A shows a structural diagram of two carbon atoms that form a single bond with each other. The left carbon atom forms single bonds with hydrogen atoms each. The right carbon forms a double bond to an oxygen atom. The right carbon also forms a single bonded to another oxygen atom. This oxygen atom also forms a single bond to a hydrogen atom.

(b)


Figure B shows a structural diagram containing a leftmost carbon that forms single bonds to three hydrogen atoms each. This leftmost carbon also forms a single bond to a second carbon atom. The second carbon atom forms a double bond with an oxygen atom. The second carbon also forms a single bond to a second oxygen atom. This oxygen atom forms a single bond to a third carbon atom. This third carbon atom forms single bonds with two hydrogen atoms each as well as a single bond with another carbon atom. The rightmost carbon atom forms a single bond with three hydrogen atoms each.

(a) CH_2O; (b) C_2H_4O

Open the Build a Molecule simulation and select the “Larger Molecules” tab. Select an appropriate atoms “Kit” to build a molecule with two carbon and six hydrogen atoms. Drag atoms into the space above the “Kit” to make a molecule. A name will appear when you have made an actual molecule that exists (even if it is not the one you want). You can use the scissors tool to separate atoms if you would like to change the connections. Click on “3D” to see the molecule, and look at both the space-filling and ball-and-stick possibilities.

1. (a) Draw the structural formula of this molecule and state its name.
2. (b) Can you arrange these atoms in any way to make a different compound?

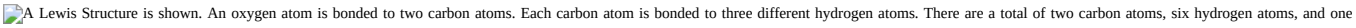
Use the Build a Molecule simulation to repeat Exercise, but build a molecule with two carbons, six hydrogens, and one oxygen.

1. (a) Draw the structural formula of this molecule and state its name.
2. (b) Can you arrange these atoms to make a different molecule? If so, draw its structural formula and state its name.
3. (c) How are the molecules drawn in (a) and (b) the same? How do they differ? What are they called (the type of relationship between these molecules, not their names).

(a) ethanol


A Lewis Structure is shown. An oxygen atom is bonded to a hydrogen atom and a carbon atom. The carbon atom is bonded to two hydrogen atoms and another carbon atom. That carbon atom is bonded to three more hydrogen atoms. There are a total of two carbon atoms, six hydrogen atoms, and one oxygen atoms.

(b) methoxymethane, more commonly known as dimethyl ether


A Lewis Structure is shown. An oxygen atom is bonded to two carbon atoms. Each carbon atom is bonded to three different hydrogen atoms. There are a total of two carbon atoms, six hydrogen atoms, and one oxygen atom.

(c) These molecules have the same chemical composition (types and number of atoms) but different chemical structures. They are structural isomers.

Use the Build a Molecule simulation to repeat Exercise, but build a molecule with three carbons, seven hydrogens, and one chlorine.

a. Draw the structural formula of this molecule and state its name.
b. Can you arrange these atoms to make a different molecule? If so, draw its structural formula and state its name.
c. How are the molecules drawn in (a) and (b) the same? How do they differ? What are they called (the type of relationship between these molecules, not their names)?

2.5: The Periodic Table

Using the periodic table, classify each of the following elements as a metal or a nonmetal, and then further classify each as a main-group (representative) element, transition metal, or inner transition metal:

a. uranium
b. bromine
c. strontium
d. neon
e. gold
f. americium
g. rhodium
h. sulfur
i. carbon
j. potassium

(a) metal, inner transition metal; (b) nonmetal, representative element; (c) metal, representative element; (d) nonmetal, representative element; (e) metal, transition metal; (f) metal, inner transition metal; (g) metal, transition metal; (h) nonmetal, representative element; (i) nonmetal, representative element; (j) metal, representative element

Using the periodic table, classify each of the following elements as a metal or a nonmetal, and then further classify each as a main-group (representative) element, transition metal, or inner transition metal:

1. (a) cobalt
2. (b) europium

3. (c) iodine
4. (d) indium
5. (e) lithium
6. (f) oxygen
7. (g) cadmium
8. (h) terbium
9. (i) rhenium

Using the periodic table, identify the lightest member of each of the following groups:

1. (a) noble gases
2. (b) alkaline earth metals
3. (c) alkali metals
4. (d) chalcogens

(a) He; (b) Be; (c) Li; (d) O

Using the periodic table, identify the heaviest member of each of the following groups:

1. (a) alkali metals
2. (b) chalcogens
3. (c) noble gases
4. (d) alkaline earth metals

1. Use the periodic table to give the name and symbol for each of the following elements:
2. (a) the noble gas in the same period as germanium
3. (b) the alkaline earth metal in the same period as selenium
4. (c) the halogen in the same period as lithium
5. (d) the chalcogen in the same period as cadmium

(a) krypton, Kr; (b) calcium, Ca; (c) fluorine, F; (d) tellurium, Te

Use the periodic table to give the name and symbol for each of the following elements:

1. (a) the halogen in the same period as the alkali metal with 11 protons
2. (b) the alkaline earth metal in the same period with the neutral noble gas with 18 electrons
3. (c) the noble gas in the same row as an isotope with 30 neutrons and 25 protons
4. (d) the noble gas in the same period as gold

Write a symbol for each of the following neutral isotopes. Include the atomic number and mass number for each.

1. (a) the alkali metal with 11 protons and a mass number of 23
2. (b) the noble gas element with and 75 neutrons in its nucleus and 54 electrons in the neutral atom
3. (c) the isotope with 33 protons and 40 neutrons in its nucleus
4. (d) the alkaline earth metal with 88 electrons and 138 neutrons

(a) $^{23}_{11}\mathrm{Na}$; (b) $^{129}_{54}\mathrm{Xe}$; (c) $^{73}_{33}\mathrm{As}$; (d) $^{226}_{88}\mathrm{Ra}$

Write a symbol for each of the following neutral isotopes. Include the atomic number and mass number for each.

1. (a) the chalcogen with a mass number of 125
2. (b) the halogen whose longest-lived isotope is radioactive
3. (c) the noble gas, used in lighting, with 10 electrons and 10 neutrons
4. (d) the lightest alkali metal with three neutrons

2.6: Molecular and Ionic Compounds

Using the periodic table, predict whether the following chlorides are ionic or covalent: KCl, NCl_3, ICl, $MgCl_2$, PCl_5, and CCl_4.

Ionic: KCl, $MgCl_2$; Covalent: NCl_3, ICl, PCl_5, CCl_4

Using the periodic table, predict whether the following chlorides are ionic or covalent: $SiCl_4$, PCl_3, $CaCl_2$, CsCl, $CuCl_2$, and $CrCl_3$.

For each of the following compounds, state whether it is ionic or covalent. If it is ionic, write the symbols for the ions involved:

1. (a) NF_3
2. (b) BaO,
3. (c) $(NH_4)_2CO_3$
4. (d) $Sr(H_2PO_4)_2$
5. (e) IBr
6. (f) Na_2O

(a) covalent; (b) ionic, Ba^{2+}, O^{2-}; (c) ionic, NH_4^+, CO_3^{2-}; (d) ionic, Sr^{2+}, $H_2PO_4^-$; (e) covalent; (f) ionic, Na^+, O^{2-}

For each of the following compounds, state whether it is ionic or covalent, and if it is ionic, write the symbols for the ions involved:

1. (a) $KClO_4$
2. (b) $MgC_2H_3O_2$
3. (c) H_2S
4. (d) Ag_2S
5. (e) N_2Cl_4
6. (f) $Co(NO_3)_2$

For each of the following pairs of ions, write the symbol for the formula of the compound they will form:

1. (a) Ca^{2+}, S^{2-}
2. (b) NH_4^+, SO_4^{2-}
3. (c) Al^{3+}, Br^-
4. (d) Na^+, HPO_4^{2-}
5. (e) Mg^{2+}, PO_4^{3-}

(a) CaS; (b) $(NH_4)_2CO_3$; (c) $AlBr_3$; (d) Na_2HPO_4; (e) $Mg_3(PO_4)_2$

For each of the following pairs of ions, write the symbol for the formula of the compound they will form:

1. (a) K^+, O^{2-}
2. (b) NH_4^+, PO_4^{3-}
3. (c) Al^{3+}, O^{2-}
4. (d) Na^+, CO_3^{2-}
5. (e) Ba^{2+}, PO_4^{3-}

2.7: Chemical Nomenclature

Name the following compounds:

1. (a) CsCl
2. (b) BaO
3. (c) K_2S
4. (d) $BeCl_2$
5. (e) HBr
6. (f) AlF_3

(a) cesium chloride; (b) barium oxide; (c) potassium sulfide; (d) beryllium chloride; (e) hydrogen bromide; (f) aluminum fluoride

Name the following compounds:

1. (a) NaF
2. (b) Rb_2O
3. (c) BCl_3
4. (d) H_2Se
5. (e) P_4O_6
6. (f) ICl_3

Write the formulas of the following compounds:

1. (a) rubidium bromide
2. (b) magnesium selenide

3. (c) sodium oxide
4. (d) calcium chloride
5. (e) hydrogen fluoride
6. (f) gallium phosphide
7. (g) aluminum bromide
8. (h) ammonium sulfate

(a) RbBr; (b) MgSe; (c) Na_2O; (d) $CaCl_2$; (e) HF; (f) GaP; (g) $AlBr_3$; (h) $(NH_4)_2SO_4$

Write the formulas of the following compounds:

1. (a) lithium carbonate
2. (b) sodium perchlorate
3. (c) barium hydroxide
4. (d) ammonium carbonate
5. (e) sulfuric acid
6. (f) calcium acetate
7. (g) magnesium phosphate
8. (h) sodium sulfite

Write the formulas of the following compounds:

1. (a) chlorine dioxide
2. (b) dinitrogen tetraoxide
3. (c) potassium phosphide
4. (d) silver(I) sulfide
5. (e) aluminum nitride
6. (f) silicon dioxide

(a) ClO_2; (b) N_2O_4; (c) K_3P; (d) Ag_2S; (e) AlN; (f) SiO_2

Write the formulas of the following compounds:

1. (a) barium chloride
2. (b) magnesium nitride
3. (c) sulfur dioxide
4. (d) nitrogen trichloride
5. (e) dinitrogen trioxide
6. (f) tin(IV) chloride

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

1. (a) Cr_2O_3
2. (b) $FeCl_2$
3. (c) CrO_3
4. (d) $TiCl_4$
5. (e) CoO
6. (f) MoS_2

(a) chromium(III) oxide; (b) iron(II) chloride; (c) chromium(VI) oxide; (d) titanium(IV) chloride; (e) cobalt(II) oxide; (f) molybdenum(IV) sulfide

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

1. (a) $NiCO_3$
2. (b) MoO_3
3. (c) $Co(NO_3)_2$
4. (d) V_2O_5
5. (e) MnO_2
6. (f) Fe_2O_3

The following ionic compounds are found in common household products. Write the formulas for each compound:

1. (a) potassium phosphate
2. (b) copper(II) sulfate
3. (c) calcium chloride
4. (d) titanium dioxide
5. (e) ammonium nitrate
6. (f) sodium bisulfate (the common name for sodium hydrogen sulfate)

(a) K_3PO_4; (b) $CuSO_4$; (c) $CaCl_2$; (d) TiO_2; (e) NH_4NO_3; (f) $NaHSO_4$

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

1. (a) $Ca(H_2PO_4)_2$
2. (b) $FeSO_4$
3. (c) $CaCO_3$
4. (d) MgO
5. (e) $NaNO_2$
6. (f) KI

What are the IUPAC names of the following compounds?

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

(a) manganese(IV) oxide; (b) mercury(I) chloride; (c) iron(III) nitrate; (d) titanium(IV) chloride; (e) copper(II) bromide

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1.2.S: Atoms, Molecules, and Ions (Study Guide)

This chapter introduced some of the fundamental concepts of chemistry, with particular attention to the basic properties of atoms and elements. These entities are the building blocks of all substances we encounter, yet most common substances do not consist of only pure elements or individual atoms. Instead, nearly all substances are chemical compounds or mixtures of chemical compounds. Although there are only about 115 elements (of which about 86 occur naturally), millions of chemical compounds are known, with a tremendous range of physical and chemical properties. Consequently, a major emphasis of modern chemistry focuses on understanding the relationship between the structures and properties of chemical compounds.

1.2.2: Early Ideas in Atomic Theory

- Dalton's atomic theory of matter:
  1. Each element is composed of extremely small particles called atoms
  2. All atoms of a given element are identical; the atoms of different elements are different and have different properties
  3. Atoms of an element are not changed into different types of atoms by chemical reactions
  4. Compounds are formed when atoms of more than one element combine
- explains the law of constant composition, law of conservation of mass

1.2.3: Evolution of Atomic Theory

- subatomic particles – what atoms are composed of
- Like charges repel each other; unlike charges attract

Cathode Rays and Electrons

- cathode rays – radiation resulting from a high voltage
- cause certain materials to give off light (fluoresce)
- mass of an electron $9.10939*10^{-28}$g
- 2000 times smaller than hydrogen

1.2.2 Radioactivity

- radioactivity – spontaneous emission of radiation
- three types of radiation: alpha (a), beta (b), gamma (g)
- alpha and beta radiation are affected by an electric field
- beta particles have a charge of 1-
- alpha particles have a charge of 2+
- gamma radiation has no particles and no charge

1.2.3 The Nuclear Atom

- Rutherford determined that there was a nucleus in every atom
- Protons discovered by Rutherford in 1919
- Neutrons discovered by James Chadwich in 1932

1.2.4: Atomic Structure and Symbolism

- charge of an electron is $–1.602*10^{-19}$
- charge of a proton is $+1.602*10^{-19}$
- $1.602*10^{-19}$ is called to electronic charge

Particle	Charge	Mass (amu)
Proton	Positive	1.0073
Neutron	None	1.0087
Electron	Negative	$5.486*10^{-4}$

- atomic mass unit (amu) – equals $1.66054*10^{-24}$ grams

- angstrom (Å) – unit of length to measure atomic dimensions
  - 1 angstrom = 10^{-10}m
- atoms have diameters of 1-5 Å
- nucleus – diameter of 10^{-4} Å
- all atoms of an element have the same number of protons in the nucleus
- isotopes - atoms of the same element that have a different number of neutrons
- atomic number – the number of protons in an atom
- mass number – number of protons + number of neutrons
- nuclide – atom of a specific isotope

1.2.5: Chemical Formulas

- empirical formula - formula showing the composition of a compound given as the simplest whole-number ratio of atoms
- molecular formula - formula indicating the composition of a molecule of a compound and giving the actual number of atoms of each element in a molecule of the compound
- isomers - compounds with the same chemical formula but different structures
- spatial isomers - compounds in which the relative orientations of the atoms in space differ
- structural isomer - one of two substances that have the same molecular formula but different physical and chemical properties because their atoms are bonded differently
- structural formula - shows the atoms in a molecule and how they are connected

1.2.6: The Periodic Table

- periodic table – the arrangement of all the elements by atomic number and similarities into a table
- columns = groups
- metallic elements – all elements on the left side and in the middle of the periodic table
- nonmetallic elements – elements on the periodic table that are divided by a diagonal steplike line from boron to astatine
- metalloids – properties of metals and nonmetals

1.2.7: Molecular and Ionic Compounds

- molecule – two or more atoms bonded together
- ion – charged particle formed by the removal or addition of an electron
- cation – ion with a positive charge
- anion – ion with a negative charge
- metal atoms tend to lose electrons, nonmetal atoms tend to gain electrons
- monatomic ion - ions formed from one atom
- polyatomic ions – joined atoms that have a net positive or negative charge
- Oxyanions - polyatomic ions that contain one or more oxygen atoms
- Predicting Ionic Charges
  - alkali metals (group 1) form 1+ ions
  - alkaline earth metals (group 2) form 2+ ions
  - halogens form 1- ions
  - group 6A from 2- ions
- ionic compound – a compound that contains positively and negatively charged ions
- ionic bond - electrostatic forces of attraction between the oppositely charged ions of an ionic compound
- ionic compounds are generally combinations of metals and nonmetals, molecular compounds are generally nonmetals only
- chemical formula – way of representing molecule
- molecular compound or covalent compound – contains more than one type of atom, pairs of electrons are shared between bonded atoms
- covalent bond - attractive force between the nuclei of a molecule's atoms and pairs of electrons between the atoms

1.2.8: Chemical Nomenclature

- chemical nomenclature – the naming of substances following a system of rules
- organic compounds – contain carbon as the principle element
- inorganic compounds – composed principally of elements other than carbon
- positive ion
  - cations formed from atoms have the same name as the metal
  - if a metal can form cations of differing charges, the positive charge is given by a roman numeral in parentheses following the name of the metal
  - cations formed from nonmetal atoms have names that end in –ium
- negative ion
  - monatomic anions have names formed by dropping the ending of the name of the element and adding the ending –ide
  - polyatomic anions containing oxygen have names ending in –ate or –ite alled oxyanions
  - anions derived by adding H^+ to an oxyanion are named by adding as a prefix the word hydrogen or dihydrogen, as appropriate
- names of ionic compounds are the cation name followed by the anion name
- names of ionic compounds containing a metal with a variable charge state the charge on the metal with a Roman numeral in parentheses after the name of the metal
- acids based on anions whose names end in –ide have associated acids that have the hydro- prefix and an –ic ending
- acids based on anions whose names end in –ate or -ite

Anion	Acid
____ide	Hydro____ic acid
____ate	_____ic acid
____ite	_____ous acid

- Names and Formulas of Binary Molecular Compounds
  - the name of the element farthest to the left in the periodic table is usually written first
  - if elements in same group lower one written first
  - name of second element is given an –ide ending
  - greek prefixes used to indicate number of atoms of each element
  - if prefix ends in a or o and the name of the anion begins with a vowel, the a or o is dropped

Prefix	Meaning
Mono-	1
Di-	2
Tri-	3
Tetra-	4
Penta-	5
Hexa-	6
Hepta-	7
Octa-	8
Nona-	9

Prefix	Meaning
Deca-	10

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SECTION OVERVIEW

1.3: Composition of Substances and Solutions

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General Chemistry

Quantitative aspects of the composition of substances and mixtures are the subject of this chapter.

1.3.1: Formula Mass and the Mole Concept

1.3.2: Determining Empirical and Molecular Formulas

1.3.3: Molarity

1.3.4: Other Units for Solution Concentrations

1.3.5: Composition of Substances and Solutions (Study Guide)

1.3.E: Composition of Substances and Solutions (Exercises)

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1.3.1: Formula Mass and the Mole Concept

Learning Objectives

- Calculate formula masses for covalent and ionic compounds
- 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

We can 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.

1.3.1.1: Formula Mass

In an earlier chapter, we 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.

1.3.1.1.1: 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 1.3.1.1outlines 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

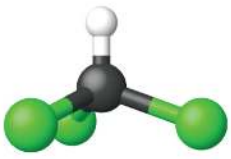


Figure 1.3.1.1: The average mass of a chloroform molecule, $CHCl_3$, is 119.37 amu, which is the sum of the average atomic masses of each of its constituent atoms. The model shows the molecular structure of chloroform.

A table and diagram are shown. The table is made up of six columns and five rows. The header row reads: "Element," "Quantity," a blank space, "Average atomic mass (a m u)," a blank space, and "Subtotal (a m u)." The first column contains the symbols "C," "H," "C l" and a blank, merged cell that runs the width of the first five columns. The second column contains the numbers "1," "1," and "3" as well as the merged cell. The third column contains the multiplication symbol in each cell except for the last, merged cell. The fourth column contains the numbers "12.01," "1.008," and "35.45" as well as the merged cell. The fifth column contains the symbol "=" in each cell except for the last, merged cell. The sixth column contains the values "12.01," "1.008," "106.35," and "119.37." There is a thick black line below the number 106.35. The merged cell under the first five columns reads "Molecular mass." To the left of the table is a diagram of a molecule. Three green spheres are attached to a slightly smaller black sphere, which is also attached to a smaller white sphere. The green spheres lie beneath and to the sides of the black sphere while the white sphere is located straight up from the black sphere.

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 1.3.1.2).

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	9	×	12.01	=	108.09
H	8	×	1.008	=	8.064
O	4	×	16.00	=	64.00
				Molecular mass	180.15

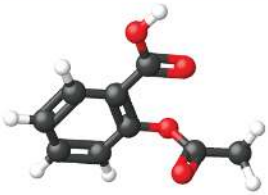


Figure 1.3.1.2: The average mass of an aspirin molecule is 180.15 amu. The model shows the molecular structure of aspirin, $C_9H_8O_4$.

A table and diagram are shown. The table is made up of six columns and five rows. The header row reads: “Element,” “Quantity,” a blank space, “Average atomic mass (a m u),” a blank space, and “Subtotal (a m u).” The first column contains the symbols “C,” “H,” “O,” and a merged cell. The merged cell runs the length of the first five columns. The second column contains the numbers “9,” “8,” and “4” as well as the merged, cell. The third column contains the multiplication symbol in each cell except for the last, merged cell. The fourth column contains the numbers “12.01,” “1.008,” and “16.00” as well as the merged cell. The fifth column contains the symbol “=” in each cell except for the last, merged cell. The sixth column contains the values: “108.09,” “8.064,” “64.00,” and “180.15.” There is a thick black line below the number 64.00. The merged cell under the first five columns reads “Molecular mass.” To the left of the table is a diagram of a molecule. Six black spheres are located in a six-sided ring and connected by alternating double and single black bonds. Attached to each of the four black spheres is one smaller white sphere. Attached to the farthest right black sphere is a red sphere, connected to two more black spheres, all in a row. Attached to the last black sphere of that row are two more white spheres. Attached to the first black sphere of that row is another red sphere. A black sphere, attached to two red spheres and a white sphere is attached to the black sphere on the top right of the six-sided ring.

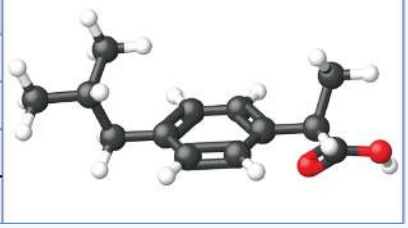
Example 1.3.1.1: Computing Molecular Mass for a Covalent Compound

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 comprised 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	=	18.114
O	2	×	16.00	=	32.00
				Molecular mass	206.27



Exercise 1.3.1.1

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?

Answer

151.16 amu

1.3.1.1.2: 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 (Figure 1.3.1.3).

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

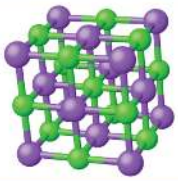


Figure 1.3.1.3: Table salt, NaCl, contains an array of sodium and chloride ions combined in a 1:1 ratio. Its formula mass is 58.44 amu.

A table and diagram are shown. The table is made up of six columns and four rows. The header row reads: “Element,” “Quantity,” a blank space, “Average atomic mass (a m u),” a blank space and “Subtotal (a m u).” The first column contains the symbols “N a”, “C l,” and a merged cell. The merged cell runs the length of the first five columns. The second column contains the numbers “1” and “1” as well as the merged cell. The third column contains the multiplication symbol in each cell except for the last, merged cell. The fourth column contains the numbers “22.99” and “35.45” as well as the merged cell. The fifth column contains the symbol “=” in each cell except for the last, merged cell. The sixth column contains the values “22.99,” “35.45,” and “58.44.” There is a thick black line below the number “35.45.” The merged cell under the first five columns reads “Formula mass.” To the left of the table is a diagram of a chemical structure. The diagram shows green and purple spheres placed in an alternating pattern, making up the corners of eight stacked cubes to form one larger cube. The green spheres are slightly smaller than the purple spheres.

Note that the average masses of neutral sodium and chlorine atoms were used in this computation, rather than the masses for sodium cations and chlorine anions. This approach is perfectly acceptable when computing the formula mass of an ionic compound. Even though a sodium cation has a slightly smaller mass than a sodium atom (since it is missing an electron), this difference will be offset by the fact that a chloride anion is slightly more massive than a chloride atom (due to the extra electron). Moreover, the mass of an electron is negligibly small with respect to the mass of a typical atom. Even when calculating the mass of an isolated ion, the missing or additional electrons can generally be ignored, since their contribution to the overall mass is negligible, reflected only in the nonsignificant digits that will be lost when the computed mass is properly rounded. The few exceptions to this guideline are very light ions derived from elements with precisely known atomic masses.

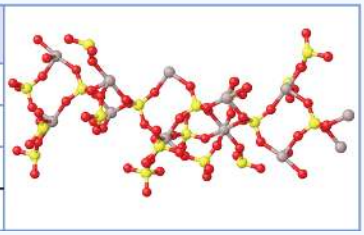
✔ Example 1.3.1.2: Computing Formula Mass for an Ionic Compound

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



? Exercise 1.3.1.2

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?

Answer

310.18 amu

1.3.1.2: The Mole

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, we possess sophisticated instruments that 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 bulk sample of matter. A mole is defined as the amount of substance containing the same number of discrete entities (such as atoms, molecules, and ions) as the number of atoms in a sample of pure ^{12}C weighing exactly 12 g. 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.

The number of entities composing a mole has been experimentally determined to be $6.02214179 \times 10^{23}$, a fundamental constant named **Avogadro’s number** (N_A) 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 $6.022 \times 10^{23}/\text{mol}$.

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) (Figure 1.3.1.4).

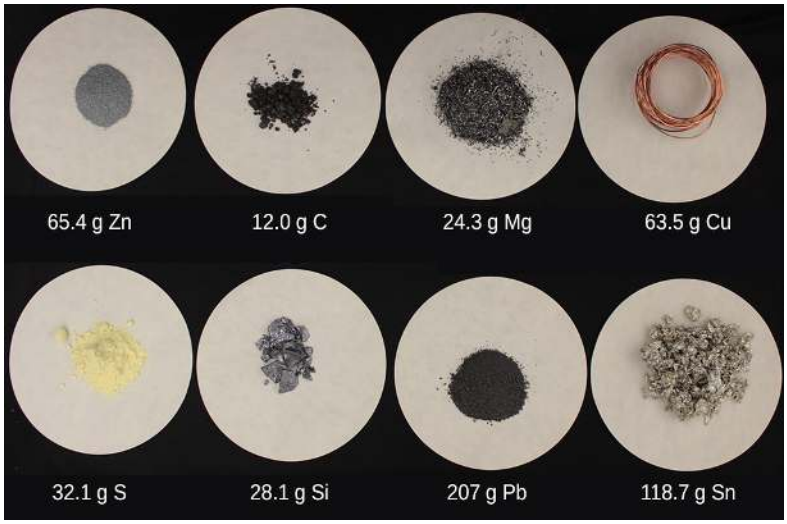
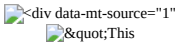


Figure 1.3.1.4: Each sample contains 6.022×10^{23} atoms —1.00 mol of atoms. From left to right (top row): 65.4 g zinc, 12.0 g carbon, 24.3 g magnesium, and 63.5 g copper. From left to right (bottom row): 32.1 g sulfur, 28.1 g silicon, 207 g lead, and 118.7 g tin. (credit: modification of work by Mark Ott).

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

Because the definitions of both the mole and the atomic mass unit are based on the same reference substance, ^{12}C, 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). According to the definition of the mole, 12 g of ^{12}C contains 1 mole of ^{12}C atoms (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 1.3.1.5).



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Figure 1.3.1.5: Each sample contains 6.022×10^{23} molecules or formula units—1.00 mol of the compound or element. Clockwise 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). (credit: Sahar Atwa).

Table 1.3.1.1: Mass of one mole of elements

Element	Average Atomic Mass (amu)	Molar Mass (g/mol)	Atoms/Mole
C	12.01	12.01	6.022×10^{23}
H	1.008	1.008	6.022×10^{23}
O	16.00	16.00	6.022×10^{23}
Na	22.99	22.99	6.022×10^{23}
Cl	33.45	35.45	6.022×10^{23}

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 after a rainfall. 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.



Video 1.3.1.1: The mole is used in chemistry to represent 6.022×10^{23} of something, but it can be difficult to conceptualize such a large number. Watch this video and then complete the “Think” questions that follow. Explore more about the mole by reviewing the information under “Dig Deeper.”

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. For example, if we know the mass and chemical composition of a substance, we can determine the number of moles and calculate number of atoms or molecules in the sample. Likewise, if we know the number of moles of a substance, we can derive the number of atoms or molecules and calculate the substance’s mass.

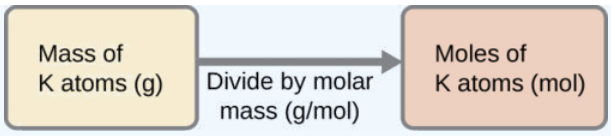
Example 1.3.1.3: Deriving Moles from Grams for an Element

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):



The factor-label method supports this mathematical approach since the unit “g” cancels and the answer has units of “mol:”

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

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

Exercise 1.3.1.3: Beryllium

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?

Answer

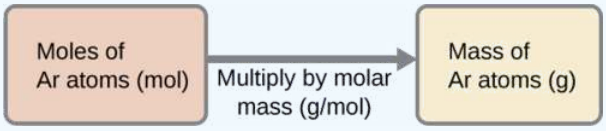
0.360 mol

Example 1.3.1.4: 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):

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

The result is in agreement with our expectations, around 0.04 g Ar.

Exercise 1.3.1.4

What is the mass of 2.561 mol of gold?

Answer

504.4 g

Example 1.3.1.6: Deriving Number of Atoms from Mass for an Element

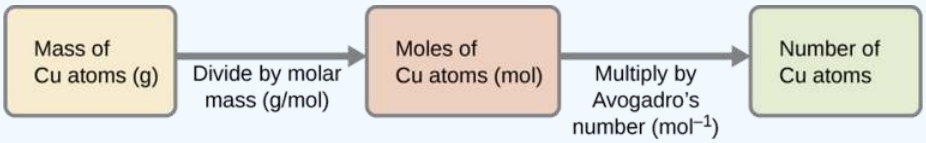
Copper is commonly used to fabricate electrical wire (Figure 1.3.1.6). How many copper atoms are in 5.00 g of copper wire?



Figure 1.3.1.6: Copper wire is composed of many, many atoms of Cu. (credit: Emilian Robert Vicol)

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:

$$5.00\ \cancel{\text{g}}\ \text{Cu}\left(\frac{\cancel{\text{mol}}\ \text{Cu}}{63.55\ \cancel{\text{g}}}\right)\left(\frac{6.022\times10^{23}\ \text{atoms}}{\cancel{\text{mol}}}\right)=4.74\times10^{22}\ \text{atoms of copper}$$

The factor-label method yields the desired cancellation of units, and the computed result is on the order of 10^{22} as expected.

? Exercise 1.3.1.6

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?

Answer

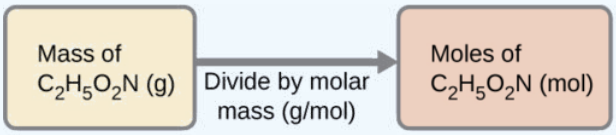
$4.586\times10^{22}\ Au$ atoms

✓ Example 1.3.1.7: Deriving Moles from Grams for a Compound

Our bodies synthesize protein from amino acids. One of these amino acids is glycine, which has the molecular formula $C_2H_5O_2N$. How many moles of glycine molecules are contained in 28.35 g of glycine?

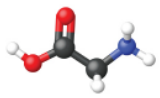
Solution

We can derive the number of moles of a compound from its mass following the same procedure we used for an element in Example 1.3.1.6:



The molar mass of glycine is required for this calculation, and it is computed in the same fashion as its molecular mass. One mole of glycine, $C_2H_5O_2N$, contains 2 moles of carbon, 5 moles of hydrogen, 2 moles of oxygen, and 1 mole of nitrogen:

Element	Quantity (mol element/ mol compound)		Molar mass (g/mol element)		Subtotal (g/mol compound)
C	2	×	12.01	=	24.02
H	5	×	1.008	=	5.040
O	2	×	16.00	=	32.00
N	1	×	14.007	=	14.007
Molecular mass (g/mol compound)					75.07



A table is shown that is made up of six columns and six rows. The header row reads: “Element,” “Quantity (mol element / mol compound,” a blank space, “Molar mass (g / mol element),” a blank space, and “Subtotal (a m u).” The first column contains the symbols “C,” “H,” “O,” “N,” and a merged cell. The merged cell runs the width of the first five columns. The second column contains the numbers “2,” “5,” “2,” and “1” as well as the merged cell. The third column contains the multiplication symbol in each cell except for the last, merged cell. The fourth column contains the numbers “12.01,” “1.008,” “16.00,” and “14.007” as well as the merged cell. The fifth column contains the symbol “=” in each cell except for the last, merged cell. The sixth column contains the values “24.02,” “5.040,” “32.00,” “14.007,” and “75.07.” There is a thick black line under the number 14.007. The merged cell under the first five columns reads “Molar mass (g / mol compound). There is a ball-and-stick drawing to the right of this table. It shows a black sphere that forms a double bond with a slightly smaller red sphere, a single bond with another red sphere, and a single bond with another black sphere. The red sphere that forms a single bond with the black sphere also forms a single bond with a smaller, white sphere. The second black sphere forms a single bond with a smaller, white sphere and a smaller blue sphere. The blue sphere forms a single bond with two smaller, white spheres each.

The provided mass of glycine (~28 g) is a bit more than one-third the molar mass (~75 g/mol), so we would expect the computed result to be a bit greater than one-third of a mole (~0.33 mol). Dividing the compound’s mass by its molar mass yields:

$$28.35\ \cancel{\text{g}}\ \text{glycine}\left(\frac{\text{mol glycine}}{75.07\ \cancel{\text{g}}}\right) = 0.378\ \text{mol glycine}$$

This result is consistent with our rough estimate.

Exercise 1.3.1.7

How many moles of sucrose, $C_{12}H_{22}O_{11}$, are in a 25-g sample of sucrose?

Answer

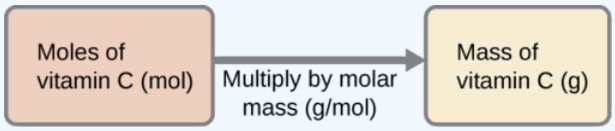
0.073 mol

Example 1.3.1.8: Deriving Grams from Moles for a Compound

Vitamin C is a covalent compound with the molecular formula $C_6H_8O_6$. The recommended daily dietary allowance of vitamin C for children aged 4–8 years is 1.42×10^{-4} mol. What is the mass of this allowance in grams?

Solution

As for elements, the mass of a compound can be derived from its molar amount as shown:



The molar mass for this compound is computed to be 176.124 g/mol. The given number of moles is a very small fraction of a mole (~10^{-4} or one-ten thousandth); therefore, we would expect the corresponding mass to be about one-ten thousandth of the molar mass (~0.02 g). Performing the calculation, we get:

$$1.42 \times 10^{-4}\ \cancel{\text{mol}}\ \text{vitamin C}\left(\frac{176.124\ \text{g}}{\cancel{\text{mol}}\ \text{vitamin C}}\right) = 0.0250\ \text{g vitamin C}$$

This is consistent with the anticipated result.

Exercise 1.3.1.8

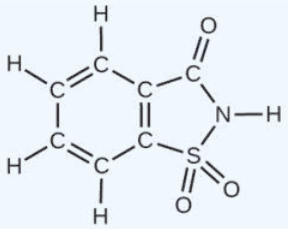
What is the mass of 0.443 mol of hydrazine, N_2H_4?

Answer

14.2 g

Example 1.3.1.9: Deriving the Number of Molecules from the Compound Mass

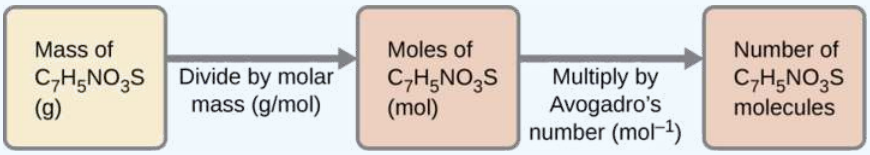
A packet of an artificial sweetener contains 40.0 mg of saccharin ($C_7H_5NO_3S$), which has the structural formula:



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 in Example 1.3.1.8, and then multiplying by Avogadro's number:



Using the provided mass and molar mass for saccharin yields:

$$0.0400\ \cancel{\text{g}}\ C_7H_5NO_3S\left(\frac{\cancel{\text{mol}}\ C_7H_5NO_3S}{183.18\ \cancel{\text{g}}\ C_7H_5NO_3S}\right)\left(\frac{6.022\times10^{23}\ C_7H_5NO_3S\ \text{molecules}}{1\ \cancel{\text{mol}}\ C_7H_5NO_3S}\right)$$
$$=1.31\times10^{20}\ C_7H_5NO_3S\ \text{molecules}$$

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

$$1.31\times10^{20}\ C_7H_5NO_3S\ \text{molecules}\left(\frac{7\ \text{C atoms}}{1\ C_7H_5NO_3S\ \text{molecule}}\right)=9.20\times10^{21}\ \text{C atoms}$$

Exercise 1.3.1.9

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

Answer

- 9.545×10^{22} molecules C_4H_{10}
- 9.545×10^{23} atoms H

Summary

The formula mass of a substance is the sum of the average atomic masses of each atom represented in the chemical formula and is expressed in atomic mass units. The formula mass of a covalent compound is also called the molecular mass. A convenient amount unit for expressing very large numbers of atoms or molecules is the mole. Experimental measurements have determined the number of entities composing 1 mole of substance to be 6.022×10^{23}, a quantity called Avogadro's number. The mass in grams of 1 mole of substance is its molar mass. Due to the use of the same reference substance in defining the atomic mass unit and the mole, the formula mass (amu) and molar mass (g/mol) for any substance are numerically equivalent (for example, one H_2O molecule weighs approximately18 amu and 1 mole of H_2O molecules weighs approximately 18 g).

Footnotes

1. 1 Omiatek, Donna M., Amanda J. Bressler, Ann-Sofie Cans, Anne M. Andrews, Michael L. Heien, and Andrew G. Ewing. "The Real Catecholamine Content of Secretory Vesicles in the CNS Revealed by Electrochemical Cytometry." *Scientific Report* 3 (2013): 1447, accessed January 14, 2015, doi:10.1038/srep01447.

Glossary

Avogadro's number (N_A)

experimentally determined value of the number of entities comprising 1 mole of substance, equal to 6.022×10^{23} mol^{-1}

formula mass

sum of the average masses for all atoms represented in a chemical formula; for covalent compounds, this is also the molecular mass

mole

amount of substance containing the same number of atoms, molecules, ions, or other entities as the number of atoms in exactly 12 grams of ^{12}C

molar mass

mass in grams of 1 mole of a substance

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1.3.2: Determining Empirical and Molecular Formulas

Learning Objectives

- Compute the percent composition of a compound
- Determine the empirical formula of a compound
- Determine the molecular formula of a compound

In the previous section, we discussed the relationship between the bulk mass of a substance and the number of atoms or molecules it contains (moles). Given the chemical formula of the substance, we were able to determine the amount of the substance (moles) from its mass, and vice versa. But what if the chemical formula of a substance is unknown? In this section, we will explore how to apply these very same principles in order to derive the chemical formulas of unknown substances from experimental mass measurements.

1.3.2.1: 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:

$$\%\mathrm{H} = \frac{\text{mass H}}{\text{mass compound}} \times 100\%$$

$$\%\mathrm{C} = \frac{\text{mass C}}{\text{mass compound}} \times 100\%$$

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:

$$\%\mathrm{H} = \frac{2.5\ \text{g H}}{10.0\ \text{g compound}} \times 100\% = 25\%$$

$$\%\mathrm{C} = \frac{7.5\ \text{g C}}{10.0\ \text{g compound}} \times 100\% = 75\%$$

Example 1.3.2.1: 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, we divide the experimentally derived mass of each element by the overall mass of the compound, and then convert to a percentage:

$$\%\mathrm{C} = \frac{7.34\ \text{g C}}{12.04\ \text{g compound}} \times 100\% = 61.0\%$$

$$\%\mathrm{H} = \frac{1.85\ \text{g H}}{12.04\ \text{g compound}} \times 100\% = 15.4\%$$

$$\%\mathrm{N} = \frac{2.85\ \text{g N}}{12.04\ \text{g compound}} \times 100\% = 23.7\%$$

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

Exercise 1.3.2.1

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?

Answer

12.1% C, 16.1% O, 71.8% Cl

1.3.2.2: Determining Percent Composition from Formula Mass

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:

$$\%\mathrm{N} = \frac{14.01\ \text{amu N}}{17.03\ \text{amu NH}_3} \times 100\% = 82.27\%$$

$$\%\mathrm{H} = \frac{3.024\ \text{amu N}}{17.03\ \text{amu NH}_3} \times 100\% = 17.76\%$$

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 1.3.2.2 As long as we know the chemical formula of the substance in question, we can easily derive percent composition from the formula mass or molar mass.

Example 1.3.2.2: 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, we need to know the masses of C, H, and O in a known mass of $C_9H_8O_4$. 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:

$$\%\mathrm{C} = \frac{9\ \text{mol C} \times \text{molar mass C}}{\text{molar mass } \mathrm{C_9H_{18}O_4}} \times 100 = \frac{9 \times 12.01\ \text{g/mol}}{180.159\ \text{g/mol}} \times 100 = \frac{108.09\ \text{g/mol}}{180.159\ \text{g/mol}} \times 100$$

$$\%\mathrm{C} = 60.00\ \%\ \mathrm{C}$$

$$\%\mathrm{H} = \frac{8\ \text{mol H} \times \text{molar mass H}}{\text{molar mass } \mathrm{C_9H_{18}O_4}} \times 100 = \frac{8 \times 1.008\ \text{g/mol}}{180.159\ \text{g/mol}} \times 100 = \frac{8.064\ \text{g/mol}}{180.159\ \text{g/mol}} \times 100$$

$$\%\mathrm{H} = 4.476\ \%\ \mathrm{H}$$

$$\%\mathrm{O} = \frac{4\ \text{mol O} \times \text{molar mass O}}{\text{molar mass } \mathrm{C_9H_{18}O_4}} \times 100 = \frac{4 \times 16.00\ \text{g/mol}}{180.159\ \text{g/mol}} \times 100 = \frac{64.00\ \text{g/mol}}{180.159\ \text{g/mol}} \times 100$$

$$\%\mathrm{O} = 35.52\%$$

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

Exercise 1.3.2.2

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

Answer

69.9% Fe

1.3.2.3: 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, we must 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. To accomplish this, we can use molar masses to convert the mass of each element to a number of moles. We then consider the moles of each element relative to each other, converting these numbers into a whole-number ratio 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:

$$1.71 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 0.142 \text{ mol C}$$

$$0.287 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 0.284 \text{ mol H}$$

Thus, we can accurately represent this compound with the formula $C_{0.142}H_{0.284}$. Of course, per accepted convention, formulas contain whole-number subscripts, which can be achieved by dividing each subscript by the smaller subscript:

$$\text{C}_{\frac{0.142}{0.142}}\ \text{H}_{\frac{0.284}{0.142}}\ \text{or}\ \text{CH}_2$$

(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, we would need additional information to make that determination (as discussed later in this section).

Consider as another example a sample of compound determined to contain 5.31 g Cl and 8.40 g O. Following the same approach yields a tentative empirical formula of:

$$\text{Cl}_{0.150}\text{O}_{0.525} = \text{Cl}_{\frac{0.150}{0.150}}\ \text{O}_{\frac{0.525}{0.150}} = \text{ClO}_{3.5}$$

In this case, dividing by the smallest subscript still leaves us with a decimal subscript in the empirical formula. To convert this into a whole number, we must multiply each of the subscripts by two, retaining the same atom ratio and yielding Cl_2O_7 as the final empirical formula.

Procedure

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 1.3.2.1outlines this procedure in flow chart fashion for a substance containing elements A and X.

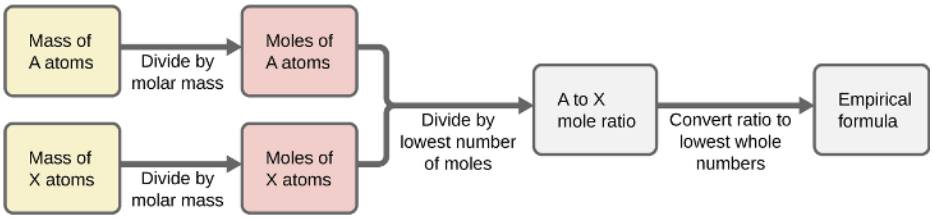


Figure 1.3.2.1: The empirical formula of a compound can be derived from the masses of all elements in the sample.

A flow chart is shown that is composed of six boxes, two of which are connected together by a right facing arrow and located above two more that are also connected by a right-facing arrow. These two rows of boxes are connected vertically by a line that leads to a right-facing arrow and the last two boxes, connected by a final right facing arrow. The first two upper boxes have the phrases, “Mass of A atoms” and “Moles of A atoms” respectively, while the arrow that connects them has the phrase, “Divide by molar mass,” written below it. The second two bottom boxes have the phrases, “Mass of X atoms” and “Moles of X atoms” respectively, while the arrow that connects them has the phrase, “Divide by molar mass” written below it. The arrow that connects the upper and lower boxes to the last two boxes has the phrase “Divide by lowest number of moles” written below it. The last two boxes have the phrases, “A to X mole ratio” and “Empirical formula” respectively, while the arrow that connects them has the phrase, “Convert ratio to lowest whole numbers” written below it.

Example 1.3.2.3: Determining an Empirical Formula from Masses of Elements

A sample of the black mineral hematite (Figure 1.3.2.2), 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?



Figure 1.3.2.2: Hematite is an iron oxide that is used in jewelry. (credit: Mauro Cateb)

Solution

For this problem, we are given the mass in grams of each element. Begin by finding the moles of each:

$$34.97\ \text{g Fe}\left(\frac{\text{mol Fe}}{55.85\ \text{g}}\right) = 0.6261\ \text{mol Fe}$$

$$15.03\ \text{g O}\left(\frac{\text{mol O}}{16.00\ \text{g}}\right) = 0.9394\ \text{mol O}$$

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

$$\frac{0.6261}{0.6261} = 1.000\ \text{mol Fe}$$

$$\frac{0.9394}{0.6261} = 1.500\ \text{mol O}$$

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:

$$2(\text{Fe}_1\text{O}_{1.5}) = \text{Fe}_2\text{O}_3$$

The empirical formula is Fe_2O_3.

Exercise 1.3.2.3

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

Answer

N_2O_5



***Video* 1.3.2.1** *: Additional worked examples illustrating the derivation of empirical formulas are presented in the brief video clip.*

1.3.2.4: 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 1.3.2.4: 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 (Figure 1.3.2.3). What is the empirical formula for this gas?



Figure 1.3.2.3: An oxide of carbon is removed from these fermentation tanks through the large copper pipes at the top. (credit: "Dual Freq"/Wikimedia Commons)

A picture is shown of four copper-colored industrial containers with a large pipe connecting to the top of each one.

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:

$$27.29\ \%\ \mathrm{C} = \frac{27.29\ \mathrm{g\ C}}{100\ \mathrm{g\ compound}}$$

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

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

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

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

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

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

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

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

? Exercise 1.3.2.4

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

Answer

CH_2O

1.3.2.5: Derivation of Molecular Formulas

Recall that empirical formulas are symbols representing the *relative* numbers of a compound's elements. Determining the *absolute* numbers of atoms that compose a single molecule of a covalent compound requires knowledge of both its empirical formula and its molecular mass or molar mass. These quantities may be determined experimentally by various measurement techniques. Molecular mass, for example, is often derived from the mass spectrum of the compound (see discussion of this technique in the previous chapter on atoms and molecules). Molar mass can be measured by a number of experimental methods, many of which will be introduced in later chapters of this text.

Molecular formulas are derived by comparing the compound's molecular or molar mass to its empirical formula mass. As the name suggests, an empirical formula mass is the sum of the average atomic masses of all the atoms represented in an empirical formula. If we know the molecular (or molar) mass of the substance, we can divide this by the empirical formula mass in order to identify the number of empirical formula units per molecule, which we designate as *n*:

$$\frac{\text{molecular or molar mass}\left(\text{amu or }\frac{\mathrm{g}}{\mathrm{mol}}\right)}{\text{empirical formula mass}\left(\text{amu or }\frac{\mathrm{g}}{\mathrm{mol}}\right)} = n\,\text{formula units/molecule}$$

The molecular formula is then obtained by multiplying each subscript in the empirical formula by *n*, as shown by the generic empirical formula A_xB_y:

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

For example, consider a covalent compound whose empirical formula is determined to be CH_2O. The empirical formula mass for this compound is approximately 30 amu (the sum of 12 amu for one C atom, 2 amu for two H atoms, and 16 amu for one O atom).

If the compound's molecular mass is determined to be 180 amu, this indicates that molecules of this compound contain six times the number of atoms represented in the empirical formula:

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

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

$$(\text{CH}_2\text{O})_6 = \text{C}_6\text{H}_{12}\text{O}_6$$

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, we are merely considering one mole of empirical formula units and molecules, as opposed to single units and molecules.

Example 1.3.2.5: Determination of the Molecular Formula for Nicotine

Nicotine, an alkaloid in the nightshade family of plants that is mainly responsible for the addictive nature of cigarettes, contains 74.02% C, 8.710% H, and 17.27% N. If 40.57 g of nicotine contains 0.2500 mol nicotine, what is the molecular formula?

Solution

Determining the molecular formula from the provided data will require comparison of the compound's empirical formula mass to its molar mass. As the first step, use the percent composition to derive the compound's empirical formula. Assuming a convenient, a 100-g sample of nicotine yields the following molar amounts of its elements:

$$(74.02\ \text{g C})\left(\frac{1\ \text{mol C}}{12.01\ \text{g C}}\right) = 6.163\ \text{mol C} \tag{1.3.2.1}$$

$$(8.710\ \text{g H})\left(\frac{1\ \text{mol H}}{1.01\ \text{g H}}\right) = 8.624\ \text{mol H} \tag{1.3.2.2}$$

$$(17.27\ \text{g N})\left(\frac{1\ \text{mol N}}{14.01\ \text{g N}}\right) = 1.233\ \text{mol N} \tag{1.3.2.3}$$

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

$$6.163\ \text{mol C}/\ 1.233\ \text{mol N} = 5$$

$$8.264\ \text{mol H}/\ 1.233\ \text{mol N} = 7$$

$$1.233\ \text{mol N}/\ 1.233\ \text{mol N} = 1$$

$$1.233/1.233 = 1.000\ \text{mol N}$$

$$6.163/1.233 = 4.998\ \text{mol C}$$

$$8.624/1.233 = 6.994\ \text{mol H}$$

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.

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

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

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

$$\frac{162.3\ \text{g/mol}}{81.13\ \dfrac{\text{g}}{\text{formula unit}}} = 2\ \text{formula units/molecule}$$

Thus, we can derive the molecular formula for nicotine from the empirical formula by multiplying each subscript by two:

$$(\text{C}_5\text{H}_7\text{N})_2 = \text{C}_{10}\text{H}_{14}\text{N}_2$$

Exercise 1.3.2.5

What is the molecular formula of a compound with a percent composition of 49.47% C, 5.201% H, 28.84% N, and 16.48% O, and a molecular mass of 194.2 amu?

Answer

$C_8H_{10}N_4O_2$

Summary

The chemical identity of a substance is defined by the types and relative numbers of atoms composing its fundamental entities (molecules in the case of covalent compounds, ions in the case of ionic compounds). A compound's percent composition provides the mass percentage of each element in the compound, and it is often experimentally determined and used to derive the compound's empirical formula. The empirical formula mass of a covalent compound may be compared to the compound's molecular or molar mass to derive a molecular formula.

1.3.2.6: Key Equations

- $\%\mathrm{X} = \dfrac{\text{mass X}}{\text{mass compound}} \times 100\%$
- $\dfrac{\text{molecular or molar mass}\left(\text{amu or } \dfrac{\text{g}}{\text{mol}}\right)}{\text{empirical formula mass}\left(\text{amu or } \dfrac{\text{g}}{\text{mol}}\right)} = n\,\text{formula units/molecule}$
- $(A_xB_y)_n = A_{nx}B_{ny}$

Glossary

percent composition

percentage by mass of the various elements in a compound

empirical formula mass

sum of average atomic masses for all atoms represented in an empirical formula

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1.3.3: Molarity

Learning Objectives

- Describe the fundamental properties of solutions
- Calculate solution concentrations using molarity
- Perform dilution calculations using the dilution equation

In preceding sections, we 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 (Figure 1.3.3.1). In this section, we will describe one of the most common ways in which the relative compositions of mixtures may be quantified.



Figure 1.3.3.1: Sugar is one of many components in the complex mixture known as coffee. The amount of sugar in a given amount of coffee is an important determinant of the beverage's sweetness. (credit: Jane Whitney)

1.3.3.1: Solutions

We have previously defined solutions 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. We will explore a more thorough treatment of solution properties in the chapter on solutions and colloids, but here we will introduce 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:

$$M = \frac{\text{mol solute}}{\text{L solution}} \tag{1.3.3.1}$$

Example 1.3.3.1: 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:

$$\begin{aligned} M &= \frac{mol\ solute}{L\ solution} \\ &= \frac{0.133\ mol}{355\ mL \times \dfrac{1\ L}{1000\ mL}} \\ &= 0.375\ M \end{aligned}$$

Exercise 1.3.3.1

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?

Answer

0.05 M

Example 1.3.3.2: Deriving Moles and Volumes from Molar Concentrations

How much sugar (mol) is contained in a modest sip (~10 mL) of the soft drink from Example 1.3.3.1?

Solution

In this case, we can rearrange the definition of molarity to isolate the quantity sought, moles of sugar. We then substitute the value for molarity that we derived in Example 3.4.2, 0.375 *M*:

$$M = \frac{\text{mol solute}}{\text{L solution}} \tag{1.3.3.2}$$

$$\text{mol solute} = \text{M} \times \text{L solution}$$

$$\text{mol solute} = 0.375\ \frac{\text{mol sugar}}{\text{L}} \times \left(10\ \text{mL} \times \frac{1\ \text{L}}{1000\ \text{mL}}\right) \qquad = 0.004\ \text{mol sugar}$$

Exercise 1.3.3.2

What volume (mL) of the sweetened tea described in Example 1.3.3.1 contains the same amount of sugar (mol) as 10 mL of the soft drink in this example?

Answer

80 mL

Example 1.3.3.3: Calculating Molar Concentrations from the Mass of Solute

Distilled white vinegar (Figure 1.3.3.2) 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?



Figure 1.3.3.3: Distilled white vinegar is a solution of acetic acid in water.
A label on a container is shown. The label has a picture of a salad with the words “Distilled White Vinegar,” and, “Reduced with water to 5% acidity,” written above it.

Solution

As in previous examples, the definition of molarity is the primary equation used to calculate the quantity sought. In this case, the mass of solute is provided instead of its molar amount, so we must use the solute’s molar mass to obtain the amount of solute in moles:

$$M = \frac{\text{mol solute}}{\text{L solution}} = \frac{25.2\ \text{g}\ \text{CH}_3\text{CO}_2\text{H} \times \frac{1\ \text{mol}\ \text{CH}_3\text{CO}_2\text{H}}{60.052\ \text{g}\ \text{CH}_3\text{CO}_2\text{H}}}{0.500\ \text{L solution}} = 0.839\ M \tag{1.3.3.3}$$

$$M = \frac{0.839\ \text{mol solute}}{1.00\ \text{L solution}}$$

Nov 29, 2019, 5:24 PM

$$M = \frac{\text{mol solute}}{\text{L solution}} = 0.839\ M \tag{1.3.3.4}$$

? Exercise 1.3.3.3

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.

Answer

0.674 M

✓ Example 1.3.3.4: Determining the Mass of Solute in a Given Volume of Solution

How many grams of NaCl are contained in 0.250 L of a 5.30-*M* solution?

Solution

The volume and molarity of the solution are specified, so the amount (mol) of solute is easily computed as demonstrated in Example 1.3.3.3

$$M = \frac{\text{mol solute}}{\text{L solution}} \tag{1.3.3.5}$$

$$\text{mol solute} = M \times \text{L solution} \tag{1.3.3.6}$$

$$\text{mol solute} = 5.30\ \frac{\text{mol NaCl}}{\text{L}} \times 0.250\ \text{L} = 1.325\ \text{mol NaCl} \tag{1.3.3.7}$$

Finally, this molar amount is used to derive the mass of NaCl:

$$1.325 \text{ mol NaCl} \times \frac{58.44 \text{ g NaCl}}{\text{mol NaCl}} = 77.4 \text{ g NaCl} \tag{1.3.3.8}$$

Exercise 1.3.3.4

How many grams of $CaCl_2$ (110.98 g/mol) are contained in 250.0 mL of a 0.200-M solution of calcium chloride?

Answer

5.55 g $CaCl_2$

When performing calculations stepwise, as in Example 1.3.3.3, it is important to refrain from rounding any intermediate calculation results, which can lead to rounding errors in the final result. In Example 1.3.3.4, the molar amount of NaCl computed in the first step, 1.325 mol, would be properly rounded to 1.32 mol if it were to be reported; however, although the last digit (5) is not significant, it must be retained as a guard digit in the intermediate calculation. If we had not retained this guard digit, the final calculation for the mass of NaCl would have been 77.1 g, a difference of 0.3 g.

In addition to retaining a guard digit for intermediate calculations, we can also avoid rounding errors by performing computations in a single step (Example 1.3.3.5). This eliminates intermediate steps so that only the final result is rounded.

Example 1.3.3.5: Determining the Volume of Solution

In Example 1.3.3.3, we found the typical concentration of vinegar to be 0.839 *M*. What volume of vinegar contains 75.6 g of acetic acid?

Solution

First, use the molar mass to calculate moles of acetic acid from the given mass:

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} = \text{mol solute} \tag{1.3.3.9}$$

Then, use the molarity of the solution to calculate the volume of solution containing this molar amount of solute:

$$\text{mol solute} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution} \tag{1.3.3.10}$$

Combining these two steps into one yields:

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution} \tag{1.3.3.11}$$

$$75.6 \text{ g } CH_3CO_2H \left(\frac{\text{mol } CH_3CO_2H}{60.05 \text{ g}}\right)\left(\frac{\text{L solution}}{0.839 \text{ mol } CH_3CO_2H}\right) = 1.50 \text{ L solution} \tag{1.3.3.12}$$

Exercise 1.3.3.5:

What volume of a 1.50-M KBr solution contains 66.0 g KBr?

Answer

0.370 L

1.3.3.2: Dilution of Solutions

Dilution is the process whereby the concentration of a solution is lessened by the addition of solvent. For example, we might say that 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 1.3.3.2).

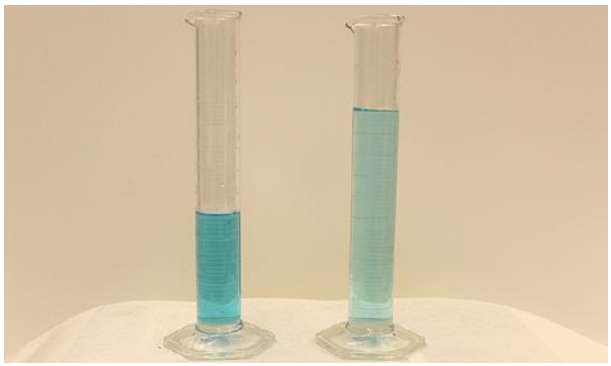


Figure 1.3.3.2: Both solutions contain the same mass of copper nitrate. The solution on the right is more dilute because the copper nitrate is dissolved in more solvent. (credit: Mark Ott).

This figure shows two graduated cylinders side-by-side. 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*, we can achieve a particular concentration. 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 (Figure 1.3.3.3).



Figure 1.3.3.3: A solution of $KMnO_4$ is prepared by mixing water with 4.74 g of KMnO4 in a flask. (credit: modification of work by Mark Ott)

This figure shows two photos. In the first, there is an empty glass container, 4.75 g of K M n O subscript 4 powder on a white circle, and a bottle of distilled water. In the second photo the powder and about half the water have been added to the glass container. The liquid in the glass container is almost black in color.

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 molar amount of solute in a solution is equal to the product of the solution's molarity and its volume in liters:

$$n = ML$$

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

$$n_1 = M_1 L_1$$

$$n_2 = M_2 L_2$$

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:

$$M_1 L_1 = M_2 L_2$$

This relation is commonly referred to as the dilution equation. Although we derived this equation using molarity as the unit of concentration and liters as the unit of volume, other units of concentration and volume may be used, so 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:

$$C_1V_1 = C_2V_2$$

where C and V are concentration and volume, respectively.

Example 1.3.3.6: 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

We are given the volume and concentration of a stock solution, V_1 and C_1, and the volume of the resultant diluted solution, V_2. We need to find the concentration of the diluted solution, C_2. We thus rearrange the dilution equation in order to isolate C_2:

$$C_1V_1 = C_2V_2$$

$$C_2 = \frac{C_1V_1}{V_2}$$

Since the stock solution is being diluted by more than two-fold (volume is increased from 0.85 L to 1.80 L), we would expect the diluted solution's concentration to be less than one-half 5 *M*. We will compare this ballpark estimate 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:

$$C_2 = \frac{0.850\ \text{L} \times 5.00\ \frac{\text{mol}}{\text{L}}}{1.80\ \text{L}} = 2.36\ M$$

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

Exercise 1.3.3.6

What is the concentration of the solution that results from diluting 25.0 mL of a 2.04-M solution of CH3OH to 500.0 mL?

Answer

0.102 M CH_3OH

Example 1.3.3.7: Volume of a Diluted Solution

What volume of 0.12 *M* HBr can be prepared from 11 mL (0.011 L) of 0.45 *M* HBr?

Solution

We are given the volume and concentration of a stock solution, V_1 and C_1, and the concentration of the resultant diluted solution, C_2. We need to find the volume of the diluted solution, V_2. We thus rearrange the dilution equation in order to isolate V_2:

$$C_1V_1 = C_2V_2$$

$$V_2 = \frac{C_1V_1}{C_2}$$

Since the diluted concentration (0.12 *M*) is slightly more than one-fourth the original concentration (0.45 *M*), we would expect the volume of the diluted solution to be roughly four times the original volume, or around 44 mL. Substituting the given values and solving for the unknown volume yields:

$$V_2 = \frac{(0.45\ M)(0.011\ \text{L})}{(0.12\ M)}$$

$$V_2 = 0.041\ \text{L}$$

The volume of the 0.12-*M* solution is 0.041 L (41 mL). The result is reasonable and compares well with our rough estimate.

? Exercise 1.3.3.7

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?

Answer

3.76 L

✓ Example 1.3.3.8: Volume of a Concentrated Solution Needed for Dilution

What volume of 1.59 *M* KOH is required to prepare 5.00 L of 0.100 *M* KOH?

Solution

We are given the concentration of a stock solution, C_1, and the volume and concentration of the resultant diluted solution, V_2 and C_2. We need to find the volume of the stock solution, V_1. We thus rearrange the dilution equation in order to isolate V_1:

$$C_1V_1 = C_2V_2$$

$$V_1 = \frac{C_2V_2}{C_1}$$

Since the concentration of the diluted solution 0.100 *M* is roughly one-sixteenth that of the stock solution (1.59 *M*), we would expect the volume of the stock solution to be about one-sixteenth that of the diluted solution, or around 0.3 liters. Substituting the given values and solving for the unknown volume yields:

$$V_1 = \frac{(0.100\ M)(5.00\ \text{L})}{1.59\ M}$$

$$V_1 = 0.314\ \text{L}$$

Thus, we would need 0.314 L of the 1.59-*M* solution to prepare the desired solution. This result is consistent with our rough estimate.

? Exercise 1.3.3.8

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?

Answer

0.261

Summary

Solutions are homogeneous mixtures. Many solutions contain one component, called the solvent, in which other components, called solutes, are dissolved. An aqueous solution is one for which the solvent is water. The concentration of a solution is a measure of the relative amount of solute in a given amount of solution. Concentrations may be measured using various units, with one very useful unit being molarity, defined as the number of moles of solute per liter of solution. The solute concentration of a solution may be decreased by adding solvent, a process referred to as dilution. The dilution equation is a simple relation between concentrations and volumes of a solution before and after dilution.

1.3.3.3: Key Equations

- $M = \frac{\text{mol solute}}{\text{L solution}}$
- $C_1V_1 = C_2V_2$

Glossary

aqueous solution
solution for which water is the solvent

concentrated
qualitative term for a solution containing solute at a relatively high concentration

concentration
quantitative measure of the relative amounts of solute and solvent present in a solution

dilute
qualitative term for a solution containing solute at a relatively low concentration

dilution
process of adding solvent to a solution in order to lower the concentration of solutes

dissolved
describes the process by which solute components are dispersed in a solvent

molarity (*M*)
unit of concentration, defined as the number of moles of solute dissolved in 1 liter of solution

solute
solution component present in a concentration less than that of the solvent

solvent
solution component present in a concentration that is higher relative to other components

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1.3.4: Other Units for Solution Concentrations

Learning Objectives

- Define the concentration units of mass percentage, volume percentage, mass-volume percentage, parts-per-million (ppm), and parts-per-billion (ppb)
- Perform computations relating a solution's concentration and its components' volumes and/or masses using these units

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

1.3.4.1: Mass Percentage

Earlier in this chapter, we introduced percent composition 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:

$$\text{mass percentage} = \frac{\text{mass of component}}{\text{mass of solution}} \times 100\% \tag{1.3.4.1}$$

We are generally most interested in the mass percentages of solutes, but it is also possible to compute the mass percentage of solvent.

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. The label of a typical liquid bleach bottle (Figure 1.3.4.1) 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 $NaOCl$.



Figure 1.3.4.1: Liquid bleach is an aqueous solution of sodium hypochlorite (NaOCl). This brand has a concentration of 7.4% NaOCl by mass.

The sides of two cylindrical containers are shown. Each container's label is partially visible. The left container's label reads "Bleach." The right label contains more information about the product including the phrase, "Contains: Sodium hypochlorite 7.4 %."

Example 1.3.4.1: 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:

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

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, we converted the units of solute in the numerator from mg to g to match the units in the denominator. We could just as easily have converted the denominator 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.

? Exercise 1.3.4.1

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?

Answer

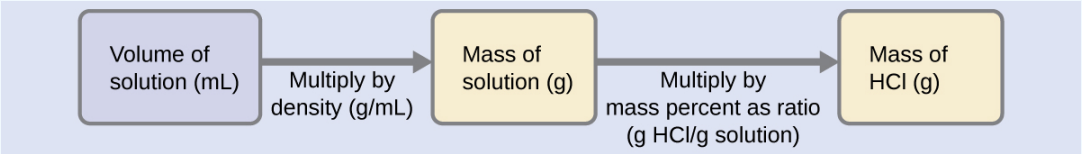
14.8%

✓ Example 1.3.4.2: 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 $5 \times 40 = 200$ g. To derive the mass of solute in a solution from its mass percentage, we need to know the corresponding mass of the solution. Using the solution density given, we can 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:



A diagram of three boxes connected by a right-facing arrow in between each is shown. The box on the left contains the phrase, "Volume of solution (m L)," the middle box reads, "Mass of solution (g)," while the one on the right contains the phrase, "Mass of H C l (g)." There is a phrase under the left arrow that says, "Multiply by density (g / m L)" and under the right arrow it states, "Multiply by mass percent as ratio (g H C l / g solution)."

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:

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

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

? Exercise 1.3.4.2

What volume of concentrated HCl solution contains 125 g of HCl?

Answer

282 mL

1.3.4.2: 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)%:

$$\text{volume percentage} = \frac{\text{volume solute}}{\text{volume solution}} \times 100\% \tag{1.3.4.2}$$

Example 1.3.4.3: 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:

$$355 \text{ mL solution}\left(\frac{70 \text{ mL isopropyl alcohol}}{100 \text{ mL solution}}\right)\left(\frac{0.785 \text{ g isopropyl alcohol}}{1 \text{ mL isopropyl alcohol}}\right) = 195 \text{ g isopropyl alcohol}$$

Exercise 1.3.4.3

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?

Answer

1.5 mol ethanol

1.3.4.3: 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 1.3.4.2).



Figure 1.3.4.2: “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. (credit a: modification of work by “The National Guard”/Flickr; credit b: modification of work by Biswarup Ganguly).

Two pictures are shown labeled a and b. Picture a depicts a clear, colorless solution in a plastic bag being held in a person’s hand. Picture b shows a person’s hand holding a detection meter with a digital readout screen while another hand holds someone’s finger up to the end of the meter. The meter is pressed to the drop of blood that is at the end of the person’s finger.

1.3.4.4: Parts per Million and Parts per Billion

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:

$$\text{ppm} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^6 \text{ ppm} \tag{1.3.4.3}$$

$$\text{ppb} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^9 \text{ ppb} \tag{1.3.4.4}$$

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 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 (Figure 1.3.4.3).

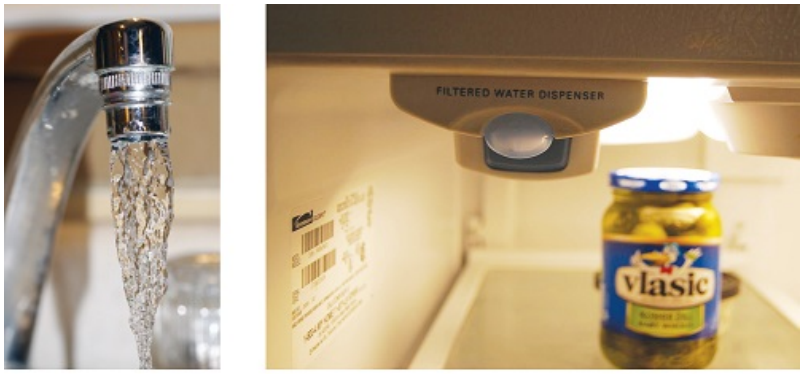


Figure 1.3.4.3: (a) In some areas, trace-level concentrations of contaminants can render unfiltered tap water unsafe for drinking and cooking. (b) Inline water filters reduce the concentration of solutes in tap water. (credit a: modification of work by Jenn Durfey; credit b: modification of work by "vastateparkstaff"/Wikimedia commons).

Two pictures are shown labeled a and b. Picture a depicts a clear, colorless solution in a plastic bag being held in a person's hand. Picture b shows a person's hand holding a detection meter with a digital readout screen while another hand holds someone's finger up to the end of the meter. The meter is pressed to the drop of blood that is at the end of the person's finger.

Example 1.3.4.4: 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:

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

The definition of the ppb unit may be used to calculate the requested mass if the mass of the solution is provided. However, only the volume of solution (300 mL) is given, so we must use the density to derive the corresponding mass. We can 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:

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

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

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

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

$$4.5 \times 10^{-6} \text{ g} \times \frac{1 \ \mu\text{g}}{10^{-6} \text{ g}} = 4.5 \ \mu\text{g}$$

? Exercise 1.3.4.4

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.

Answer

9.6 ppm, 9600 ppb

Summary

In addition to molarity, a number of other solution concentration units are used in various applications. Percentage concentrations based on the solution components' masses, volumes, or both are useful for expressing relatively high concentrations, whereas lower concentrations are conveniently expressed using ppm or ppb units. These units are popular in environmental, medical, and other fields where mole-based units such as molarity are not as commonly used.

Glossary

mass percentage
ratio of solute-to-solution mass expressed as a percentage

mass-volume percent
ratio of solute mass to solution volume, expressed as a percentage

parts per billion (ppb)
ratio of solute-to-solution mass multiplied by 10^9

parts per million (ppm)
ratio of solute-to-solution mass multiplied by 10^6

volume percentage
ratio of solute-to-solution volume expressed as a percentage

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1.3.5: Composition of Substances and Solutions (Study Guide)

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1.3.E: Composition of Substances and Solutions (Exercises)

1.3.E.1: Formula Mass and the Mole Concept

Exercise 1.3.E.1

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.

Answer

Formic acid. Its formula has twice as many oxygen atoms as the other two compounds (one each). Therefore, 0.60 mol of formic acid would be equivalent to 1.20 mol of a compound containing a single oxygen atom.

Exercise 1.3.E.2

Determine the mass of each of the following:

1. 0.0146 mol KOH
2. 10.2 mol ethane, C_2H_6
3. 1.6×10^{-3} mol $Na_2 SO_4$
4. 6.854×10^3 mol glucose, $C_6 H_{12} O_6$
5. 2.86 mol $Co(NH_3)_6Cl_3$

Answer

1. 0.819 g;
2. 307 g;
3. 0.23 g;
4. 1.235×10^6 g (1235 kg);
5. 765 g

Exercise 1.3.E.3

A certain nut crunch cereal contains 11.0 grams of sugar (sucrose, $C_{12}H_{22}O_{11}$) per serving size of 60.0 grams. How many servings of this cereal must be eaten to consume 0.0278 moles of sugar?

Answer

0.865 servings, or about 1 serving.

Exercise 1.3.E.4

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.

Answer

$Mg_3Si_2H_3O_8$ (empirical formula), $Mg_6Si_4H_6O_{16}$ (molecular formula)

Exercise 1.3.E.5

A major textile dye manufacturer developed a new yellow dye. The dye has a percent composition of 75.95% C, 17.72% N, and 6.33% H by mass with a molar mass of about 240 g/mol. Determine the molecular formula of the dye.

Answer

$C_{15}H_{15}N_3$?)

Exercise 1.3.E.6

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

Answer

Exercise 1.3.E.7

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?

Answer

0.5000 L

Exercise 1.3.E.8

A 2.00-L bottle of a solution of concentrated HCl was purchased for the general chemistry laboratory. The solution contained 868.8 g of HCl. What is the molarity of the solution?

Answer

11.9 M

Exercise 1.3.E.9

What volume of a 0.33-*M* $C_{12}H_{22}O_{11}$ solution can be diluted to prepare 25 mL of a solution with a concentration of 0.025 *M*?

Answer

1.9 mL

Exercise 1.3.E.10

Determine the molarity of each of the following solutions:

a. 1.457 mol KCl in 1.500 L of solution
b. 0.515 g of H_2SO_4 in 1.00 L of solution
c. 20.54 g of $Al(NO_3)_3$ in 1575 mL of solution
d. 2.76 kg of $CuSO_4 \cdot 5H_2O$ in 1.45 L of solution
e. 0.005653 mol of Br_2 in 10.00 mL of solution
f. 0.000889 g of glycine, $C_2H_5NO_2$, in 1.05 mL of solution

Answer

(a) 37.0 mol H_2SO_4; 3.63×10^3 g H_2SO_4;

(b) 3.8×10^{-6} mol NaCN; 1.9×10^{-4} g NaCN;

(c) 73.2 mol H_2CO; 2.20 kg H_2CO;

(d) 5.9×10^{-7} mol $FeSO_4$; 8.9×10^{-5} g $FeSO_4$

MORE *unformatted* Exercises

What is the total mass (amu) of carbon in each of the following molecules?

1. (a) CH_4
2. (b) $CHCl_3$
3. (c) $C_{12}H_{10}O_6$
4. (d) $CH_3CH_2CH_2CH_2CH_3$

(a) 12.01 amu; (b) 12.01 amu; (c) 144.12 amu; (d) 60.05 amu

What is the total mass of hydrogen in each of the molecules?

1. (a) CH_4
2. (b) $CHCl_3$
3. (c) $C_{12}H_{10}O_6$
4. (d) $CH_3CH_2CH_2CH_2CH_3$

Calculate the molecular or formula mass of each of the following:

(a) P_4

(b) H_2O

(c) $Ca(NO_3)_2$

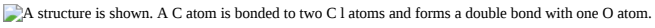
(d) CH_3CO_2H (acetic acid)

(e) $C_{12}H_{22}O_{11}$ (sucrose, cane sugar).

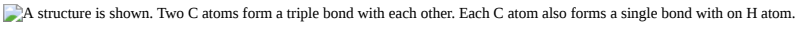
(a) 123.896 amu; (b) 18.015 amu; (c) 164.086 amu; (d) 60.052 amu; (e) 342.297 amu

Determine the molecular mass of the following compounds:

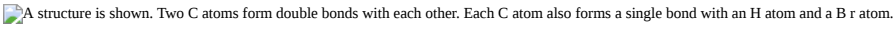
(a)



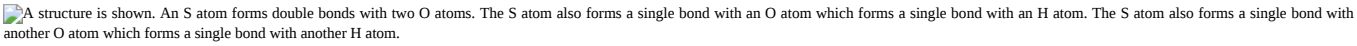
(b)



(c)

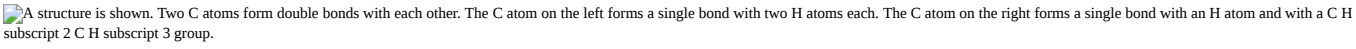


(d)

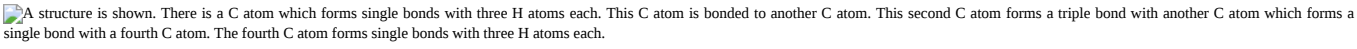


Determine the molecular mass of the following compounds:

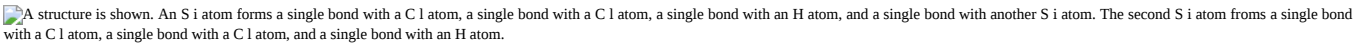
(a)



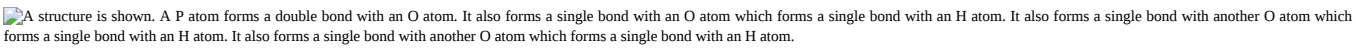
(b)



(c)



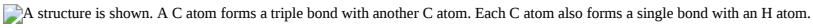
(d)



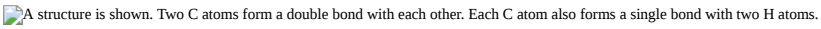
1. (a) 56.107 amu;
2. (b) 54.091 amu;
3. (c) 199.9976 amu;
4. (d) 97.9950 amu

Which molecule has a molecular mass of 28.05 amu?

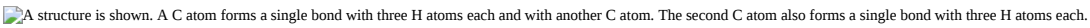
(a)



(b)



(c)



Write a sentence that describes how to determine the number of moles of a compound in a known mass of the compound if we know its molecular formula.

Use the molecular formula to find the molar mass; to obtain the number of moles, divide the mass of compound by the molar mass of the compound expressed in grams.

Compare 1 mole of H_2, 1 mole of O_2, and 1 mole of F_2.

1. (a) Which has the largest number of molecules? Explain why.
2. (b) Which has the greatest mass? Explain why.

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.

How are the molecular mass and the molar mass of a compound similar and how are they different?

The two masses have the same numerical value, but the units are different: The molecular mass is the mass of 1 molecule while the molar mass is the mass of 6.022×10^{23} molecules.

Calculate the molar mass of each of the following compounds:

1. (a) hydrogen fluoride, HF
2. (b) ammonia, NH_3
3. (c) nitric acid, HNO_3
4. (d) silver sulfate, Ag_2SO_4
5. (e) boric acid, $B(OH)_3$

Calculate the molar mass of each of the following:

1. (a) S_8
2. (b) C_5H_{12}
3. (c) $Sc_2(SO_4)_3$
4. (d) CH_3COCH_3 (acetone)
5. (e) $C_6H_{12}O_6$ (glucose)

(a) 256.528 g/mol; (b) 72.150 g mol^{-1}; (c) 378.103 g mol^{-1}; (d) 58.080 g mol^{-1}; (e) 180.158 g mol^{-1}

Calculate the empirical or molecular formula mass and the molar mass of each of the following minerals:

1. (a) limestone, $CaCO_3$
2. (b) halite, NaCl
3. (c) beryl, $Be_3Al_2Si_6O_{18}$
4. (d) malachite, $Cu_2(OH)_2CO_3$
5. (e) turquoise, $CuAl_6(PO_4)_4(OH)_8(H_2O)_4$

Calculate the molar mass of each of the following:

1. (a) the anesthetic halothane, $C_2HBrClF_3$

2. (b) the herbicide paraquat, $C_{12}H_{14}N_2Cl_2$
3. (c) caffeine, $C_8H_{10}N_4O_2$
4. (d) urea, $CO(NH_2)_2$
5. (e) a typical soap, $C_{17}H_{35}CO_2Na$

(a) 197.382 g mol^{-1}; (b) 257.163 g mol^{-1}; (c) 194.193 g mol^{-1}; (d) 60.056 g mol^{-1}; (e) 306.464 g mol^{-1}

Determine the number of moles of compound and the number of moles of each type of atom in each of the following:

1. (a) 25.0 g of propylene, C_3H_6
2. (b) 3.06×10^{-3} g of the amino acid glycine, $C_2H_5NO_2$
3. (c) 25 lb of the herbicide Treflan, $C_{13}H_{16}N_2O_4F$ (1 lb = 454 g)
4. (d) 0.125 kg of the insecticide Paris Green, $Cu_4(AsO_3)_2(CH_3CO_2)_2$
5. (e) 325 mg of aspirin, $C_6H_4(CO_2H)(CO_2CH_3)$

Determine the number of moles of the compound and determine the number of moles of each type of atom in each of the following:

1. (a) 2.12 g of potassium bromide, KBr
2. (b) 0.1488 g of phosphoric acid, H_3PO_4
3. (c) 23 kg of calcium carbonate, $CaCO_3$
4. (d) 78.452 g of aluminum sulfate, $Al_2(SO_4)_3$
5. (e) 0.1250 mg of caffeine, $C_8H_{10}N_4O_2$

Determine the mass of each of the following:

1. (a) 2.345 mol LiCl
2. (b) 0.0872 mol acetylene, C_2H_2
3. (c) 3.3×10^{-2} mol $Na_2\ CO_3$
4. (d) 1.23×10^{3} mol fructose, $C_6\ H_{12}\ O_6$
5. (e) 0.5758 mol $FeSO_4(H_2O)_7$

1. (a) 99.41 g;
2. (b) 2.27 g;
3. (c) 3.5 g;
4. (d) 222 kg;
5. (e) 160.1 g

The approximate minimum daily dietary requirement of the amino acid leucine, $C_6H_{13}NO_2$, is 1.1 g. What is this requirement in moles?

Determine the mass in grams of each of the following:

1. (a) 0.600 mol of oxygen atoms
2. (b) 0.600 mol of oxygen molecules, O_2
3. (c) 0.600 mol of ozone molecules, O_3

1.

(a) 9.60 g; (b) 19.2 g; (c) 28.8 g

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?

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.

zirconium: 2.038×10^{23} atoms; 30.87 g; silicon: 2.038×10^{23} atoms; 9.504 g; oxygen: 8.151×10^{23} atoms; 21.66 g

Determine which of the following contains the greatest mass of hydrogen: 1 mol of CH_4, 0.6 mol of C_6H_6, or 0.4 mol of C_3H_8.

Determine which of the following contains the greatest mass of aluminum: 122 g of $AlPO_4$, 266 g of Al_2Cl_6, or 225 g of Al_2S_3.

$AlPO_4$: 1.000 mol

Al_2Cl_6: 1.994 mol

Al_2S_3: 3.00 mol

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?

The Cullinan diamond was the largest natural diamond ever found (January 25, 1905). It weighed 3104 carats (1 carat = 200 mg). How many carbon atoms were present in the stone?

3.113×10^{25} C atoms

One 55-gram serving of a particular cereal supplies 270 mg of sodium, 11% of the recommended daily allowance. How many moles and atoms of sodium are in the recommended daily allowance?

A certain nut crunch cereal contains 11.0 grams of sugar (sucrose, $C_{12}H_{22}O_{11}$) per serving size of 60.0 grams. How many servings of this cereal must be eaten to consume 0.0278 moles of sugar?

0.865 servings, or about 1 serving.

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?

Which of the following represents the least number of molecules?

a. 20.0 g of H_2O (18.02 g/mol)
b. 77.0 g of CH_4 (16.06 g/mol)
c. 68.0 g of CaH_2 (42.09 g/mol)
d. 100.0 g of N_2O (44.02 g/mol)
e. 84.0 g of HF (20.01 g/mol)

20.0 g H_2O represents the least number of molecules since it has the least number of moles.

1.3.E.2: Determining Empirical and Molecular Formulas

What information do we need to determine the molecular formula of a compound from the empirical formula?

Calculate the following to four significant figures:

a. (a) the percent composition of ammonia, NH_3
b. (b) the percent composition of photographic “hypo,” $Na_2S_2O_3$
c. (c) the percent of calcium ion in $Ca_3(PO_4)_2$

(a) % N = 82.24%

% H = 17.76%;

(b) % Na = 29.08%

% S = 40.56%

% O = 30.36%;

(c) % Ca^{2+} = 38.76%

Determine the following to four significant figures:

a. the percent composition of hydrazoic acid, HN_3
b. the percent composition of TNT, $C_6H_2(CH_3)(NO_2)_3$
c. the percent of SO_4^{2-} in $Al_2(SO_4)_3$

Determine the percent ammonia, NH_3, in $Co(NH_3)_6Cl_3$, to three significant figures.

% NH_3 = 38.2%

Determine the percent water in $CuSO_4 \cdot 5H_2O$ to three significant figures.

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

(a) CS_2

(b) CH_2O

Determine the empirical formulas for compounds with the following percent compositions:

(a) 43.6% phosphorus and 56.4% oxygen

(b) 28.7% K, 1.5% H, 22.8% P, and 47.0% O

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?

C_6H_6

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?

Polymers are large molecules composed of simple units repeated many times. Thus, they often have relatively simple empirical formulas. Calculate the empirical formulas of the following polymers:

a. Lucite (Plexiglas); 59.9% C, 8.06% H, 32.0% O
b. Saran; 24.8% C, 2.0% H, 73.1% Cl
c. polyethylene; 86% C, 14% H
d. polystyrene; 92.3% C, 7.7% H
e. Orlon; 67.9% C, 5.70% H, 26.4% N

1.3.E.3: Molarity

1.3.E.3.1: Questions

Explain what changes and what stays the same when 1.00 L of a solution of NaCl is diluted to 1.80 L.

What information do we need to calculate the molarity of a sulfuric acid solution?

We need to know the number of moles of sulfuric acid dissolved in the solution and the volume of the solution.

What does it mean when we say that 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?

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

a. (a) 0.679 *M*;
b. (b) 1.00 *M*;
c. (c) 0.06998 *M*;
d. (d) 1.75 *M*;
e. (e) 0.070 *M*;
f. (f) 6.6 *M*

Consider this question: What is the mass of the solute in 0.500 L of 0.30 *M* glucose, $C_6H_{12}O_6$, used for intravenous injection?

(a) Outline the steps necessary to answer the question.

(b) Answer the question.

(a) determine the number of moles of glucose in 0.500 L of solution; determine the molar mass of glucose; determine the mass of glucose from the number of moles and its molar mass; (b) 27 g

Consider this question: What is the mass of solute in 200.0 L of a 1.556-*M* solution of KBr?

1. (a) Outline the steps necessary to answer the question.
2. (b) Answer the question.

Answer:

(a)

1. Calculate to moles of KBr by multiplying the Molarity by the amount of solution (200.0 L)
2. Find the Molar Mass of KBr and convert moles of solute to grams

(b)

$$\frac{1.556\ moles\ \text{KBr}}{1\ \cancel{L}} \times 200.0\ \cancel{L} = 311.2\ moles\ \text{KBr}$$

$$311.2\ \cancel{moles}\ \text{KBr} \times \frac{119.0\ g\ \text{KBr}}{1\ \cancel{mole}\ \text{KBr}} = 37,030\ g$$

37,030g; 37.03 kg

Calculate the number of moles and the mass of the solute in each of the following solutions:

a. 325 mL of 8.23×10^{-5} *M* KI, a source of iodine in the diet
b. 75.0 mL of 2.2×10^{-5} *M* H_2SO_4, a sample of acid rain
c. 0.2500 L of 0.1135 *M* K_2CrO_4, an analytical reagent used in iron assays
d. 10.5 L of 3.716 *M* $(NH_4)_2SO_4$, a liquid fertilizer

Answers:

a. 2.67×10^{-5} moles KI; 4.44×10^{-3}g KI

b. 1.7×10^{-6} moles H_2SO_4 ; 1.6×10^{-4} g H_2SO_4

c. 2.838×10^{-2} moles K_2CrO_4 ; 5.510g K_2CrO_4

d. 39.0 moles $(NH_4)_2SO_4$; 5,160 g $(NH_4)_2SO_4$

Consider this question: What is the molarity of $KMnO_4$ in a solution of 0.0908 g of $KMnO_4$ in 0.500 L of solution?

1. (a) Outline the steps necessary to answer the question.
2. (b) Answer the question.

(a) Determine the molar mass of $KMnO_4$; determine the number of moles of $KMnO_4$ in the solution; from the number of moles and the volume of solution, determine the molarity; (b) 1.15×10^{-3} *M*

Consider this question: What is the molarity of HCl if 35.23 mL of a solution of HCl contain 0.3366 g of HCl?

1. (a) Outline the steps necessary to answer the question.
2. (b) Answer the question.

Answer:

(a)

1. Convert g of HCl to moles of HCl and convert mL of solution to L of solution
2. Divide moles of HCl by L of solution

(b)

$$0.3366\ \cancel{g}\ \text{HCl} \times \frac{1\ mole\ \text{HCl}}{36.46\ \cancel{g}\ \text{HCl}} = 9.232 \times 10^{-3}\ moles\ \text{HCl}$$

$$35.23\ mL = 0.03523\ L$$

$$\frac{9.232 \times 10^{-3}\ moles\ \text{HCl}}{0.03523\ L} = 0.2621\ M\ \text{HCl}$$

0.2621 M ;

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

(a) 5.04×10^{-3} *M*;

(b) 0.499 *M*;

(c) 9.92 *M*;

(d) 1.1×10^{-3} *M*

Calculate the molarity of each of the following solutions:

a. 293 g HCl in 666 mL of solution, a concentrated HCl solution
b. 2.026 g $FeCl_3$ in 0.1250 L of a solution used as an unknown in general chemistry laboratories
c. 0.001 mg Cd^{2+} in 0.100 L, the maximum permissible concentration of cadmium in drinking water
d. 0.0079 g $C_7H_5SNO_3$ in one ounce (29.6 mL), the concentration of saccharin in a diet soft drink.

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?

0.025 *M*

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*?

If 4.12 L of a 0.850 *M*-H_3PO_4 solution is be diluted to a volume of 10.00 L, what is the concentration the resulting solution?

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?

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

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

1. (a) 0.125 *M*;
2. (b) 0.04888 *M*;
3. (c) 0.206 *M*;
4. (e) 0.0056 *M*

What is the final concentration of the solution produced when 225.5 mL of a 0.09988-*M* solution of Na_2CO_3 is allowed to evaporate until the solution volume is reduced to 45.00 mL?

An experiment in a general chemistry laboratory calls for a 2.00-*M* solution of HCl. How many mL of 11.9 *M* HCl would be required to make 250 mL of 2.00 *M* HCl?

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

1.6 L

The US Environmental Protection Agency (EPA) places limits on the quantities of toxic substances that may be discharged into the sewer system. Limits have been established for a variety of substances, including hexavalent chromium, which is limited to 0.50 mg/L. If an industry is discharging hexavalent chromium as potassium dichromate ($K_2Cr_2O_7$), what is the maximum permissible molarity of that substance?

1.3.E.4: 3.4: Other Units for Solution Concentrations

1.3.E.4.1: Questions

1. Consider this question: What mass of a concentrated solution of nitric acid (68.0% HNO3 by mass) is needed to prepare 400.0 g of a 10.0% solution of HNO3 by mass?
   a. Outline the steps necessary to answer the question.
   b. Answer the question.
2. What mass of a 4.00% NaOH solution by mass contains 15.0 g of NaOH?
3. 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.
4. 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?
5. The hardness of water (hardness count) is usually expressed in parts per million (by mass) of $\mathrm{CaCO_3}$, which is equivalent to milligrams of $\mathrm{CaCO_3}$ 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?
6. The level of mercury in a stream was suspected to be above the minimum considered safe (1 part per billion by weight). An analysis indicated that the concentration was 0.68 parts per billion. Assume a density of 1.0 g/mL and calculate the molarity of mercury in the stream.
7. 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 mM is observed, what is the concentration of glucose ($C_6H_{12}O_6$) in mg/dL?
8. A throat spray is 1.40% by mass phenol, $\mathrm{C_6H_5OH}$, in water. If the solution has a density of 0.9956 g/mL, calculate the molarity of the solution.
9. Copper(I) iodide (CuI) is often added to table salt as a dietary source of iodine. How many moles of CuI are contained in 1.00 lb (454 g) of table salt containing 0.0100% CuI by mass?
10. 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.
11. D5W is a solution used as an intravenous fluid. It is a 5.0% by mass solution of dextrose ($\mathrm{C_6H_{12}O_6}$) in water. If the density of D5W is 1.029 g/mL, calculate the molarity of dextrose in the solution.
12. Find the molarity of a 40.0% by mass aqueous solution of sulfuric acid, $\mathrm{H_2SO_4}$, for which the density is 1.3057 g/mL.

1.3.E.4.2: Solutions

1

- (a) The dilution equation can be used, appropriately modified to accommodate mass-based concentration units:

$$\%\,\mathrm{mass}_1 \times \mathrm{mass}_1 = \%\,\mathrm{mass}_2 \times \mathrm{mass}_2 \tag{1.3.E.1}$$

  This equation can be rearranged to isolate mass_1 and the given quantities substituted into this equation.
- (b) 58.8 g

3. 114 g5. $1.75 \times 10^{-3} M$ 7 95 mg/dL9 2.38×10^{-4} mol 11 0.29mol

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SECTION OVERVIEW

1.4: Stoichiometry of Chemical Reactions

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General Chemistry

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*.

1.4.1: Prelude to Stoichiometry

1.4.2: Writing and Balancing Chemical Equations

1.4.3: Classifying Chemical Reactions

1.4.4: Reaction Stoichiometry

1.4.5: Reaction Yields

1.4.6: Quantitative Chemical Analysis

1.4.E: Stoichiometry of Chemical Reactions (Exercises)

1.4.S: Stoichiometry of Chemical Reactions (Summary)

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1.4.1: Prelude to Stoichiometry

Solid-fuel rockets are a central feature in the world's space exploration programs, including the new Space Launch System being developed by the National Aeronautics and Space Administration (NASA) to replace the retired Space Shuttle fleet (Figure 1.4.1.1). 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*.



Figure 1.4.1.1: Many modern rocket fuels are solid mixtures of substances combined in carefully measured amounts and ignited to yield a thrust-generating chemical reaction. (credit: modification of work by NASA)

An image is shown of a rocket that appears to have just passed through a layer of clouds as it travels skyward. A bright white light is seen in the upper right corner of the image. To the lower left appears the layer of clouds and the bottom of the rocket with fire projecting from the fuel cones at its base.

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1.4.2: Writing and Balancing Chemical Equations

Learning Objectives

- Derive chemical equations from narrative descriptions of chemical reactions.
- Write and balance chemical equations in molecular, total ionic, and net ionic formats.

The preceding chapter 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 molecule (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 1.4.2.1, with space-filling molecular models shown in the lower half of the figure.

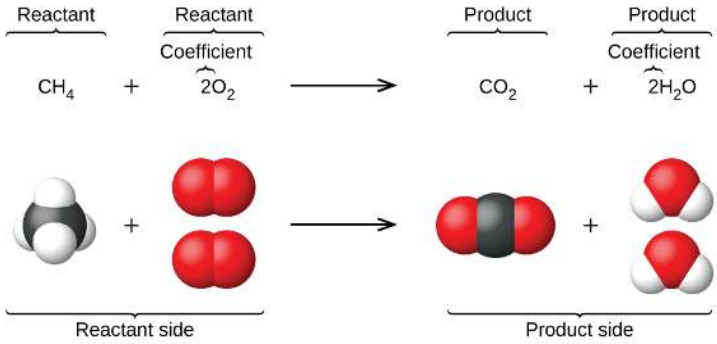


Figure 1.4.2.1: The reaction between methane and oxygen to yield carbon dioxide and water (shown at bottom) may be represented by a chemical equation using formulas (top).

This figure shows a balanced chemical equation followed below by a representation of the equation using space-filling models. The equation reads C H subscript 4 plus 2 O subscript 2 arrow C O subscript 2 plus 2 H subscript 2 O. Under the C H subscript 4, the molecule is shown with a central black sphere, representing a C atom, to which 4 smaller white spheres, representing H atoms, are distributed evenly around. All four H atoms are bonded to the central black C atom. This is followed by a plus sign. Under the 2 O subscript 2, two molecules are shown. The molecules are each composed of two red spheres bonded together. The red spheres represent O atoms. To the right of an arrow and under the C O subscript 2, appears a single molecule with a black central sphere with two red spheres bonded to the left and right. Following a plus sign and under the 2 H subscript 2 O, are two molecules, each with a central red sphere and two smaller white spheres attached to the lower right and lower left sides of the central red sphere. Note that in space filling models of molecules, spheres appear slightly compressed in regions where there is a bond between two atoms.

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 sight 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 1.4.2.2). 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.

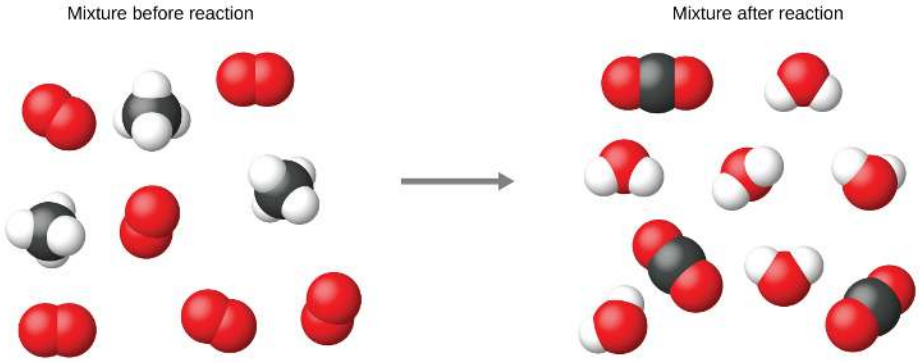


Figure 1.4.2.2: Regardless of the absolute number of molecules involved, the ratios between numbers of molecules of each species that react (the reactants) and molecules of each species that form (the products) are the same and are given in the chemical equation.

1.4.2.1: Balancing Equations

When a chemical equation is balanced it means 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, $\mathrm{CO_2}$ and $\mathrm{H_2O}$, contain the element oxygen, and so the number of oxygen atoms on the product side of the equation is

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

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:

$$\mathrm{CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O}$$

Equation for the reaction

$$\mathrm{CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O}$$

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:

$$\mathrm{H_2O \rightarrow H_2 + O_2} \qquad \text{(unbalanced)}$$

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

Comparisons between H and O atoms

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.

$$2\,H_2O \rightarrow H_2 + O_2 \qquad \text{(unbalanced)}$$

O atom balance may be achieved by changing the coefficient for H2O to 2

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.

$$2\,H_2O \rightarrow 2\,H_2 + O_2 \qquad \text{(balanced)}$$

H atom balance upset but easily reestablished by changing the coefficient for the H2 product to 2.

Element	Reactants	Products	Balanced?
H	2 × 2 = 4	**2** × 2 = 2	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:

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

Example 1.4.2.1: 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.

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

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

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).

$$\mathrm{N_2 + 5\,O_2 \rightarrow 2\,N_2O_5} \qquad \text{(unbalanced)}$$

$$\mathrm{N_2 + 5\,O_2 \rightarrow 2\,N_2O_5} \qquad \text{(unbalanced)}$$

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 $\mathrm{N_2}$ to 2.

$$\mathrm{2\,N_2 + 5\,O_2 \rightarrow 2\,N_2O_5}$$

N atom balance upset but restored by changing the coefficient for the reactant N2 to 2.

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.

? Exercise 1.4.2.1

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.)

Answer

$$\mathrm{2\,NH_4NO_3 \rightarrow 2\,N_2 + O_2 + 4\,H_2O}$$

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

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 ($\mathrm{C_2H_6}$) with oxygen to yield $\mathrm{H_2O}$ and $\mathrm{CO_2}$, represented by the unbalanced equation:

$$\mathrm{C_2H_6 + O_2 \rightarrow H_2O + CO_2} \qquad \text{(unbalanced)}$$

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

$$\mathrm{C_2H_6 + O_2 \rightarrow 3\,H_2O + 2\,CO_2} \qquad \text{(unbalanced)}$$

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

$$\mathrm{C_2H_6 + \tfrac{7}{2}\,O_2 \rightarrow 3\,H_2O + 2\,CO_2}$$

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

$$\mathrm{2\,C_2H_6 + 7\,O_2 \rightarrow 6\,H_2O + 4\,CO_2}$$

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,

$$3\,\mathrm{N_2} + 9\,\mathrm{H_2} \rightarrow 6\,\mathrm{NH_3}$$

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:

$$\mathrm{N_2} + 3\,\mathrm{H_2} \rightarrow 2\,\mathrm{NH_3}$$

Phet Simulation

Use this interactive tutorial for additional practice balancing equations.

1.4.2.2: 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*, as introduced in the preceding chapter). These notations are illustrated in the example equation here:

$$2\,\mathrm{Na(s)} + 2\,\mathrm{H_2O(l)} \rightarrow 2\,\mathrm{NaOH(aq)} + \mathrm{H_2(g)}$$

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.

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

Other examples of these special conditions will be encountered in more depth in later chapters.

1.4.2.3: 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 $\mathrm{CaCl_2}$ and $\mathrm{AgNO_3}$ are mixed, a reaction takes place producing aqueous $\mathrm{Ca(NO_3)_2}$ and solid AgCl:

$$\mathrm{CaCl_2}(aq) + 2\,\mathrm{AgNO_3}(aq) \rightarrow \mathrm{Ca(NO_3)_2}(aq) + 2\,\mathrm{AgCl}(s)$$

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 (a thorough discussion of this important process is provided in the chapter on solutions). Ionic compounds dissolved in water are, therefore, more realistically represented as dissociated ions, in this case:

$$\mathrm{CaCl_2}(aq) \rightarrow \mathrm{Ca^{2+}}(aq) + 2\,\mathrm{Cl^-}(aq)$$

$$2\,\mathrm{AgNO_3}(aq) \rightarrow 2\,\mathrm{Ag^+}(aq) + 2\,\mathrm{NO_3^-}(aq)$$

$$\mathrm{Ca(NO_3)_2}(aq) \rightarrow \mathrm{Ca^{2+}}(aq) + 2\,\mathrm{NO_3^-}(aq)$$

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:

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

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:

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

$$2\,Cl^{-}(aq) + 2\,Ag^{+}(aq) \rightarrow 2\,AgCl(s)$$

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

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

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 1.4.2.2: 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:

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

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

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

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

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

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:

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

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

Exercise 1.4.2.2

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.

Answer

Balanced molecular equation:

$$2\,NaCl(aq) + 2\,H_2O(l) \longrightarrow 2\,NaOH(aq) + H_2(g) + Cl_2(g)$$

Balanced ionic equation:

$$2\,Na^+(aq) + 2\,Cl^-(aq) + 2\,H_2O(l) \longrightarrow 2\,Na^+(aq) + 2\,OH^-(aq) + H_2(g) + Cl_2(g)$$

Balanced net ionic equation:

$$2\,Cl^-(aq) + 2\,H_2O(l) \longrightarrow 2\,OH^-(aq) + H_2(g) + Cl_2(g)$$

1.4.2.4: Key Concepts and Summary

Chemical equations are symbolic representations of chemical and physical changes. Formulas for the substances undergoing the change (reactants) and substances generated by the change (products) are separated by an arrow and preceded by integer coefficients indicating their relative numbers. Balanced equations are those whose coefficients result in equal numbers of atoms for each element in the reactants and products. Chemical reactions in aqueous solution that involve ionic reactants or products may be represented more realistically by complete ionic equations and, more succinctly, by net ionic equations.

Glossary

balanced equation
chemical equation with equal numbers of atoms for each element in the reactant and product

chemical equation
symbolic representation of a chemical reaction

coefficient
number placed in front of symbols or formulas in a chemical equation to indicate their relative amount

complete ionic equation
chemical equation in which all dissolved ionic reactants and products, including spectator ions, are explicitly represented by formulas for their dissociated ions

molecular equation
chemical equation in which all reactants and products are represented as neutral substances

net ionic equation
chemical equation in which only those dissolved ionic reactants and products that undergo a chemical or physical change are represented (excludes spectator ions)

product
substance formed by a chemical or physical change; shown on the right side of the arrow in a chemical equation

reactant
substance undergoing a chemical or physical change; shown on the left side of the arrow in a chemical equation

spectator ion
ion that does not undergo a chemical or physical change during a reaction, but its presence is required to maintain charge neutrality

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1.4.3: Classifying Chemical Reactions

Learning Objectives

- Define three common types of chemical reactions (precipitation, acid-base, and oxidation-reduction)
- Classify chemical reactions as one of these three types given appropriate descriptions or chemical equations
- Identify common acids and bases
- Predict the solubility of common inorganic compounds by using solubility rules
- Compute the oxidation states for elements in compounds

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: precipitation, acid-base, and oxidation-reduction.

1.4.3.1: 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 (see the last module of this chapter).

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 solubilities are said to be soluble. A substance will precipitate when solution conditions are such that its concentration exceeds its solubility. Substances with relatively low solubilities are said to be insoluble, and these are the substances that readily precipitate from solution. More information on these important concepts is provided in the text chapter on solutions. 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 1.4.3.1).

Table 1.4.3.1: Solubilities of Common Ionic Compounds in Water

Soluble compounds contain	**Exceptions** to these solubility rules include
• group 1 metal cations (Li^+, Na^+, K^+, Rb^+, and Cs^+) and ammonium ion (NH_4^+) • the halide ions (Cl^-, Br^-, and I^-) • the acetate ($C_2H_3O_2^-$), bicarbonate (HCO_3^-), nitrate (NO_3^-), and chlorate (ClO_3^-) ions • the sulfate (SO_4^-) ion	• halides of Ag^+, Hg_2^{2+}, and Pb^{2+} • sulfates of Ag^+, Ba^{2+}, Ca^{2+}, Hg_2^{2+}, Pb^{2+}, and Sr^{2+}
Insoluble compounds contain	**Exceptions** to these insolubility rules include
• carbonate (CO_3^{2-}), chromate (CrO_4^{2-}), phosphate (PO_4^{3-}), and sulfide (S^{2-}) ions • hydroxide ion (OH^-)	• compounds of these anions with group 1 metal cations and ammonium ion • hydroxides of group 1 metal 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:

$$2\,KI(aq) + Pb(NO_3)_2(aq) \rightarrow PbI_2(s) + 2\,KNO_3(aq)$$

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:

$$\mathrm{Pb^{2+}}(aq) + 2\,\mathrm{I^-}(aq) \rightarrow \mathrm{PbI_2}(s)$$

Lead iodide is a bright yellow solid that was formerly used as an artist's pigment known as iodine yellow (Figure 1.4.3.1). The properties of pure PbI_2 crystals make them useful for fabrication of X-ray and gamma ray detectors.



Figure 1.4.3.1: A precipitate of PbI_2 forms when solutions containing Pb^{2+} and I^- are mixed. (credit: Der Kreole/Wikimedia Commons)

A photograph is shown of a yellow green opaque substance swirled through a clear, colorless liquid in a test tube.

The solubility guidelines in Table 1.4.3.1 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:

$$\mathrm{NaF}(aq) + \mathrm{AgNO_3}(aq) \rightarrow \mathrm{AgF}(s) + \mathrm{NaNO_3}(aq) \quad \text{(molecular)}$$

$$\mathrm{Ag^+}(aq) + \mathrm{F^-}(aq) \rightarrow \mathrm{AgF}(s) \quad \text{(net ionic)}$$

Example 1.4.3.1: 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, derived in the manner detailed in the previous module, is

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

(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, derived in the manner detailed in

the previous module, is

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

(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, derived in the manner detailed in the previous module, is

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

? Exercise 1.4.3.1

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?

Answer

sodium sulfate, $BaSO_4$

1.4.3.2: 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 later in the text.

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:

$$\mathrm{HCl}(aq) + \mathrm{H_2O}(aq) \rightarrow \mathrm{Cl^-}(aq) + \mathrm{H_3O^+}(aq)$$

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 1.4.3.2).

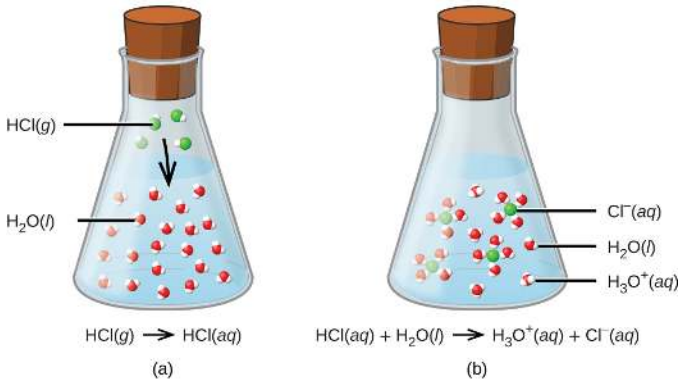


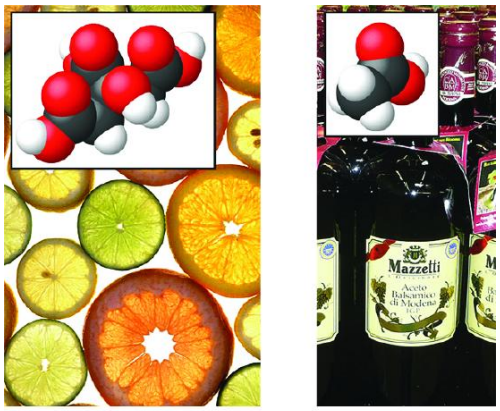
Figure 1.4.3.2: When hydrogen chloride gas dissolves in water, (a) it reacts as an acid, transferring protons to water molecules to yield (b) hydronium ions (and solvated chloride ions)

This figure shows two flasks, labeled a and b. The flasks are both sealed with stoppers and are nearly three-quarters full of a liquid. Flask a is labeled H C l followed by g in parentheses. In the liquid there are approximately twenty space-filling molecular models composed of one red sphere and two smaller attached white spheres. The label H subscript 2 O followed by a q in parentheses is connected with a line to one of these models. In the space above the liquid in the flask, four space filling molecular models composed of one larger green sphere to which a smaller white sphere is bonded are shown. To one of these models, the label H C l followed by g in parentheses is attached with a line segment. An arrow is drawn from the space above the liquid pointing down into the liquid below. Flask b is labeled H subscript 3 O superscript positive sign followed by a q in parentheses. This is followed by a plus sign and C l superscript negative sign which is also followed by a q in parentheses. In this flask, no molecules are shown in the open space above the liquid. A label, C l superscript negative sign followed by a q in parentheses, is connected with a line segment to a green sphere. This sphere is surrounded by four molecules composed each of one red sphere and two white smaller spheres. A few of these same molecules appear separate from the green spheres in the liquid. A line segment connects one of them to the label H subscript 2 O which is followed by l in parentheses. There are a few molecules formed from one central larger red sphere to which three smaller white spheres are bonded. A line segment is drawn from one of these to the label H subscript 3 O superscript positive sign, followed by a q in parentheses.

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 1.4.3.1). 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:

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{CH_3CO_2^-}(aq) + \mathrm{H_3O^+}(aq)$$

When dissolved in water under typical conditions, only about 1% of acetic acid molecules are present in the ionized form, $\mathrm{CH_3CO_2^-}$ (Figure 1.4.3.3). (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.)



(a) (b)

Figure 1.4.3.3: (a) Fruits such as oranges, lemons, and grapefruit contain the weak acid citric acid. (b) Vinegars contain the weak acid acetic acid. (credit a: modification of work by Scott Bauer; credit b: modification of work by Brücke-Osteuropa/Wikimedia Commons)

This figure contains two images, each with an associated structural formula provided in the lower left corner of the image. The first image is a photograph of a variety of thinly sliced, circular cross sections of citrus fruits ranging in color for green to yellow, to orange and reddish-orange. The slices are closely packed on a white background. The structural formula with this picture shows a central chain of five C atoms. The leftmost C atom has an O atom double bonded above and to the left and a singly bonded O atom below and to the left. This single bonded O atom has an H atom indicated in red on its left side which is highlighted in pink. The second C atom moving to the right has H atoms bonded above and below. The third C atom has a single bonded O atom above which has an H atom on its right. This third C atom has a C atom bonded below it which has an O atom double bonded below and to the left and a singly bonded O atom below and to the right. An H atom appears in red and is highlighted in pink to the right of the singly bonded O atom. The fourth C atom has H atoms bonded above and below. The fifth C atom is at the right end of the structure. It has an O atom double bonded above and to the right and a singly bonded O atom below and to the right. This single bonded O atom has a red H atom on its right side which is highlighted in pink. The second image is a photograph of bottles of vinegar. The bottles are labeled, “Balsamic Vinegar,” and appear to be clear and colorless. The liquid in this bottle appears to be brown. The structural formula that appears with this image shows a chain of two C atoms. The leftmost C atom has H atoms bonded above, below, and to the left. The C atom on the right has a doubly bonded O atom above and to the right and a singly bonded O atom below and to the right. This O atom has an H atom bonded to its right which is highlighted in pink.

Table 1.4.3.2: 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 $Ca(OH)_2$. When these compounds dissolve in water, hydroxide ions are released 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:

$$\mathrm{NaOH}(s) \rightarrow \mathrm{Na}^+(aq) + \mathrm{OH}^-(aq)$$

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 1.4.3.4). When dissolved in water, ammonia reacts partially to yield hydroxide ions, as shown here:

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

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



Figure 1.4.3.4: 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. (credit a: modification of work by National Resources Conservation Service; credit b: modification of work by pat00139)

This photograph shows a large agricultural tractor in a field pulling a field sprayer and a large, white cylindrical tank which is labeled “Caution Ammonia.”

The chemical reactions described in which acids and bases dissolved in water produce hydronium and hydroxide ions, respectively, are, by definition, acid-base reactions. In these reactions, water serves as both a solvent *and* a reactant. A neutralization reaction is a specific type of acid-base reaction in which the reactants are an acid and a base, the products are often a salt and water, and neither reactant is the water itself:

$$\mathrm{acid} + \mathrm{base} \rightarrow \mathrm{salt} + \mathrm{water}$$

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

$$\mathrm{Mg(OH)_2}(s) + 2\,\mathrm{HCl}(aq) \rightarrow \mathrm{MgCl_2}(aq) + 2\,\mathrm{H_2O}(l).$$

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

Example 1.4.3.2: 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 $\mathrm{H_2O}$. Since the substance is reported to be an acid, its reaction with water will involve the transfer of $\mathrm{H^+}$ from HOCl to $\mathrm{H_2O}$ to generate hydronium ions, $\mathrm{H_3O^+}$ and hypochlorite ions, $\mathrm{OCl^-}$.

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

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

$$\mathrm{Ba(OH)_2}(aq) + 2\,\mathrm{HNO_3}(aq) \rightarrow \mathrm{Ba(NO_3)_2}(aq) + 2\,\mathrm{H_2O}(l)$$

? Exercise 1.4.3.21

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.)

Answer

$$\mathrm{H_3O^+}(aq) + \mathrm{OH^-}(aq) \rightarrow 2\,\mathrm{H_2O}(l)$$

> *Explore the microscopic view of strong and weak acids and bases.*

1.4.3.3: 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:

$$2\,\mathrm{Na}(s) + \mathrm{Cl_2}(g) \rightarrow 2\,\mathrm{NaCl}(s)$$

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:

$$2\,\mathrm{Na}(s) \rightarrow 2\,\mathrm{Na^+}(s) + 2\,\mathrm{e^-}$$
$$\mathrm{Cl_2}(g) + 2\,\mathrm{e^-} \rightarrow 2\,\mathrm{Cl^-}(s)$$

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:

$$\textbf{oxidation} = \text{loss of electrons} \tag{1.4.3.1}$$
$$\textbf{reduction} = \text{gain of electrons} \tag{1.4.3.2}$$

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.

$$\textbf{reducing agent} = \text{species that is oxidized} \tag{1.4.3.3}$$
$$\textbf{oxidizing agent} = \text{species that is reduced} \tag{1.4.3.4}$$

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

$$\mathrm{H_2}(g) + \mathrm{Cl_2}(g) \rightarrow 2\,\mathrm{HCl}(g)$$

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 $-\frac{1}{2}$ (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 1.4.3.3: 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:

$$\text{charge on } H_2S = 0 = (2 \times +1) + (1 \times x)$$
$$x = 0 - (2 \times +1) = -2$$

(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:

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

(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:

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

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

Exercise 1.4.3.3

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

a. $K\underline{N}O_3$
b. $\underline{Al}H_3$
c. $\underline{N}H_4^+$
d. $H_2\underline{P}O_4^-$

Answer a

N, +5

Answer b

Al, +3

Answer c

N, −3

Answer d

P, +5

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 as shown below\). Definitions for the complementary processes of this reaction class are correspondingly revised as shown here:

$$\textbf{oxidation} = \text{increase in oxidation number} \tag{1.4.3.5}$$

$$\textbf{reduction} = \text{decrease in oxidation number} \tag{1.4.3.6}$$

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 such as the one depicted below are combustion processes. A typical propellant reaction in which solid aluminum is oxidized by ammonium perchlorate is represented by this equation:

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

Watch a brief video showing the test firing of a small-scale, prototype, hybrid rocket engine planned for use in the new Space Launch System being developed by NASA. The first engines firing at 3 s (green flame) use a liquid fuel/oxidant mixture, and the second, more powerful engines firing at 4 s (yellow flame) use a solid mixture.



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:

$$\mathrm{Zn}(s) + 2\,\mathrm{HCl}(aq) \rightarrow \mathrm{ZnCl_2}(aq) + \mathrm{H_2}(g)$$

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

$$\mathrm{Cu}(s) + 2\,\mathrm{AgNO_3}(aq) \rightarrow \mathrm{Cu(NO_3)_2}(aq) + 2\,\mathrm{Ag}(s)$$

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 1.4.3.4).

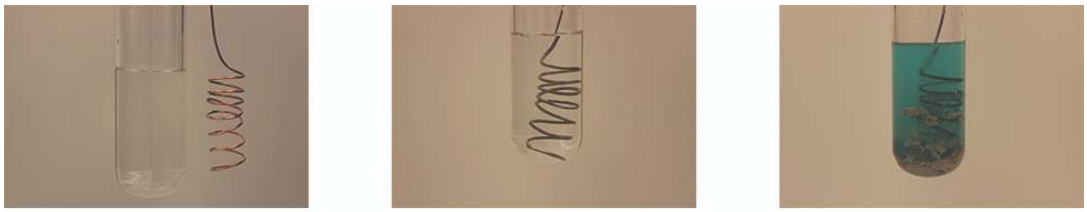


Figure 1.4.3.4: (a) A copper wire is shown next to a solution containing silver(I) ions. (b) Displacement of dissolved silver ions by copper ions results in (c) accumulation of gray-colored silver metal on the wire and development of a blue color in the solution, due to dissolved copper ions. (credit: modification of work by Mark Ott)

This figure contains three photographs. In a, a coiled copper wire is shown beside a test tube filled with a clear, colorless liquid. In b, the wire has been inserted into the test tube with the clear, colorless liquid. In c, the test tube contains a light blue liquid and the coiled wire appears to have a fuzzy silver gray coating.

Example 1.4.3.4: 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. $\mathrm{ZnCO_3}(s) \rightarrow \mathrm{ZnO}(s) + \mathrm{CO_2}(g)$
b. $2\,\mathrm{Ga}(l) + 3\,\mathrm{Br_2}(l) \rightarrow 2\,\mathrm{GaBr_3}(s)$
c. $2\,\mathrm{H_2O_2}(aq) \rightarrow 2\,\mathrm{H_2O}(l) + \mathrm{O_2}(g)$
d. $\mathrm{BaCl_2}(aq) + \mathrm{K_2SO_4}(aq) \rightarrow \mathrm{BaSO_4}(s) + 2\,\mathrm{KCl}(aq)$
e. $\mathrm{C_2H_4}(g) + 3\,\mathrm{O_2}(g) \rightarrow 2\,\mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l)$

Solution

Redox reactions are identified per definition if one or more elements undergo a change in oxidation number.

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).

Exercise 1.4.3.4

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

$$\mathrm{Sn}(s) + 2\,\mathrm{HCl}(g) \rightarrow \mathrm{SnCl_2}(s) + \mathrm{H_2}(g)$$

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

Answer

Yes, a single-replacement reaction. Sn(s) is the reductant, HCl(g) is the oxidant.

1.4.3.3.1: 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[1] 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:
   - Add OH^- ions to both sides of the equation in numbers equal to the number of H^+ ions.
   - On the side of the equation containing both H^+ and OH^- ions, combine these ions to yield water molecules.
   - Simplify the equation by removing any redundant water molecules.
9. Finally, check to see that both the number of atoms and the total charges[2] are balanced.

Example 1.4.3.5: 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.

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

Solution

Write the two half-reactions.

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

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

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.

$$\mathrm{Fe^{2+} \rightarrow Fe^{3+}}$$
$$\mathrm{Cr_2O_7^{2-} \rightarrow 2\,Cr^{3+}}$$

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.

$$\mathrm{Fe^{2+} \rightarrow Fe^{3+}}$$
$$\mathrm{Cr_2O_7^{2-} \rightarrow 2\,Cr^{3+} + 7\,H_2O}$$

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.

$$\mathrm{Fe^{2+} \rightarrow Fe^{3+}}$$
$$\mathrm{Cr_2O_7^{2-} + 14\,H^+ \rightarrow 2\,Cr^{3+} + 7\,H_2O}$$

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 bring 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.

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$
$$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \rightarrow 2\,Cr^{3+} + 7\,H_2O$$

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.

$6\,Fe^{2+} \rightarrow 6\,Fe^{3+} + 6\,e^-$
$Cr_2O_7^{2-} + 6\,e^- + 14\,H^+ \rightarrow 2\,Cr^{3+} + 7\,H_2O$

Add the balanced half-reactions and cancel species that appear on both sides of the equation.

$$6\,Fe^{2+} + Cr_2O_7^{2-} + 6\,e^- + 14\,H^+ \rightarrow 6\,Fe^{3+} + 6\,e^- + 2\,Cr^{3+} + 7\,H_2O$$

Only the six electrons are redundant species. Removing them from each side of the equation yields the simplified, balanced equation here:

$$6\,Fe^{2+} + Cr_2O_7^{2-} + 14\,H^+ \rightarrow 6\,Fe^{3+} + 2\,Cr^{3+} + 7\,H_2O$$

A final check of atom and charge balance confirms the equation is balanced.

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+

? Exercise 1.4.3.5

In acidic solution, hydrogen peroxide reacts with Fe^{2+} to produce Fe^{3+} and H_2O. Write a balanced equation for this reaction.

Answer

$$H_2O_2(aq) + 2\,H^+(aq) + 2\,Fe^{2+} \rightarrow 2\,H_2O(l) + 2\,Fe^{3+}$$

Summary

Chemical reactions are classified according to similar patterns of behavior. A large number of important reactions are included in three categories: precipitation, acid-base, and oxidation-reduction (redox). Precipitation reactions involve the formation of one or more insoluble products. Acid-base reactions involve the transfer of hydrogen ions between reactants. Redox reactions involve a change in oxidation number for one or more reactant elements. Writing balanced equations for some redox reactions that occur in aqueous solutions is simplified by using a systematic approach called the half-reaction method.

1.4.3.3.1: Footnotes

1. 1 The requirement of “charge balance” is just a specific type of “mass balance” in which the species in question are electrons. An equation must represent equal numbers of electrons on the reactant and product sides, and so both atoms and charges must be balanced.
2. 2 The requirement of “charge balance” is just a specific type of “mass balance” in which the species in question are electrons. An equation must represent equal numbers of electrons on the reactant and product sides, and so both atoms and charges must be balanced.

1.4.3.3.2: Glossary

acid

substance that produces H_3O^+ when dissolved in water

acid-base reaction

reaction involving the transfer of a hydrogen ion between reactant species

base

substance that produces OH^- when dissolved in water

combustion reaction

vigorous redox reaction producing significant amounts of energy in the form of heat and, sometimes, light

half-reaction

an equation that shows whether each reactant loses or gains electrons in a reaction.

insoluble

of relatively low solubility; dissolving only to a slight extent

neutralization reaction

reaction between an acid and a base to produce salt and water

oxidation

process in which an element’s oxidation number is increased by loss of electrons

oxidation-reduction reaction

(also, redox reaction) reaction involving a change in oxidation number for one or more reactant elements

oxidation number

(also, oxidation state) the charge each atom of an element would have in a compound if the compound were ionic

oxidizing agent

(also, oxidant) substance that brings about the oxidation of another substance, and in the process becomes reduced

precipitate

insoluble product that forms from reaction of soluble reactants

precipitation reaction

reaction that produces one or more insoluble products; when reactants are ionic compounds, sometimes called double-displacement or metathesis

reduction

process in which an element’s oxidation number is decreased by gain of electrons

reducing agent

(also, reductant) substance that brings about the reduction of another substance, and in the process becomes oxidized

salt
ionic compound that can be formed by the reaction of an acid with a base that contains a cation and an anion other than hydroxide or oxide

single-displacement reaction
(also, replacement) redox reaction involving the oxidation of an elemental substance by an ionic species

soluble
of relatively high solubility; dissolving to a relatively large extent

solubility
the extent to which a substance may be dissolved in water, or any solvent

strong acid
acid that reacts completely when dissolved in water to yield hydronium ions

strong base
base that reacts completely when dissolved in water to yield hydroxide ions

weak acid
acid that reacts only to a slight extent when dissolved in water to yield hydronium ions

weak base
base that reacts only to a slight extent when dissolved in water to yield hydroxide ions

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1.4.4: Reaction Stoichiometry

Learning Objectives

- Explain the concept of stoichiometry as it pertains to chemical reactions
- Use balanced chemical equations to derive stoichiometric factors relating amounts of reactants and products
- Perform stoichiometric calculations involving mass, moles, and solution molarity

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.

The general approach to using stoichiometric relationships is similar in concept to the way people go about many common activities. Cooking, for example, offers an appropriate comparison. Suppose a recipe for making eight pancakes calls for 1 cup pancake mix, $\frac{3}{4}$ cup milk, and one egg. The "equation" representing the preparation of pancakes per this recipe is

$$1 \text{ cup mix} + \frac{3}{4} \text{ cup milk} + 1 \text{ egg} \rightarrow 8 \text{ pancakes} \tag{1.4.4.1}$$

If two dozen pancakes are needed for a big family breakfast, the ingredient amounts must be increased proportionally according to the amounts given in the recipe. For example, the number of eggs required to make 24 pancakes is

$$24 \cancel{\text{ pancakes}} \times \frac{1 \text{ egg}}{8 \cancel{\text{ pancakes}}} = 3 \text{ eggs} \tag{1.4.4.2}$$

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:

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightarrow 2\,\mathrm{NH_3}(g) \tag{1.4.4.3}$$

This equation shows that ammonia molecules are produced from hydrogen molecules in a 2:3 ratio, and stoichiometric factors may be derived using any amount (number) unit:

$$\frac{2\,\mathrm{NH_3} \text{ molecules}}{3\,\mathrm{H_2} \text{ molecules}} \text{ or } \frac{2 \text{ doz } \mathrm{NH_3} \text{ molecules}}{3 \text{ doz } \mathrm{H_2} \text{ molecules}} \text{ or } \frac{2 \text{ mol } \mathrm{NH_3} \text{ molecules}}{3 \text{ mol } \mathrm{H_2} \text{ molecules}} \tag{1.4.4.4}$$

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 1.4.4.1: Moles of Reactant Required in a Reaction

How many moles of $\mathrm{I_2}$ are required to react with 0.429 mol of Al according to the following equation (see Figure 1.4.4.2)?

$$2\,\mathrm{Al} + 3\,\mathrm{I_2} \rightarrow 2\,\mathrm{AlI_3} \tag{1.4.4.5}$$

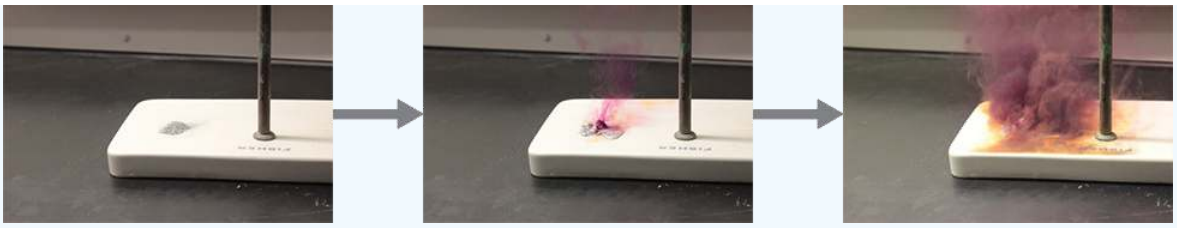
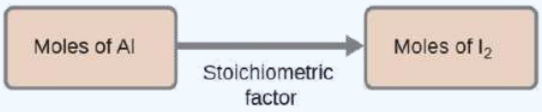


Figure 1.4.4.1: Aluminum and iodine react to produce aluminum iodide. The heat of the reaction vaporizes some of the solid iodine as a purple vapor. (credit: modification of work by Mark Ott)

Three pictures showing the progression of the reaction between iodine and aluminum. The first diagram shows only a pile of silver powder while the second diagram shows small amount of vapor forming. The final picture shows a large release of purple vapor.

Solution

Referring to the balanced chemical equation, the stoichiometric factor relating the two substances of interest is $\frac{3\ \text{mol}\ \text{I}_2}{2\ \text{mol}\ \text{Al}}$. The molar amount of iodine is derived by multiplying the provided molar amount of aluminum by this factor:



$$\begin{aligned}\text{mol I}_2 &= 0.429\ \cancel{\text{mol Al}} \times \frac{3\ \text{mol I}_2}{2\ \cancel{\text{mol Al}}} \\ &= 0.644\ \text{mol I}_2\end{aligned}$$

? Exercise 1.4.4.1

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 $3\,Ca(OH)_2 + 2\,H_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6\,H_2O$?

Answer

2.04 mol

✔ Example 1.4.4.2: 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?

$$C_3H_8 + 5\,O_2 \rightarrow 3\,CO_2 + 4\,H_2O \tag{1.4.4.6}$$

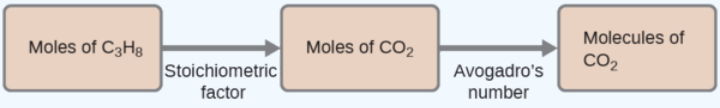
Solution

The approach here is the same as for Example 1.4.4.1, 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:

\[\ce{\dfrac{3\: mol\: CO2}{1\: mol\: C3H8}} \label{4.4.7} \]

Using this stoichiometric factor, the provided molar amount of propane, and Avogadro's number,



$$0.75\ \cancel{\text{mol C}_3\text{H}_8} \times \frac{3\ \cancel{\text{mol CO}_2}}{1\ \cancel{\text{mol C}_3\text{H}_8}} \times \frac{6.022 \times 10^{23}\ \text{CO}_2\ \text{molecules}}{\cancel{\text{mol CO}_2}} = 1.4 \times 10^{24}\ \text{CO}_2\ \text{molecules} \tag{1.4.4.7}$$

Exercise 1.4.4.1

How many NH_3 molecules are produced by the reaction of 4.0 mol of $Ca(OH)_2$ according to the following equation:

$$(NH_4)_2SO_4 + Ca(OH)_2 \rightarrow 2\,NH_3 + CaSO_4 + 2\,H_2O \tag{1.4.4.8}$$

Answer

4.8×10^{24} NH_3 molecules

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.

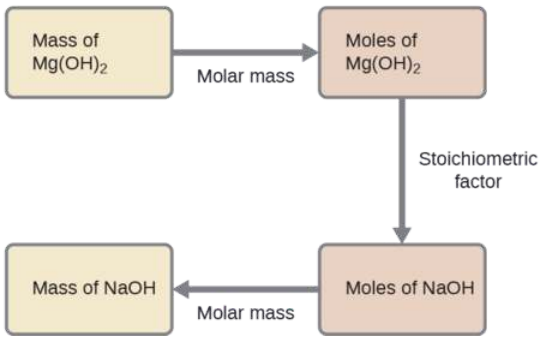
Example 1.4.4.3: Relating Masses of Reactants and Products

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?

$$MgCl_2(aq) + 2\,NaOH(aq) \rightarrow Mg(OH)_2(s) + 2\,NaCl(aq)$$

Solution

The approach used previously in Examples 1.4.4.1 and 1.4.4.2 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:



$$16\ \text{g}\ \cancel{Mg(OH)_2} \times \frac{1\ \text{mol}\ \cancel{Mg(OH)_2}}{58.3\ \text{g}\ \cancel{Mg(OH)_2}} \times \frac{2\ \text{mol}\ \cancel{NaOH}}{1\ \text{mol}\ \cancel{Mg(OH)_2}} \times \frac{40.0\ \text{g NaOH}}{\text{mol}\ \cancel{NaOH}} = 22\ \text{g NaOH}$$

Exercise 1.4.4.3

What mass of gallium oxide, Ga_2O_3, can be prepared from 29.0 g of gallium metal? The equation for the reaction is $4\,Ga + 3\,O_2 \rightarrow 2\,Ga_2O_3$.

Answer

39.0 g

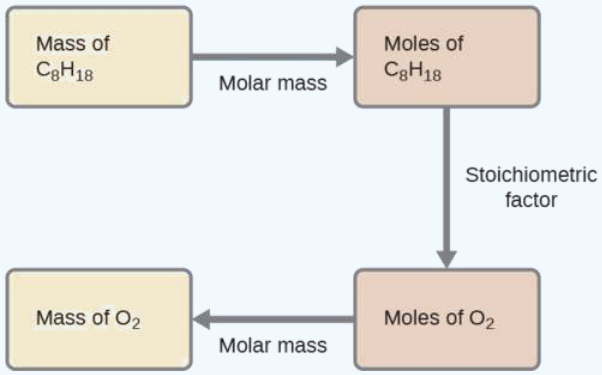
Example 1.4.4.4: Relating Masses of Reactants

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?

$$2\,C_8H_{18} + 25\,O_2 \rightarrow 16\,CO_2 + 18\,H_2O$$

Solution

The approach required here is the same as for the Example 1.4.4.3, differing only in that the provided and requested masses are both for reactant species.



$$702\ \text{g}\ \cancel{\text{C}_8\text{H}_{18}} \times \frac{1\ \text{mol}\ \cancel{\text{C}_8\text{H}_{18}}}{114.23\ \text{g}\ \cancel{\text{C}_8\text{H}_{18}}} \times \frac{25\ \text{mol}\ \cancel{\text{O}_2}}{2\ \text{mol}\ \cancel{\text{C}_8\text{H}_{18}}} \times \frac{32.00\ \text{g}\ \text{O}_2}{\cancel{\text{mol}\ \text{O}_2}} = 2.46 \times 10^3\ \text{g}\ \text{O}_2$$

? Exercise 1.4.4.4

What mass of CO is required to react with 25.13 g of Fe_2O_3 according to the equation $\text{Fe}_2\text{O}_3 + 3\,\text{CO} \rightarrow 2\,\text{Fe} + 3\,\text{CO}_2$?

Answer

13.22 g

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 1.4.4.2 provides a general outline of the various computational steps associated with many reaction stoichiometry calculations.

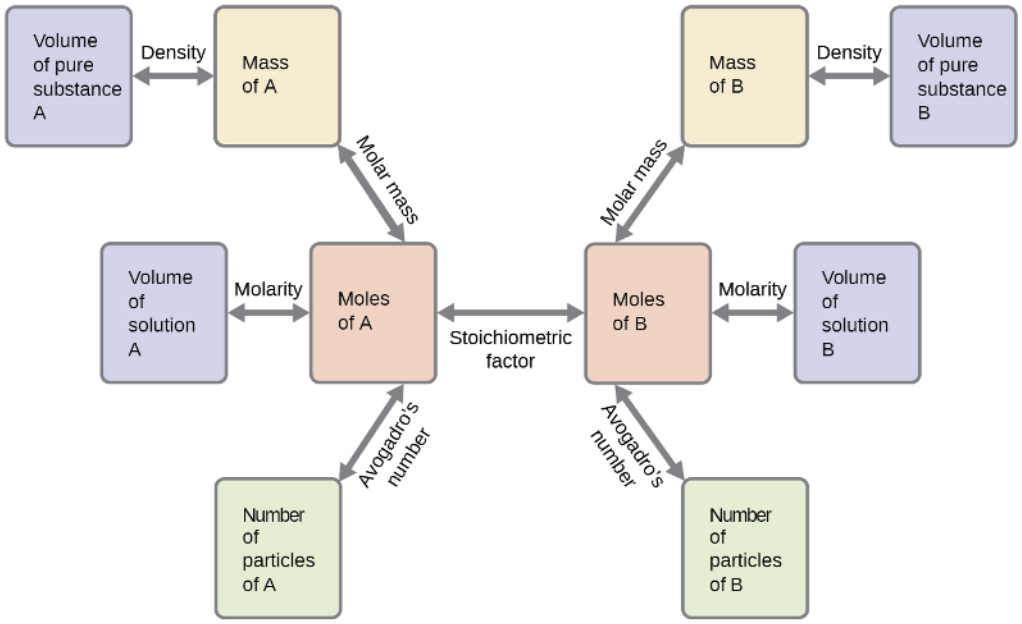


Figure 1.4.4.2: The flowchart depicts the various computational steps involved in most reaction stoichiometry calculations.

Schematic flowchart showing how density is used for converting volume of pure substance to mass, molar mass for mass and moles, molarity for moles and volume of solution, Avogadro's number for moles and number of particles, and stoichiometric factor for relating moles of one substance to another.

Airbags

Airbags (Figure 1.4.4.3) 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:

$$2\,NaN_3(s) \rightarrow 3\,N_2(g) + 2\,Na(s)$$

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 1.4.4.3: Airbags deploy upon impact to minimize serious injuries to passengers. (credit: Jon Seidman)

Summary

A balanced chemical equation may be used to describe a reaction's stoichiometry (the relationships between amounts of reactants and products). Coefficients from the equation are used to derive stoichiometric factors that subsequently may be used for computations relating reactant and product masses, molar amounts, and other quantitative properties.

1.4.4.0.1: Glossary

stoichiometric factor
: ratio of coefficients in a balanced chemical equation, used in computations relating amounts of reactants and products

stoichiometry
: relationships between the amounts of reactants and products of a chemical reaction

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1.4.5: Reaction Yields

Learning Objectives

- Explain the concepts of theoretical yield and limiting reactants/reagents.
- Derive the theoretical yield for a reaction under specified conditions.
- Calculate the percent yield for a reaction.

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.

1.4.5.1: Limiting Reactant

Consider another food analogy, making grilled cheese sandwiches (Figure 1.4.5.1):

$$1 \text{ slice of cheese} + 2 \text{ slices of bread} \rightarrow 1 \text{ sandwich} \tag{1.4.5.1}$$

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*.

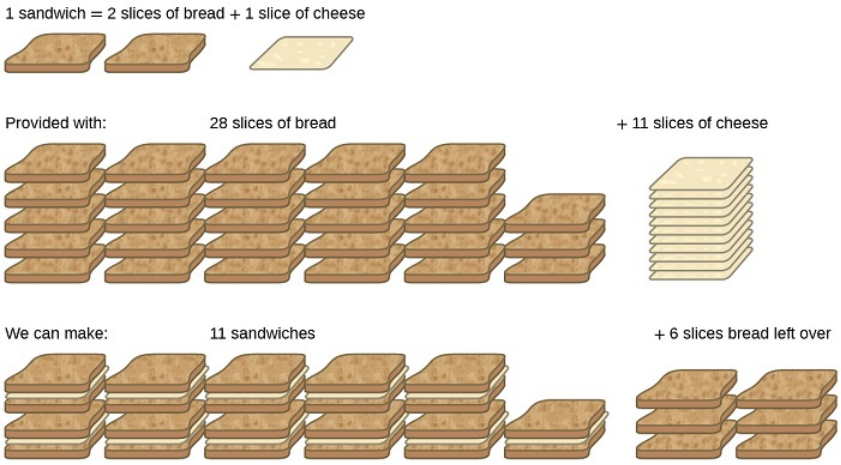


Figure 1.4.5.1: Sandwich making can illustrate the concepts of limiting and excess reactants.

This figure has three rows showing the ingredients needed to make a sandwich. The first row reads, “1 sandwich = 2 slices of bread + 1 slice of cheese.” Two slices of bread and one slice of cheese are shown. The second row reads, “Provided with: 28 slices of bread + 11 slices of cheese.” There are 28 slices of bread and 11 slices of cheese shown. The third row reads, “We can make: 11 sandwiches + 6 slices of bread left over.” 11 sandwiches are shown with six extra slices of bread.

Consider this concept now with regard to a chemical process, the reaction of hydrogen with chlorine to yield hydrogen chloride:

$$\mathrm{H_2}(g) + \mathrm{Cl_2}(g) \rightarrow 2\,\mathrm{HCl}(g)$$

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 6 moles of $\mathrm{H_2}$ and 4 moles of $\mathrm{Cl_2}$. 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, the complete reaction of the hydrogen would yield

$$\text{mol HCl produced} = 6 \text{ mol } H_2 \times \frac{2 \text{ mol HCl}}{1 \text{ mol } H_2} = 12 \text{ mol HCl}$$

The complete reaction of the provided chlorine would produce

$$\text{mol HCl produced} = 4 \text{ mol } Cl_2 \times \frac{2 \text{ mol HCl}}{1 \text{ mol } Cl_2} = 8 \text{ mol HCl}$$

The chlorine will be completely consumed once 8 moles of HCl have been produced. Since enough hydrogen was provided to yield 12 moles of HCl, there will be non-reacted hydrogen remaining once this reaction is complete. Chlorine, therefore, is the limiting reactant and hydrogen is the excess reactant (Figure 1.4.5.2). To determine the amount of excess reactant that remains, the amount of hydrogen consumed in the reaction can be subtracted from the starting quantity of hydrogen.

The amount of hydrogen consumed is

$$\text{mol } H_2 \text{ produced} = 8 \text{ mol HCl} \times \frac{1 \text{ mol } H_2}{2 \text{ mol HCl}} = 4 \text{ mol } H_2$$

Subtract the hydrogen consumed from the starting quantity

$$\text{mole of excess } H_2 = 6 \text{ mol } H_2 \text{ starting } - 4 \text{ mol } H_2 \text{ consumed } = 2 \text{ mol } H_2 \text{ excess}$$

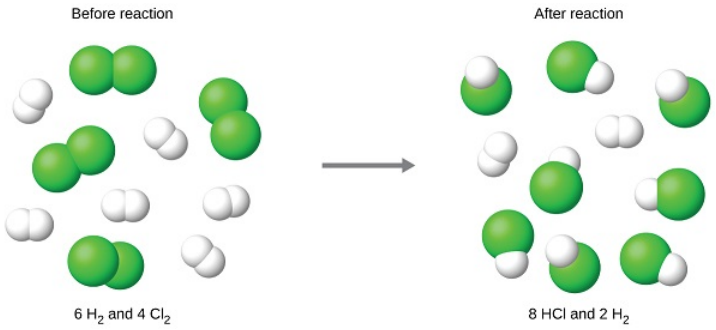


Figure 1.4.5.2: When H_2 and Cl_2 are combined in nonstoichiometric amounts, one of these reactants will limit the amount of HCl that can be produced. This illustration shows a reaction in which hydrogen is present in excess and chlorine is the limiting reactant.

The figure shows a space-filling molecular models reacting. There is a reaction arrow pointing to the right in the middle. To the left of the reaction arrow there are three molecules each consisting of two green spheres bonded together. There are also five molecules each consisting of two smaller, white spheres bonded together. Above these molecules is the label, "Before reaction," and below these molecules is the label, "6 H subscript 2 and 4 C l subscript 2." To the right of the reaction arrow, there are eight molecules each consisting of one green sphere bonded to a smaller white sphere. There are also two molecules each consisting of two white spheres bonded together. Above these molecules is the label, "After reaction," and below these molecules is the label, "8 H C l and 2 H subscript 2."

Example 1.4.5.1: 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:

$$3\,Si(s) + 2\,N_2(g) \rightarrow Si_3N_4(s)$$

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.

$$\text{mol Si} = 2.00\ \cancel{\text{g Si}} \times \frac{1\ \text{mol Si}}{28.09\ \cancel{\text{g Si}}} = 0.0712\ \text{mol Si}$$

$$\text{mol } N_2 = 1.50\ \cancel{\text{g } N_2} \times \frac{1\ \text{mol } N_2}{28.02\ \cancel{\text{g } N_2}} = 0.0535\ \text{mol } N_2$$

The provided Si:N_2 molar ratio is:

$$\frac{0.0712\ \text{mol Si}}{0.0535\ \text{mol } N_2} = \frac{1.33\ \text{mol Si}}{1\ \text{mol } N_2}$$

The stoichiometric Si:N_2 ratio is:

$$\frac{3\ \text{mol Si}}{2\ \text{mol } N_2} = \frac{1.5\ \text{mol Si}}{1\ \text{mol } N_2}$$

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

$$\text{mol } Si_3N_4 \text{ produced} = 0.0712\ \text{mol Si} \times \frac{1\ \text{mol } Si_3N_4}{3\ \text{mol Si}} = 0.0237\ \text{mol } Si_3N_4$$

while the 0.0535 moles of nitrogen would produce

$$\text{mol } Si_3N_4 \text{ produced} = 0.0535\ \text{mol } N_2 \times \frac{1\ \text{mol } Si_3N_4}{2\ \text{mol } N_2} = 0.0268\ \text{mol } Si_3N_4$$

Since silicon yields the lesser amount of product, it is the limiting reactant.

? Exercise 1.4.5.1

Which is the limiting reactant when 5.00 g of H_2 and 10.0 g of O_2 react and form water?

Answer

O_2

1.4.5.2: 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 (consider the partial reactions of weak acids and bases discussed earlier in this text). 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:

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

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 1.4.5.2: 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:

$$\mathrm{CuSO_4}(aq) + \mathrm{Zn}(s) \rightarrow \mathrm{Cu}(s) + \mathrm{ZnSO_4}(aq)$$

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:

$$1.274\ \text{g}\ \cancel{\mathrm{CuSO_4}} \times \frac{1\ \text{mol}\ \cancel{\mathrm{CuSO_4}}}{159.62\ \text{g}\ \cancel{\mathrm{CuSO_4}}} \times \frac{1\ \text{mol}\ \cancel{\mathrm{Cu}}}{1\ \text{mol}\ \cancel{\mathrm{CuSO_4}}} \times \frac{63.55\ \text{g Cu}}{1\ \text{mol}\ \cancel{\mathrm{Cu}}} = 0.5072\ \text{g Cu}$$

Using this theoretical yield and the provided value for actual yield, the percent yield is calculated to be

$$\text{percent yield} = \left(\frac{\text{actual yield}}{\text{theoretical yield}}\right) \times 100$$

$$\text{percent yield} = \left(\frac{0.392\ \text{g Cu}}{0.5072\ \text{g Cu}}\right) \times 100$$

$$= 77.3\%$$

Exercise 1.4.5.2

What is the percent yield of a reaction that produces 12.5 g of the gas Freon $\mathrm{CF_2Cl_2}$ from 32.9 g of $\mathrm{CCl_4}$ and excess HF?

$$\mathrm{CCl_4} + 2\,\mathrm{HF} \rightarrow \mathrm{CF_2Cl_2} + 2\,\mathrm{HCl}$$

Answer

48.3%

Green Chemistry and Atom Economy

The purposeful design of chemical products and processes that minimize the use of environmentally hazardous substances and the generation of waste is known as *green chemistry*. Green chemistry is a philosophical approach that is being applied to many areas of science and technology, and its practice is summarized by guidelines known as the "Twelve Principles of Green Chemistry". One of the 12 principles is aimed specifically at maximizing the efficiency of processes for synthesizing chemical products. The *atom economy* of a process is a measure of this efficiency, defined as the percentage by mass of the final product of a synthesis relative to the masses of *all* the reactants used:

$$\text{atom economy} = \frac{\text{mass of product}}{\text{mass of reactants}} \times 100\%$$

Though the definition of atom economy at first glance appears very similar to that for percent yield, be aware that this property represents a difference in the *theoretical* efficiencies of *different* chemical processes. The percent yield of a given chemical process, on the other hand, evaluates the efficiency of a process by comparing the yield of product actually obtained to the maximum yield predicted by stoichiometry.

The synthesis of the common nonprescription pain medication, ibuprofen, nicely illustrates the success of a green chemistry approach (Figure 1.4.5.3). First marketed in the early 1960s, ibuprofen was produced using a six-step synthesis that required 514 g of reactants to generate each mole (206 g) of ibuprofen, an atom economy of 40%. In the 1990s, an alternative process was developed by the BHC Company (now BASF Corporation) that requires only three steps and has an atom economy of

~80%, nearly twice that of the original process. The BHC process generates significantly less chemical waste; uses less-hazardous and recyclable materials; and provides significant cost-savings to the manufacturer (and, subsequently, the consumer). In recognition of the positive environmental impact of the BHC process, the company received the Environmental Protection Agency's Greener Synthetic Pathways Award in 1997.

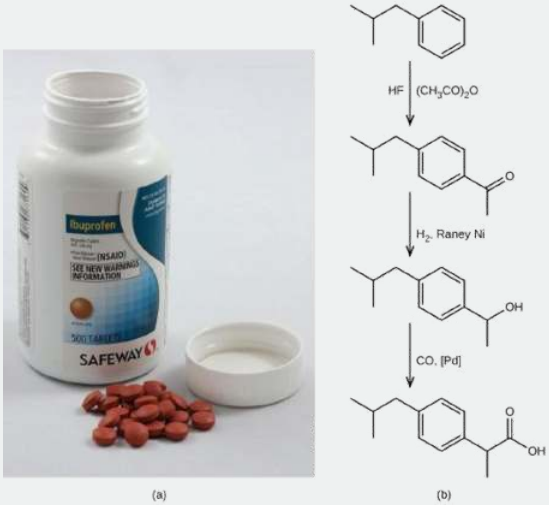


Figure 1.4.5.3: (a) Ibuprofen is a popular nonprescription pain medication commonly sold as 200 mg tablets. (b) The BHC process for synthesizing ibuprofen requires only three steps and exhibits an impressive atom economy. (credit a: modification of work by Derrick Coetzee)

Summary

When reactions are carried out using less-than-stoichiometric quantities of reactants, the amount of product generated will be determined by the limiting reactant. The amount of product generated by a chemical reaction is its actual yield. This yield is often less than the amount of product predicted by the stoichiometry of the balanced chemical equation representing the reaction (its theoretical yield). The extent to which a reaction generates the theoretical amount of product is expressed as its percent yield.

1.4.5.3: Key Equations

- $\text{percent yield} = \left(\dfrac{\text{actual yield}}{\text{theoretical yield}}\right) \times 100$

Glossary

actual yield
amount of product formed in a reaction

excess reactant
reactant present in an amount greater than required by the reaction stoichiometry

limiting reactant
reactant present in an amount lower than required by the reaction stoichiometry, thus limiting the amount of product generated

percent yield
measure of the efficiency of a reaction, expressed as a percentage of the theoretical yield

theoretical yield
amount of product that may be produced from a given amount of reactant(s) according to the reaction stoichiometry

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1.4.6: Quantitative Chemical Analysis

Learning Objectives

- Describe the fundamental aspects of titrations and gravimetric analysis.
- Perform stoichiometric calculations using typical titration and gravimetric data.

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:

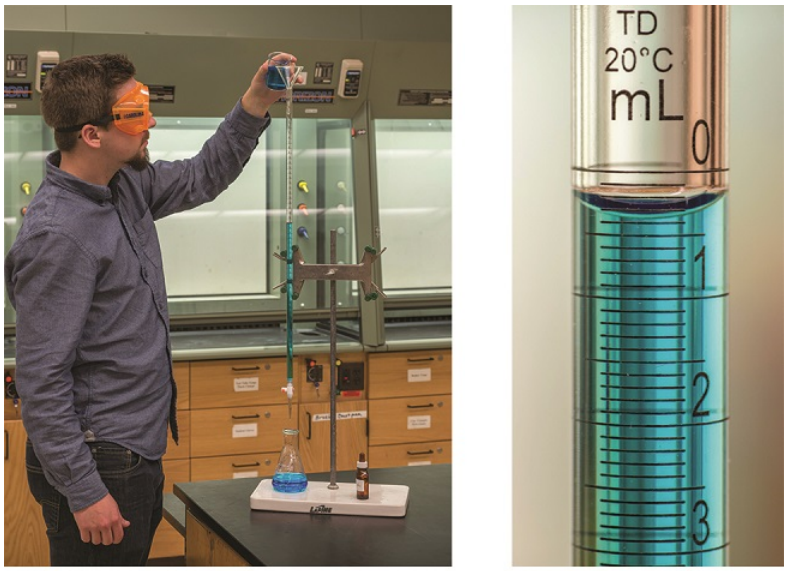
$$2\,\mathrm{CH_3CO_2H}(aq) + \mathrm{K_2CO_3}(s) \rightarrow 2\mathrm{KCH_3CO_3}(aq) + \mathrm{CO_2}(g) + \mathrm{H_2O}(l)$$

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.

1.4.6.1: 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 1.4.6.1) 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, the three described in this chapter (precipitation, acid-base, and redox) are most common. Additional details regarding titration analysis are provided in the chapter on acid-base equilibria.



(a) (b)

Figure 1.4.6.1: (a) A student fills a buret in preparation for a titration analysis. (b) A typical buret permits volume measurements to the nearest 0.1 mL. (credit a: modification of work by Mark Blaser and Matt Evans; credit b: modification of work by Mark Blaser and Matt Evans)

Two pictures are shown. In a, a person is shown pouring a liquid from a small beaker into a buret. The person is wearing goggles and gloves as she transfers the solution into the buret. In b, a close up view of the markings on the side of the buret is shown. The markings for 10, 15, and 20 are clearly shown with horizontal rings printed on the buret. Between each of these whole number markings, half markings are also clearly shown with horizontal line segment markings.

Example 1.4.6.1: 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:

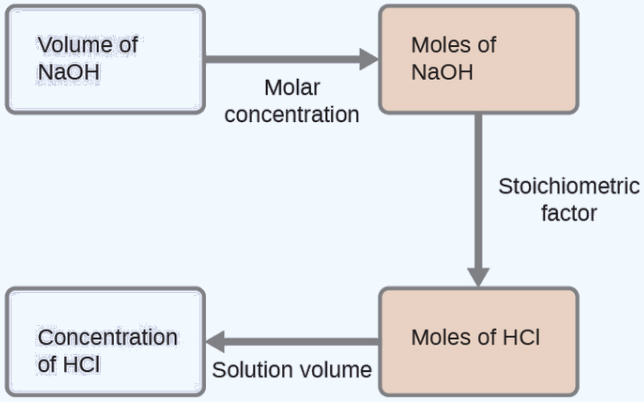
$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \rightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l)$$

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:



This figure shows four rectangles. The first is shaded lavender and is labeled, “Volume of N a O H.” This rectangle is followed by an arrow pointing right which is labeled, “Molar concentration,” to a second rectangle. This second rectangle is shaded pink and is labeled, “Moles of N a O H.” This rectangle is followed by an arrow pointing right which is labeled, “Stoichiometric factor,” to a third rectangle which is shaded pink and is labeled, “Moles of H C l.” This rectangle is followed by an arrow labeled, “Solution volume,” which points right to a fourth rectangle. This fourth rectangle is shaded lavender and is labeled, “Concentration of H C l.”

The molar amount of HCl is calculated to be:

$$35.23\ \text{mL}\ \cancel{\text{NaOH}} \times \frac{1\ \cancel{\text{L}}}{1000\ \cancel{\text{mL}}} \times \frac{0.250\ \text{mol}\ \cancel{\text{NaOH}}}{1\ \cancel{\text{L}}} \times \frac{1\ \text{mol HCl}}{1\ \text{mol}\ \cancel{\text{NaOH}}} = 8.81 \times 10^{-3}\ \text{mol HCl}$$

Using the provided volume of HCl solution and the definition of molarity, the HCl concentration is:

$$M = \frac{\text{mol HCl}}{\text{L solution}}$$

$$M = \frac{8.81 \times 10^{-3}\ \text{mol HCl}}{50.00\ \text{mL} \times \dfrac{1\ \text{L}}{1000\ \text{mL}}}$$

$$M = 0.176\ M$$

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:

$$M = \frac{\text{mol solute}}{\text{L solution}} \times \frac{\dfrac{10^3\ \text{mmol}}{\text{mol}}}{\dfrac{10^3\ \text{mL}}{\text{L}}} = \frac{\text{mmol solute}}{\text{mL solution}}$$

Using this version of the molarity unit will shorten the calculation by eliminating two conversion factors:

$$\frac{35.23\ \text{mL NaOH} \times \dfrac{0.250\ \text{mmol NaOH}}{\text{mL NaOH}} \times \dfrac{1\ \text{mmol HCl}}{1\ \text{mmol NaOH}}}{50.00\ \text{mL solution}} = 0.176\ M\,\text{HCl}$$

? Exercise 1.4.6.1

A 20.00-mL sample of aqueous oxalic acid, $H_2C_2O_4$, was titrated with a 0.09113-*M* solution of potassium permanganate, $KMnO_4$.

$$2\,\text{MnO}_4^-(aq) + 5\,\text{H}_2\text{C}_2\text{O}_4(aq) + 6\,\text{H}^+(aq) \rightarrow 10\,\text{CO}_2(g) + 2\,\text{Mn}^{2+}(aq) + 8\,\text{H}_2\text{O}(l)$$

A volume of 23.24 mL was required to reach the end point. What is the oxalic acid molarity?

Answer

0.2648 *M*

1.4.6.2: 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 1.4.6.2). The mass of the precipitate may then be used, along with relevant stoichiometric relationships, to calculate analyte concentration.



Figure 1.4.6.2: Precipitate may be removed from a reaction mixture by filtration.

"A photo is shown of a flask and funnel used for filtration. The flask contains a slightly opaque liquid filtrate with a slight yellow tint. A funnel, which contains a bright yellow and orange material, sits atop the flask. The flask is held in place by a clamp and is connected to a vacuum line. The connection between the funnel and flask is sealed with a rubber bung or gasket."

Example 1.4.6.2: Gravimetric Analysis

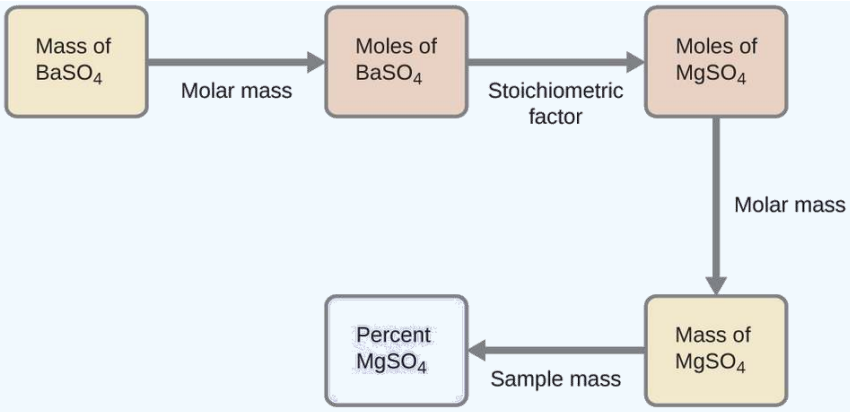
A 0.4550-g solid mixture containing $MgSO_4$ is dissolved in water and treated with an excess of $Ba(NO_3)_2$, resulting in the precipitation of 0.6168 g of $BaSO_4$.

$$MgSO_4(aq) + Ba(NO_3)_2(aq) \rightarrow BaSO_4(s) + Mg(NO_3)_2(aq)$$

What is the concentration (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.



"This figure shows five rectangles. The first is shaded yellow and is labeled “Mass of B a S O subscript 4.” This rectangle is followed by an arrow pointing right to a second rectangle. The arrow is labeled, “Molar mass.” The second rectangle is shaded pink and is labeled, “Moles of B a S O subscript 4.” This rectangle is followed by an arrow pointing right to a third rectangle. The arrow is labeled, “Stoichiometric factor.” This third rectangle is shaded pink and is labeled, “Moles of M g S O subscript 4.” This rectangle is followed by an arrow labeled, “Molar mass,” which points downward to a fourth rectangle. This fourth rectangle is shaded yellow and is labeled, “Mass of M g S O subscript 4.” This rectangle is followed by an arrow labeled, “Sample mass,” which points left to a fifth rectangle. This fifth rectangle is shaded lavender and is labeled, “Percent M g S O subscript 4."

The mass of $MgSO_4$ that would yield the provided precipitate mass is

$$0.6168\ \text{g}\ \cancel{\text{BaSO}_4} \times \frac{1\ \text{mol}\ \cancel{\text{BaSO}_4}}{233.43\ \text{g}\ \cancel{\text{BaSO}_4}} \times \frac{1\ \text{mol}\ \cancel{\text{MgSO}_4}}{1\ \text{mol}\ \cancel{\text{BaSO}_4}} \times \frac{120.37\ \text{g}\ \text{MgSO}_4}{1\ \text{mol}\ \cancel{\text{MgSO}_4}} = 0.3181\ \text{g}\ \text{MgSO}_4$$

The concentration of $MgSO_4$ in the sample mixture is then calculated to be

$$\text{percent}\ \text{MgSO}_4 = \frac{\text{mass}\ \text{MgSO}_4}{\text{mass sample}} \times 100\%$$

$$\frac{0.3181\ \text{g}}{0.4550\ \text{g}} \times 100\% = 69.91\%$$

? Exercise 1.4.6.2

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^+?

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

Answer

23.76%

1.4.6.3: Combustion Analysis

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 1.4.6.3). 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.

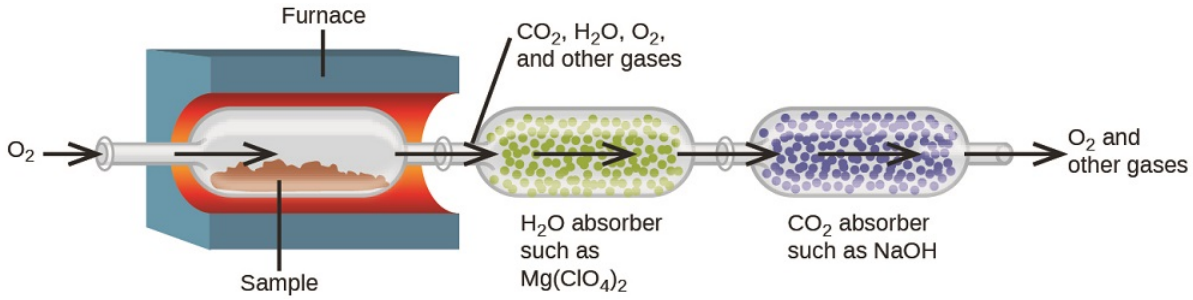


Figure 1.4.6.3: This schematic diagram illustrates the basic components of a combustion analysis device for determining the carbon and hydrogen content of a sample.

This diagram shows an arrow pointing from O subscript 2 into a tube that leads into a vessel containing a red material, labeled “Sample.” This vessel is inside a blue container with a red inner lining which is labeled “Furnace.” An arrow points from the tube to the right into the vessel above the red sample material. An arrow leads out of this vessel through a tube into a second vessel outside the furnace. An line points from this tube to a label above the diagram that reads “C O subscript 2, H subscript 2 O, O subscript 2, and other gases.” Many small green spheres are visible in the second vessel which is labeled below, “H subscript 2 O absorber such as M g (C l O subscript 4) subscript 2.” An arrow points to the right through the vessel, and another arrow points right heading out of the vessel through a tube into a third vessel. The third vessel contains many small blue spheres. It is labeled “C O subscript 2 absorber such as N a O H.” An arrow points right through this vessel, and a final arrow points out of a tube at the right end of the vessel. Outside the end of this tube at the end of the arrow is the label, “O subscript 2 and other gases.”

Example 1.4.6.3: 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?

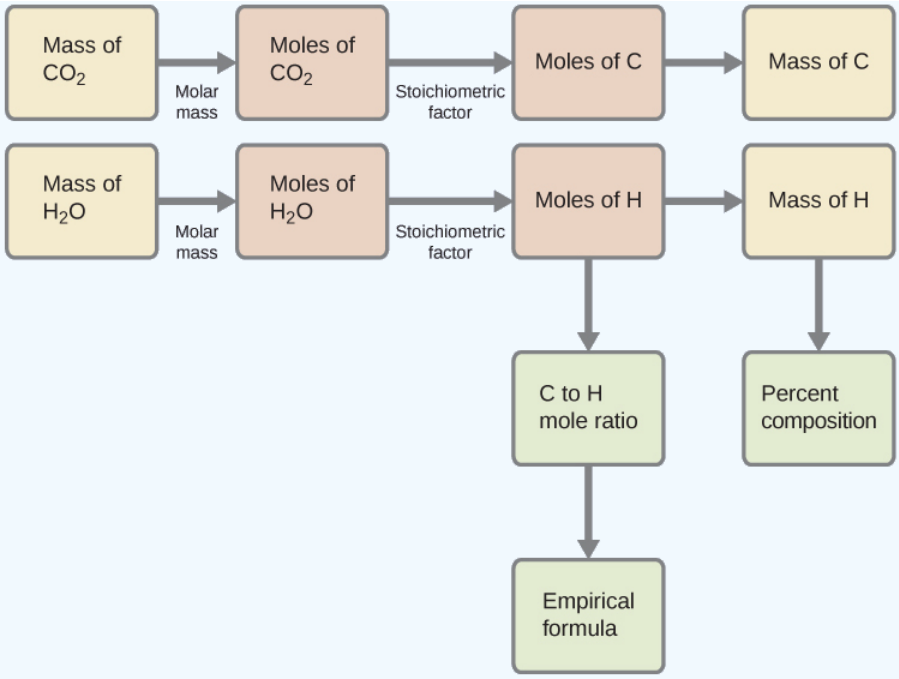
Solution

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:

$$\mathrm{C_xH_y}(s) + \text{excess } \mathrm{O_2}(g) \rightarrow x\mathrm{CO_2}(g) + \frac{y}{2}\mathrm{H_2O}(g)$$

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:



This figure shows two flowcharts. The first row is a single flow chart. In this row, a rectangle at the left is shaded yellow and is labeled, “Mass of C O subscript 2.” This rectangle is followed by an arrow pointing right to a second rectangle. The arrow is labeled, “Molar mass.” The second rectangle is shaded pink and is labeled, “Moles of C O subscript 2.” This rectangle is followed by an arrow pointing right to a third rectangle. The arrow is labeled, “Stoichiometric factor.” The third rectangle is shaded pink and is labeled, “Moles of C.” This rectangle is followed by an arrow labeled “Molar mass” which points right to a fourth rectangle. The fourth rectangle is shaded yellow and is labeled “Mass of C.” Below, is a second flowchart. It begins with a yellow shaded rectangle on the left which is labeled, “Mass of H subscript 2 O.” This rectangle is followed by an arrow labeled, “Molar mass,” which points right to a second rectangle. The second rectangle is shaded pink and is labeled, “Moles of H subscript 2 O.” This rectangle is followed by an arrow pointing right to a third rectangle. The arrow is labeled, “Stoichiometric factor.” The third rectangle is shaded pink and is labeled “Moles of H.” This rectangle is followed to the right by an arrow labeled, “Molar mass,” which points to a fourth rectangle. The fourth rectangle is shaded yellow and is labeled “Mass of H.” An arrow labeled, “Sample mass” points down beneath this rectangle to a green shaded rectangle. This rectangle is labeled, “Percent composition.” An arrow extends beneath the pink rectangle labeled, “Moles of H,” to a green shaded rectangle labeled, “C to H mole ratio.” Beneath this rectangle, an arrow extends to a second green shaded rectangle which is labeled, “Empirical formula.”

$$\text{mol C} = 0.00394 \text{ g } CO_2 \times \frac{1 \text{ mol } CO_2}{44.01 \text{ g/mol}} \times \frac{1 \text{ mol C}}{1 \text{ mol } CO_2} = 8.95 \times 10^{-5} \text{ mol C}$$

$$\text{mol H} = 0.00161 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g/mol}} \times \frac{2 \text{ mol H}}{1 \text{ mol } H_2O} = 1.79 \times 10^{-4} \text{ mol H}$$

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

$$\frac{\text{mol H}}{\text{mol C}} = \frac{1.79 \times 10^{-4} \text{ mol H}}{8.95 \times 10^{-5} \text{ mol C}} = \frac{2 \text{ mol H}}{1 \text{ mol C}}$$

and the empirical formula for polyethylene is CH_2.

? Exercise 1.4.6.3

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?

Answer

CH

Summary

The stoichiometry of chemical reactions may serve as the basis for quantitative chemical analysis methods. Titrations involve measuring the volume of a titrant solution required to completely react with a sample solution. This volume is then used to calculate the concentration of analyte in the sample using the stoichiometry of the titration reaction. Gravimetric analysis involves separating the analyte from the sample by a physical or chemical process, determining its mass, and then calculating its concentration in the sample based on the stoichiometry of the relevant process. Combustion analysis is a gravimetric method used to determine the elemental composition of a compound by collecting and weighing the gaseous products of its combustion.

Glossary

analyte
chemical species of interest

buret
device used for the precise delivery of variable liquid volumes, such as in a titration analysis

combustion analysis
gravimetric technique used to determine the elemental composition of a compound via the collection and weighing of its gaseous combustion products

end point
measured volume of titrant solution that yields the change in sample solution appearance or other property expected for stoichiometric equivalence (see *equivalence point*)

equivalence point
volume of titrant solution required to react completely with the analyte in a titration analysis; provides a stoichiometric amount of titrant for the sample's analyte according to the titration reaction

gravimetric analysis
quantitative chemical analysis method involving the separation of an analyte from a sample by a physical or chemical process and subsequent mass measurements of the analyte, reaction product, and/or sample

indicator
substance added to the sample in a titration analysis to permit visual detection of the end point

quantitative analysis
the determination of the amount or concentration of a substance in a sample

titrant
solution containing a known concentration of substance that will react with the analyte in a titration analysis

titration analysis
quantitative chemical analysis method that involves measuring the volume of a reactant solution required to completely react with the analyte in a sample

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1.4.E: Stoichiometry of Chemical Reactions (Exercises)

1.4.E.1: 4.1: Writing and Balancing Chemical Equations

1.4.E.1.1: Q4.1.1

What does it mean to say an equation is balanced? Why is it important for an equation to be balanced?

1.4.E.1.2: S4.1.1

An equation is balanced when the same number of each element is represented on the reactant and product sides. Equations must be balanced to accurately reflect the law of conservation of matter.

1.4.E.1.3: Q4.1.2

Consider molecular, complete ionic, and net ionic equations.

a. What is the difference between these types of equations?
b. In what circumstance would the complete and net ionic equations for a reaction be identical?

1.4.E.1.4: Q4.1.3

Balance the following equations:

a. $\mathrm{PCl_5}(s) + \mathrm{H_2O}(l) \rightarrow \mathrm{POCl_3}(l) + \mathrm{HCl}(aq)$
b. $\mathrm{Cu}(s) + \mathrm{HNO_3}(aq) \rightarrow \mathrm{Cu(NO_3)_2}(aq) + \mathrm{H_2O}(l) + \mathrm{NO}(g)$
c. $\mathrm{H_2}(g) + \mathrm{I_2}(s) \rightarrow \mathrm{HI}(s)$
d. $\mathrm{Fe}(s) + \mathrm{O_2}(g) \rightarrow \mathrm{Fe_2O_3}(s)$
e. $\mathrm{Na}(s) + \mathrm{H_2O}(l) \rightarrow \mathrm{NaOH}(aq) + \mathrm{H_2}(g)$
f. $\mathrm{(NH_4)_2Cr_2O_7}(s) \rightarrow \mathrm{Cr_2O_3}(s) + \mathrm{N_2}(g) + \mathrm{H_2O}(g)$
g. $\mathrm{P_4}(s) + \mathrm{Cl_2}(g) \rightarrow \mathrm{PCl_3}(l)$
h. $\mathrm{PtCl_4}(s) \rightarrow \mathrm{Pt}(s) + \mathrm{Cl_2}(g)$

1.4.E.1.5: S4.1.3

a. $\mathrm{PCl_5}(s) + \mathrm{H_2O}(l) \rightarrow \mathrm{POCl_3}(l) + 2\,\mathrm{HCl}(aq)$;
b. $3\,\mathrm{Cu}(s) + 8\,\mathrm{HNO_3}(aq) \rightarrow 3\,\mathrm{Cu(NO_3)_2}(aq) + 4\,\mathrm{H_2O}(l) + 2\,\mathrm{NO}(g)$;
c. $\mathrm{H_2}(g) + \mathrm{I_2}(s) \rightarrow 2\,\mathrm{HI}(s)$;
d. $4\,\mathrm{Fe}(s) + 3\,\mathrm{O_2}(g) \rightarrow 2\,\mathrm{Fe_2O_3}(s)$;
e. $2\,\mathrm{Na}(s) + 2\,\mathrm{H_2O}(l) \rightarrow 2\,\mathrm{NaOH}(aq) + \mathrm{H_2}(g)$;
f. $\mathrm{(NH_4)_2Cr_{52}O_7}(s) \rightarrow \mathrm{Cr_2O_3}(s) + \mathrm{N_2}(g) + 4\,\mathrm{H_2O}(g)$;
g. $\mathrm{P_4}(s) + 6\,\mathrm{Cl_2}(g) \rightarrow 4\,\mathrm{PCl_3}(l)$;
h. $\mathrm{PtCl_4}(s) \rightarrow \mathrm{Pt}(s) + 2\,\mathrm{Cl_2}(g)$

1.4.E.2: Q4.1.4

Balance the following equations:

a. $\mathrm{Ag}(s) + \mathrm{H_2S}(g) + \mathrm{O_2}(g) \rightarrow \mathrm{Ag_2S}(s) + \mathrm{H_2O}(l)$
b. $\mathrm{P_4}(s) + \mathrm{O_2}(g) \rightarrow \mathrm{P_4O_{10}}(s)$
c. $\mathrm{Pb}(s) + \mathrm{H_2O}(l) + \mathrm{O_2}(g) \rightarrow \mathrm{Pb(OH)_2}(s)$
d. $\mathrm{Fe}(s) + \mathrm{H_2O}(l) \rightarrow \mathrm{Fe_3O_4}(s) + \mathrm{H_2}(g)$
e. $\mathrm{Sc_2O_3}(s) + \mathrm{SO_3}(l) \rightarrow \mathrm{Sc_2(SO_4)_3}(s)$
f. $\mathrm{Ca_3(PO_4)_2}(aq) + \mathrm{H_3PO_4}(aq) \rightarrow \mathrm{Ca(H_2PO_4)_2}(aq)$
g. $\mathrm{Al}(s) + \mathrm{H_2SO_4}(aq) \rightarrow \mathrm{Al_2(SO_4)_3}(s) + \mathrm{H_2}(g)$
h. $\mathrm{TiCl_4}(s) + \mathrm{H_2O}(g) \rightarrow \mathrm{TiO_2}(s) + \mathrm{HCl}(g)$

1.4.E.2.1: S4.1.4

a. $4\,\mathrm{Ag}(s) + 2\,\mathrm{H_2S}(g) + \mathrm{O_2}(g) \rightarrow 2\,\mathrm{Ag_2S}(s) + 2\,\mathrm{H_2O}(l)$
b. $\mathrm{P_4}(s) + 5\,\mathrm{O_2}(g) \rightarrow \mathrm{P_4O_{10}}(s)$
c. $2\,\mathrm{Pb}(s) + 2\,\mathrm{H_2O}(l) + \mathrm{O_2}(g) \rightarrow 2\,\mathrm{Pb(OH)_2}(s)$
d. $3\,\mathrm{Fe}(s) + 4\,\mathrm{H_2O}(l) \rightarrow \mathrm{Fe_3O_4}(s) + 4\,\mathrm{H_2}(g)$
e. $\mathrm{Sc_2O_3}(s) + 3\,\mathrm{SO_3}(l) \rightarrow \mathrm{Sc_2(SO_4)_3}(s)$

f. $Ca_3(PO_4)_2(aq) + 4\,H_3PO_4(aq) \rightarrow 3\,Ca(H_2PO_4)_2(aq)$
g. $2\,Al(s) + 3\,H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(s) + 3\,H_2(g)$
h. $TiCl_4(s) + 2\,H_2O(g) \rightarrow TiO_2(s) + 4\,HCl(g)$

1.4.E.2.2: Q4.1.5

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.

1.4.E.2.3: S4.1.5

a. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$;
b. $2\,C_4H_{10}(g) + 13\,O_2(g) \rightarrow 8\,CO_2(g) + 10\,H_2O(g)$;
c. $MgCl_2(aq) + 2\,NaOH(aq) \rightarrow Mg(OH)_2(s) + 2\,NaCl(aq)$;
d. $2\,H_2O(g) + 2\,Na(s) \rightarrow 2\,NaOH(s) + H_2(g)$

1.4.E.2.4: Q4.1.6

Write a balanced equation describing each of the following chemical reactions.

a. Solid potassium chlorate, $KClO_3$, decomposes to form solid potassium chloride and diatomic oxygen gas.
b. Solid aluminum metal reacts with solid diatomic iodine to form solid Al_2I_6.
c. When solid sodium chloride is added to aqueous sulfuric acid, hydrogen chloride gas and aqueous sodium sulfate are produced.
d. Aqueous solutions of phosphoric acid and potassium hydroxide react to produce aqueous potassium dihydrogen phosphate and liquid water.

1.4.E.2.5: Q4.1.7

Colorful fireworks often involve the decomposition of barium nitrate and potassium chlorate and the reaction of the metals magnesium, aluminum, and iron with oxygen.

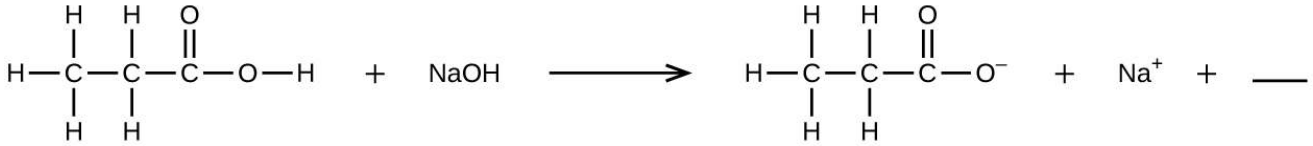
a. Write the formulas of barium nitrate and potassium chlorate.
b. The decomposition of solid potassium chlorate leads to the formation of solid potassium chloride and diatomic oxygen gas. Write an equation for the reaction.
c. The decomposition of solid barium nitrate leads to the formation of solid 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.)

1.4.E.2.6: Q4.1.7

a. $Ba(NO_3)_2$, $KClO_3$;
b. $2\,KClO_3(s) \rightarrow 2\,KCl(s) + 3\,O_2(g)$;
c. $2\,Ba(NO_3)_2(s) \rightarrow 2\,BaO(s) + 2\,N_2(g) + 5\,O_2(g)$;
d. $2\,Mg(s) + O_2(g) \rightarrow 2\,MgO(s)$; $4\,Al(s) + 3\,O_2(g) \rightarrow 2\,Al_2O_3(g)$; $4\,Fe(s) + 3\,O_2(g) \rightarrow 2\,Fe_2O_3(s)$

1.4.E.2.7: Q4.1.8

Fill in the blank with a single chemical formula for a covalent compound that will balance the equation:



1.4.E.2.8: Q4.1.9

Aqueous hydrogen fluoride (hydrofluoric acid) is used to etch glass and to analyze minerals for their silicon content. Hydrogen fluoride will also react with sand (silicon dioxide).

a. Write an equation for the reaction of solid silicon dioxide with hydrofluoric acid to yield gaseous silicon tetrafluoride and liquid water.

b. The mineral fluorite (calcium fluoride) occurs extensively in Illinois. Solid calcium fluoride can also be prepared by the reaction of aqueous solutions of calcium chloride and sodium fluoride, yielding aqueous sodium chloride as the other product. Write complete and net ionic equations for this reaction.

1.4.E.2.9: S4.1.9

a. $4\,HF(aq) + SiO_2(s) \rightarrow SiF_4(g) + 2\,H_2O(l)$;
b. complete ionic equation: $2\,Na^+(aq) + 2\,F^-(aq) + Ca^{2+}(aq) + 2\,Cl^-(aq) \rightarrow CaF_2(s) + 2\,Na^+(aq) + 2\,Cl^-(aq)$, net ionic equation: $2\,F^-(aq) + Ca^{2+}(aq) \rightarrow CaF_2(s)$

1.4.E.2.10: Q4.1.10

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.

1.4.E.2.11: Q4.1.11

From the balanced molecular equations, write the complete ionic and net ionic equations for the following:

a. $K_2C_2O_4(aq) + Ba(OH)_2(aq) \rightarrow 2\,KOH(aq) + BaC_2O_2(s)$
b. $Pb(NO_3)_2(aq) + H_2SO_4(aq) \rightarrow PbSO_4(s) + 2\,HNO_3(aq)$
c. $CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + CO_2(g) + H_2O(l)$

1.4.E.2.12: S4.1.11

a.
$$2\,K^+(aq) + C_2O_4^{2-}(aq) + Ba^{2+}(aq) + 2\,OH^-(aq) \rightarrow 2\,K^+(aq) + 2\,OH^-(aq) + BaC_2O_4(s) \quad \text{(complete)} \tag{1.4.E.1}$$

$$Ba^{2+}(aq) + C_2O_4^{2-}(aq) \rightarrow BaC_2O_4(s) \quad \text{(net)} \tag{1.4.E.2}$$

b.
$$Pb^{2+}(aq) + 2\,NO_3^-(aq) + 2\,H^+(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2\,H^+(aq) + 2\,NO_3^-(aq) \quad \text{(complete)} \tag{1.4.E.3}$$

$$Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) \quad \text{(net)} \tag{1.4.E.4}$$

c.
$$CaCO_3(s) + 2\,H^+(aq) + SO_4^{2-}(aq) \rightarrow CaSO_4(s) + CO_2(g) + H_2O(l) \quad \text{(complete)} \tag{1.4.E.5}$$

$$CaCO_3(s) + 2\,H^+(aq) + SO_4^{2-}(aq) \rightarrow CaSO_4(s) + CO_2(g) + H_2O(l) \quad \text{(net)} \tag{1.4.E.6}$$

1.4.E.3: 4.2: Classifying Chemical Reactions

1.4.E.3.1: Q4.2.1

Use the following equations to answer the next five questions:

i. $H_2O(s) \rightarrow H_2O(l)$
ii. $Na^+(aq) + Cl^-(aq)Ag^+(aq) + NO_3^-(aq) \rightarrow AgCl(s) + Na^+(aq) + NO_3^-(aq)$
iii. $CH_3OH(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$
iv. $2\,H_2O(l) \rightarrow 2\,H_2(g) + O_2(g)$
v. $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

a. Which equation describes a physical change?
b. Which equation identifies the reactants and products of a combustion reaction?
c. Which equation is not balanced?
d. Which is a net ionic equation?

1.4.E.3.2: S4.2.1

a.) **i.** $H_2O(solid) \rightarrow H_2O(liquid)$

b.) **iii.**

c.) **iii.** $2\,CH_3OH(g) + 3\,O_2(g) \rightarrow 2\,CO_2(g) + 4\,H_2O(g)$

d.) **v.**

1.4.E.3.3: Q4.2.2

Indicate what type, or types, of reaction each of the following represents:

a. $Ca(s) + Br_2(l) \rightarrow CaBr_2(s)$
b. $Ca(OH)_2(aq) + 2\,HBr(aq) \rightarrow CaBr_2(aq) + 2\,H_2O(l)$
c. $C_6H_{12}(l) + 9\,O_2(g) \rightarrow 6\,CO_2(g) + 6\,H_2O(g)$

1.4.E.3.4: S4.2.2

oxidation-reduction (addition); acid-base (neutralization); oxidation-reduction (combustion)

<

1.4.E.3.5: Q4.2.3

Indicate what type, or types, of reaction each of the following represents:

a. $H_2O(g) + C(s) \rightarrow CO(g) + H_2(g)$
b. $2\,KClO_3(s) \rightarrow 2\,KCl(s) + 3\,O_2(g)$
c. $Al(OH)_3(aq) + 3\,HCl(aq) \rightarrow AlBr_3(aq) + 3\,H_2O(l)$
d. $Pb(NO_3)_2(aq) + H_2SO_4(aq) \rightarrow PbSO_4(s) + 2\,HNO_3(aq)$

1.4.E.3.6: Q4.2.4

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? Explain your answer.

1.4.E.3.7: S4.2.4

It is an oxidation-reduction reaction because the oxidation state of the silver changes during the reaction.

1.4.E.3.8: Q4.2.5

Determine the oxidation states of the elements in the following compounds:

a. NaI
b. $GdCl_3$
c. $LiNO_3$
d. H_2Se
e. Mg_2Si
f. RbO_2, rubidium superoxide
g. HF

1.4.E.3.9: Q4.2.6

Determine the oxidation states of the elements in the compounds listed. None of the oxygen-containing compounds are peroxides or superoxides.

a. H_3PO_4
b. $Al(OH)_3$
c. SeO_2
d. KNO_2
e. In_2S_3
f. P_4O_6

1.4.E.3.10: S4.2.6

H +1, P +5, O −2; Al +3, H +1, O −2; Se +4, O −2; K +1, N +3, O −2; In +3, S −2; P +3, O −2

1.4.E.3.11: Q4.2.7

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

1.4.E.3.12: S4.2.7

a. H^{1+}, O^{2-}, S^{6+}
b. H^{1+}, O^{2-}, Ca^{+2}
c. H^{1+}, O^{2-}, Br^{1+}
d. O^{2-}, Cl^{1-}, N^{5+}
e. Cl^{1-}, Ti^{4+}
f. H^{1+}, Na^{1-}

1.4.E.3.13: Q4.2.8

Classify the following as acid-base reactions or oxidation-reduction reactions:

a. $Na_2S(aq) + 2\,HCl(aq) \rightarrow 2\,NaCl(aq) + H_2S(g)$
b. $2\,Na(s) + 2\,HCl(aq) \rightarrow 2\,NaCl(aq) + H_2(g)$
c. $Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$
d. $MgO(s) + 2\,HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)$
e. $K_3P(s) + 2\,O_2(g) \rightarrow K_3PO_4(s)$
f. $3\,KOH(aq) + H_3PO_4(aq) \rightarrow K_3PO_4(aq) + 3\,H_2O(l)$

1.4.E.3.14: S4.2.9

acid-base; oxidation-reduction: Na is oxidized, H^+ is reduced; oxidation-reduction: Mg is oxidized, Cl_2 is reduced; acid-base; oxidation-reduction: P^{3-} is oxidized, O_2 is reduced; acid-base

1.4.E.3.15: Q4.2.10

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. $Mg(s) + NiCl_2(aq) \rightarrow MgCl_2(aq) + Ni(s)$
b. $PCl_3(l) + Cl_2(g) \rightarrow PCl_5(s)$
c. $C_2H_4(g) + 3\,O_2(g) \rightarrow 2\,CO_2(g) + 2\,H_2O(g)$
d. $Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$
e. $2\,K_2S_2O_3(s) + I_2(s) \rightarrow K_2S_4O_6(s) + 2\,KI(s)$
f. $3\,Cu(s) + 8\,HNO_3(aq) \rightarrow 3\,Cu(NO_3)_2(aq) + 2\,NO(g) + 4\,H_2O(l)$

1.4.E.3.16: Q4.2.11

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.

1.4.E.3.17: S4.2.11

a. $2\,HCl(g) + Ca(OH)_2(s) \rightarrow CaCl_2(s) + 2\,H_2O(l)$;
b. $Sr(OH)_2(aq) + 2\,HNO_3(aq) \rightarrow Sr(NO_3)_2(aq) + 2\,H_2O(l)$

1.4.E.3.18: Q4.2.12

Complete and balance the following acid-base equations:

a. A solution of $HClO_4$ is added to a solution of LiOH.
b. Aqueous H_2SO_4 reacts with NaOH.
c. $Ba(OH)_2$ reacts with HF gas.

1.4.E.3.19: Q4.2.13

Complete and balance the following oxidation-reduction reactions, which give the highest possible oxidation state for the oxidized atoms.

a. $Al(s) + F_2(g) \rightarrow$

b. $\mathrm{Al}(s) + \mathrm{CuBr_2}(aq) \rightarrow$ (single displacement)
c. $\mathrm{P_4}(s) + \mathrm{O_2}(g) \rightarrow$
d. $\mathrm{Ca}(s) + \mathrm{H_2O}(l) \rightarrow$ (products are a strong base and a diatomic gas)

1.4.E.3.20: S4.2.13

a. $2\,\mathrm{Al}(s) + 3\,\mathrm{F_2}(g) \rightarrow 2\,\mathrm{AlF_3}(s)$;
b. $2\,\mathrm{Al}(s) + 3\,\mathrm{CuBr_2}(aq) \rightarrow 3\,\mathrm{Cu}(s) + 2\,\mathrm{AlBr_3}(aq)$;
c. $\mathrm{P_4}(s) + 5\,\mathrm{O_2}(g) \rightarrow \mathrm{P_4O_{10}}(s)$; $\mathrm{Ca}(s) + 2\,\mathrm{H_2O}(l) \rightarrow \mathrm{Ca(OH)_2}(aq) + \mathrm{H_2}(g)$

1.4.E.3.21: Q4.2.14

Complete and balance the following oxidation-reduction reactions, which give the highest possible oxidation state for the oxidized atoms.

a. $\mathrm{K}(s) + \mathrm{H_2O}(l) \rightarrow$
b. $\mathrm{Ba}(s) + \mathrm{HBr}(aq) \rightarrow$
c. $\mathrm{Sn}(s) + \mathrm{I_2}(s) \rightarrow$

1.4.E.3.22: Q4.2.15

Complete and balance the equations for the following acid-base neutralization reactions. If water is used as a solvent, write the reactants and products as aqueous ions. In some cases, there may be more than one correct answer, depending on the amounts of reactants used.

a. $\mathrm{Mg(OH)_2}(s) + \mathrm{HClO_4}(aq) \rightarrow$
b. $\mathrm{SO_3}(g) + \mathrm{H_2O}(l) \rightarrow$ (assume an excess of water and that the product dissolves)
c. $\mathrm{SrO}(s) + \mathrm{H_2SO_4}(l) \rightarrow$

1.4.E.3.23: S4.2.15

a. $\mathrm{Mg(OH)_2}(s) + 2\,\mathrm{HClO_4}(aq) \rightarrow \mathrm{Mg^{2+}}(aq) + 2\,\mathrm{ClO_4^-}(aq) + 2\,\mathrm{H_2O}(l)$;
b. $\mathrm{SO_3}(g) + 2\,\mathrm{H_2O}(l) \rightarrow \mathrm{H_3O^+}(aq) + \mathrm{HSO_4^-}(aq)$, (a solution of $\mathrm{H_2SO_4}$);
c. $\mathrm{SrO}(s) + \mathrm{H_2SO_4}(l) \rightarrow \mathrm{SrSO_4}(s) + \mathrm{H_2O}$

1.4.E.3.24: Q4.2.16

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.

1.4.E.3.25: Q4.2.17

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?

1.4.E.3.26: S4.2.17

$\mathrm{H_2}(g) + \mathrm{F_2}(g) \rightarrow 2\,\mathrm{HF}(g)$

1.4.E.3.27: Q4.2.18

Write the molecular, total ionic, and net ionic equations for the following reactions:

a. $\mathrm{Ca(OH)_2}(aq) + \mathrm{HC_2H_3O_2}(aq) \rightarrow$
b. $\mathrm{H_3PO_4}(aq) + \mathrm{CaCl_2}(aq) \rightarrow$

1.4.E.3.28: Q4.2.19

Great Lakes Chemical Company produces bromine, $\mathrm{Br_2}$, from bromide salts such as NaBr, in Arkansas brine by treating the brine with chlorine gas. Write a balanced equation for the reaction of NaBr with $\mathrm{Cl_2}$.

1.4.E.3.29: S4.2.19

$2\,\mathrm{NaBr}(aq) + \mathrm{Cl_2}(g) \rightarrow 2\,\mathrm{NaCl}(aq) + \mathrm{Br_2}(l)$

1.4.E.3.30: Q4.2.20

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 $\mathrm{Mg_3N_2}$, a compound formed as some of the magnesium reacts with nitrogen. Write a balanced equation for each reaction.

1.4.E.3.31: Q4.2.21

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.)

1.4.E.3.32: S4.2.21

$2\,\mathrm{LiOH}(aq) + \mathrm{CO_2}(g) \rightarrow \mathrm{Li_2CO_3}(aq) + \mathrm{H_2O}(l)$

1.4.E.3.33: Q4.2.22

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.

1.4.E.3.34: Q4.2.23

Complete and balance the equations of the following reactions, each of which could be used to remove hydrogen sulfide from natural gas:

a. $\mathrm{Ca(OH)_2}(s) + \mathrm{H_2S}(g) \rightarrow$
b. $\mathrm{Na_2CO_3}(aq) + \mathrm{H_2S}(g) \rightarrow$

1.4.E.3.35: S4.2.23

a. $\mathrm{Ca(OH)_2}(s) + \mathrm{H_2S}(g) \rightarrow \mathrm{CaS}(s) + 2\,\mathrm{H_2O}(l)$;
b. $\mathrm{Na_2CO_3}(aq) + \mathrm{H_2S}(g) \rightarrow \mathrm{Na_2S}(aq) + \mathrm{CO_2}(g) + \mathrm{H_2O}(l)$

1.4.E.3.36: Q4.2.24

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.

1.4.E.3.37: Q4.2.25

Write balanced chemical equations for the reactions used to prepare each of the following compounds from the given starting material(s). In some cases, additional reactants may be required.

a. solid ammonium nitrate from gaseous molecular nitrogen via a two-step process (first reduce the nitrogen to ammonia, then neutralize the ammonia with an appropriate acid)
b. gaseous hydrogen bromide from liquid molecular bromine via a one-step redox reaction
c. gaseous H_2S from solid Zn and S via a two-step process (first a redox reaction between the starting materials, then reaction of the product with a strong acid)

1.4.E.3.38: S4.2.25

a. step 1: $\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightarrow 2\,\mathrm{NH_3}(g)$, step 2: $\mathrm{NH_3}(g) + \mathrm{HNO_3}(aq) \rightarrow \mathrm{NH_4NO_3}(aq) \rightarrow \mathrm{NH_4NO_3}(s)(\text{after drying})$;
b. $\mathrm{H_2}(g) + \mathrm{Br_2}(l) \rightarrow 2\,\mathrm{HBr}(g)$;
c. $\mathrm{Zn}(s) + \mathrm{S}(s) \rightarrow \mathrm{ZnS}(s)$ and $\mathrm{ZnS}(s) + 2\,\mathrm{HCl}(aq) \rightarrow \mathrm{ZnCl_2}(aq) + \mathrm{H_2S}(g)$

1.4.E.3.39: Q4.2.26

Calcium cyclamate $Ca(C_6H_{11}NHSO_3)_2$ is an artificial sweetener used in many countries around the world but is banned in the United States. It can be purified industrially by converting it to the barium salt through reaction of the acid $C_6H_{11}NHSO_3H$ with barium carbonate, treatment with sulfuric acid (barium sulfate is very insoluble), and then neutralization with calcium hydroxide. Write the balanced equations for these reactions.

1.4.E.3.40: Q4.2.27

Complete and balance each of the following half-reactions (steps 2–5 in half-reaction method):

a. $\mathrm{Sn^{4+}}(aq) \rightarrow \mathrm{Sn^{2+}}(aq)$
b. $[\mathrm{Ag(NH_3)_2}]^+(aq) \rightarrow \mathrm{Ag}(s) + \mathrm{NH_3}(aq)$
c. $\mathrm{Hg_2Cl_2}(s) \rightarrow \mathrm{Hg}(l) + \mathrm{Cl^-}(aq)$
d. $\mathrm{H_2O}(l) \rightarrow \mathrm{O_2}(g)$ (in acidic solution)
e. $\mathrm{IO_3^-}(aq) \rightarrow \mathrm{I_2}(s)$
f. $\mathrm{SO_3^{2-}}(aq) \rightarrow \mathrm{SO_4^{2-}}(aq)$ (in acidic solution)
g. $\mathrm{MnO_4^-}(aq) \rightarrow \mathrm{Mn^{2+}}(aq)$ (in acidic solution)

h. $Cl^-(aq) \rightarrow ClO_3^-(aq)$ (in basic solution)

1.4.E.3.41: S4.2.27

a. $Sn^{4+}(aq) + 2\,e^- \rightarrow Sn^{2+}(aq)$,
b. $[Ag(NH_3)_2]^+(aq) + e^- \rightarrow Ag(s) + 2\,NH_3(aq)$;
c. $Hg_2Cl_2(s) + 2\,e^- \rightarrow 2\,Hg(l) + 2\,Cl^-(aq)$;
d. $2\,H_2O(l) \rightarrow O_2(g) + 4\,H^+(aq) + 4\,e^-$;
e. $6\,H_2O(l) + 2\,IO_3^-(aq) + 10\,e^- \rightarrow I_2(s) + 12\,OH^-(aq)$;
f. $H_2O(l) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + 2\,H^+(aq) + 2\,e^-$;
g. (g) $8\,H^+(aq) + MnO_4^-(aq) + 5\,e^- \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)$;
h. (h) $Cl^-(aq) + 6\,OH^-(aq) \rightarrow ClO_3^-(aq) + 3\,H_2O(l) + 6\,e^-$

1.4.E.3.42: Q4.2.28

Complete and balance each of the following half-reactions (steps 2–5 in half-reaction method):

a. $Cr^{2+}(aq) \rightarrow Cr^{3+}(aq)$
b. $Hg(l) + Br^-(aq) \rightarrow HgBr_4^{2-}(aq)$
c. $ZnS(s) \rightarrow Zn(s) + S^{2-}(aq)$
d. $H_2(g) \rightarrow H_2O(l)$ (in basic solution)
e. $H_2(g) \rightarrow H_3O^+(aq)$ (in acidic solution)
f. $NO_3^-(aq) \rightarrow HNO_2(aq)$ (in acidic solution)
g. $MnO_2(s) \rightarrow MnO_4^-(aq)$ (in basic solution)
h. $Cl^-(aq) \rightarrow ClO_3^-(aq)$ (in acidic solution)

1.4.E.3.43: Q4.2.29

Balance each of the following equations according to the half-reaction method:

a. $Sn^{2+}(aq) + Cu^{2+}(aq) \rightarrow Sn^{4+}(aq) + Cu^+(aq)$
b. $H_2S(g) + Hg_2^{2+}(aq) \rightarrow Hg(l) + S(s)$ (in acid)
c. $CN^-(aq) + ClO_2(aq) \rightarrow CNO^-(aq) + Cl^-(aq)$ (in acid)
d. $Fe^{2+}(aq) + Ce^{4+}(aq) \rightarrow Fe^{3+}(aq) + Ce^{3+}(aq)$
e. $HBrO(aq) \rightarrow Br^-(aq) + O_2(g)$ (in acid)

1.4.E.3.44: S4.2.29

a. $Sn^{2+}(aq) + 2\,Cu^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2\,Cu^+(aq)$;
b. $H_2S(g) + Hg_2^{2+}(aq) + 2\,H_2O(l) \rightarrow 2\,Hg(l) + S(s) + 2\,H_3O^+(aq)$;
c. $5\,CN^-(aq) + 2\,ClO_2(aq) + 3\,H_2O(l) \rightarrow 5\,CNO^-(aq) + 2\,Cl^-(aq) + 2\,H_3O^+(aq)$;
d. $Fe^{2+}(aq) + Ce^{4+}(aq) \rightarrow Fe^{3+}(aq) + Ce^{3+}(aq)$;
e. $2\,HBrO(aq) + 2\,H_2O(l) \rightarrow 2\,H_3O^+(aq) + 2\,Br^-(aq) + O_2(g)$

1.4.E.3.45: Q4.2.30

Balance each of the following equations according to the half-reaction method:

a. $Zn(s) + NO_3^-(aq) \rightarrow Zn^{2+}(aq) + N_2(g)$ (in acid)
b. $Zn(s) + NO_3^-(aq) \rightarrow Zn^{2+}(aq) + NH_3(aq)$ (in base)
c. $CuS(s) + NO_3^-(aq) \rightarrow Cu^{2+}(aq) + S(s) + NO(g)$ (in acid)
d. $NH_3(aq) + O_2(g) \rightarrow NO_2(g)$ (gas phase)
e. $Cl_2(g) + OH^-(aq) \rightarrow Cl^-(aq) + ClO_3^-(aq)$ (in base)
f. $H_2O_2(aq) + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + O_2(g)$ (in acid)
g. $NO_2(g) \rightarrow NO_3^-(aq) + NO_2^-(aq)$ (in base)
h. $Fe^{3+}(aq) + I^-(aq) \rightarrow Fe^{2+}(aq) + I_2(aq)$

1.4.E.3.46: Q4.2.31

Balance each of the following equations according to the half-reaction method:

a. $MnO_4^-(aq) + NO_2^-(aq) \rightarrow MnO_2(s) + NO_3^-(aq)$ (in base)
b. $MnO_4^{2-}(aq) \rightarrow MnO_4^-(aq) + MnO_2(s)$ (in base)
c. $Br_2(l) + SO_2(g) \rightarrow Br^-(aq) + SO_4^{2-}(aq)$ (in acid)

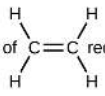
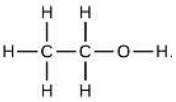
1.4.E.3.47: S4.2.31

a. $2\,\mathrm{MnO_4^-}(aq) + 3\,\mathrm{NO_2^-}(aq) + \mathrm{H_2O}(l) \rightarrow 2\,\mathrm{MnO_2}(s) + 3\,\mathrm{NO_3^-}(aq) + 2\,\mathrm{OH^-}(aq)$;
b. $3\,\mathrm{MnO_4^{2-}}(aq) + 2\,\mathrm{H_2O}(l) \rightarrow 2\,\mathrm{MnO_4^-}(aq) + 4\,\mathrm{OH^-}(aq) + \mathrm{MnO_2}(s)\ (\text{in base})$;
c. $\mathrm{Br_2}(l) + \mathrm{SO_2}(g) + 2\,\mathrm{H_2O}(l) \rightarrow 4\,\mathrm{H^+}(aq) + 2\,\mathrm{Br^-}(aq) + \mathrm{SO_4^{2-}}(aq)$

1.4.E.4: 4.3: Reaction Stoichiometry

1.4.E.4.1: Q4.3.1

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 chlorine, Cl_2, required to react with 10.0 g of sodium metal, Na, to produce sodium chloride, NaCl.
b. The number of moles and the mass of oxygen formed by the decomposition of 1.252 g of mercury(II) oxide.
c. The number of moles and the mass of sodium nitrate, $NaNO_3$, required to produce 128 g of oxygen. ($NaNO_2$ is the other product.)
d. The number of moles and the mass of carbon dioxide formed by the combustion of 20.0 kg of carbon in an excess of oxygen.
e. The number of moles and the mass of copper(II) carbonate needed to produce 1.500 kg of copper(II) oxide. (CO_2 is the other product.)
f. The number of moles and the mass of  required to react with H_2O to produce 9.55 g of .

1.4.E.4.2: Q4.3.2

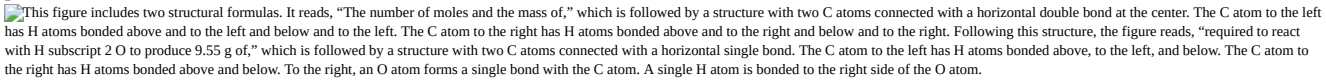
Determine the number of moles and the mass requested for each reaction in Exercise.

1.4.E.4.3: S4.3.2

0.435 mol Na, 0.217 mol Cl_2, 15.4 g Cl_2; 0.005780 mol HgO, 2.890×10^{-3} mol O_2, 9.248×10^{-2} g O_2; 8.00 mol $NaNO_3$, 6.8×10^2 g $NaNO_3$; 1665 mol CO_2, 73.3 kg CO_2; 18.86 mol CuO, 2.330 kg $CuCO_3$; 0.4580 mol $C_2H_4Br_2$, 86.05 g $C_2H_4Br_2$

1.4.E.4.4: Q4.3.3

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.)
f. 

1.4.E.4.5: Q4.3.4

Determine the number of moles and the mass requested for each reaction in Exercise.

1.4.E.4.6: S4.3.4

0.0686 mol Mg, 1.67 g Mg; 2.701×10^{-3} mol O_2, 0.08644 g O_2; 6.43 mol $MgCO_3$, 542 g $MgCO_3$ 713 mol H_2O, 12.8 kg H_2O; 16.31 mol BaO_2, 2762 g BaO_2; 0.207 mol C_2H_4, 5.81 g C_2H_4

1.4.E.4.7: Q4.3.5

H_2 is produced by the reaction of 118.5 mL of a 0.8775-M solution of H_3PO_4 according to the following equation: $2\,\mathrm{Cr} + 2\,\mathrm{H_3PO_4} \rightarrow 3\,\mathrm{H_2} + 2\,\mathrm{CrPO_4}$.

a. Outline the steps necessary to determine the number of moles and mass of H_2.
b. Perform the calculations outlined.

1.4.E.4.8: S4.3.5

a.)

1. Convert mL to L

2. Multiply L by the molarity to determine moles of H_3PO_4
3. Convert moles of H_3PO_4 to moles of H_2
4. Multiply moles of H_2 by the molar mass of H_2 to get the answer in grams

b.)

1. $118.5\ mL \times \dfrac{1\ L}{1000\ mL} = 0.1185\ L$
2. $0.1185\ L \times \dfrac{0.8775\ moles\ H_3PO_4}{1\ L} = 0.1040\ moles\ H_3PO_4$
3. $0.1040\ moles\ H_3PO_4 \times \dfrac{3\ moles\ H_2}{2\ moles\ H_3PO_4} = 0.1560\ moles\ H_2$
4. $0.1560\ moles\ H_2 \times \dfrac{2.02g}{1\ mole} = 0.3151g\ H_2$

1.4.E.4.9: Q4.3.6

Gallium chloride is formed by the reaction of 2.6 L of a 1.44 M solution of HCl according to the following equation: $2\ Ga + 6\ HCl \rightarrow 2\ GaCl_3 + 3\ H_2$.

a. Outline the steps necessary to determine the number of moles and mass of gallium chloride.
b. Perform the calculations outlined.

1.4.E.4.10: S4.3.6

volume HCl solution → mol HCl → mol $GaCl_3$; 1.25 mol $GaCl_3$, 2.2×10^2 g $GaCl_3$

1.4.E.4.11: Q4.3.7

I_2 is produced by the reaction of 0.4235 mol of $CuCl_2$ according to the following equation: $2\ CuCl_2 + 4\ KI \rightarrow 2\ CuI + 4\ KCl + I_2$.

a. How many molecules of I_2 are produced?
b. What mass of I_2 is produced?

1.4.E.4.12: Q4.3.8

Silver is often extracted from ores as $K[Ag(CN)_2]$ and then recovered by the reaction

$2\ K[Ag(CN)_2](aq) + Zn(s) \rightarrow 2\ Ag(s) + Zn(CN)_2(aq) + 2\ KCN(aq)$

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?

1.4.E.4.13: S4.3.8

5.337×10^{22} molecules; 10.41 g $Zn(CN)_2$

1.4.E.4.14: Q4.3.9

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?

$2\ C_{10}H_{10}N_4SO_2 + Ag_2O \rightarrow 2\ AgC_{10}H_9N_4SO_2 + H_2O$

1.4.E.4.15: Q4.3.10

Carborundum is silicon carbide, SiC, a very hard material used as an abrasive on sandpaper and in other applications. It is prepared by the reaction of pure sand, SiO_2, with carbon at high temperature. Carbon monoxide, CO, is the other product of this reaction. Write the balanced equation for the reaction, and calculate how much SiO_2 is required to produce 3.00 kg of SiC.

1.4.E.4.16: S4.3.10

$SiO_2 + 3\ C \rightarrow SiC + 2\ CO$, 4.50 kg SiO_2

1.4.E.4.17: Q4.3.11

Automotive air bags inflate when a sample of sodium azide, NaN_3, is very rapidly decomposed.

$2\ NaN_3(s) \rightarrow 2\ Na(s) + 3\ N_2(g)$

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?

1.4.E.4.18: S4.3.11

142g NaN_3

1.4.E.4.19: Q4.3.12

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 1.00×10^3 kg of carbon followed by the reaction?

$$\mathrm{CO_2}(g) + 2\,\mathrm{NH_3}(g) \rightarrow \mathrm{CO(NH_2)_2}(s) + \mathrm{H_2O}(l) \tag{1.4.E.7}$$

1.4.E.4.20: S4.3.12

5.00×10^3 kg

1.4.E.4.21: Q4.3.13

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?

1.4.E.4.22: Q4.3.14

A compact car gets 37.5 miles per gallon on the highway. If gasoline contains 84.2% carbon by mass and has a density of 0.8205 g/mL, determine the mass of carbon dioxide produced during a 500-mile trip (3.785 liters per gallon).

1.4.E.4.23: S4.3.14

1.28×10^5 g CO_2

1.4.E.4.24: Q4.3.15

What volume of a 0.750 M solution of hydrochloric acid, a solution of HCl, can be prepared from the HCl produced by the reaction of 25.0 g of NaCl with an excess of sulfuric acid?

$$\mathrm{NaCl}(s) + \mathrm{H_2SO_4}(l) \rightarrow \mathrm{HCl}(g) + \mathrm{NaHSO_4}(s) \tag{1.4.E.8}$$

1.4.E.4.25: Q4.3.16

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 $Cu(NO_3)_2$?

$$2\,\mathrm{Cu(NO_3)_2} + 4\,\mathrm{KI} \rightarrow 2\,\mathrm{CuI} + \mathrm{I_2} + 4\,\mathrm{KNO_3} \tag{1.4.E.9}$$

1.4.E.4.26: S4.3.16

161.40 mL KI solution

1.4.E.4.27: Q4.3.17

A mordant is a substance that combines with a dye to produce a stable fixed color in a dyed fabric. Calcium acetate is used as a mordant. It is prepared by the reaction of acetic acid with calcium hydroxide.

$$2\,\mathrm{CH_3CO_2H} + \mathrm{Ca(OH)_2} \rightarrow \mathrm{Ca(CH_3CO_2)_2} + 2\,\mathrm{H_2O} \tag{1.4.E.10}$$

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?

1.4.E.4.28: Q4.3.18

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?

$$2\,\mathrm{FeTiO_3} + 4\,\mathrm{HCl} + \mathrm{Cl_2} \rightarrow 2\,\mathrm{FeCl_3} + 2\,\mathrm{TiO_2} + 2\,\mathrm{H_2O} \tag{1.4.E.11}$$

1.4.E.4.29: S4.3.18

176 g TiO_2

1.4.E.5: 4.4: Reaction Yields

1.4.E.5.1: Q4.4.1

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 ?

1.4.E.5.2: Q4.4.2

What is the limiting reactant in a reaction that produces sodium chloride from 8 g of sodium and 8 g of diatomic chlorine?

1.4.E.5.3: S4.4.2

The limiting reactant is Cl_2.

1.4.E.5.4: Q4.4.3

Which of the postulates of Dalton's atomic theory explains why we can calculate a theoretical yield for a chemical reaction?

1.4.E.5.5: Q4.4.4

A student isolated 25 g of a compound following a procedure that would theoretically yield 81 g. What was his percent yield?

1.4.E.5.6: S4.4.4

$\text{Percent yield} = 31\%$

1.4.E.5.7: Q4.4.5

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?

$$\mathrm{CaCO_3}(s) \rightarrow \mathrm{CaO}(s) + \mathrm{CO_2}(s) \tag{1.4.E.12}$$

1.4.E.5.8: Q4.4.6

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.

1.4.E.5.9: S4.4.6

$\text{g } \mathrm{CCl_4} \rightarrow \text{mol } \mathrm{CCl_4} \rightarrow \text{mol } \mathrm{CCl_2F_2} \rightarrow \text{g } \mathrm{CCl_2F_2}, \text{ percent yield} = 48.3\%$

1.4.E.5.10: Q4.4.7

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

$$\mathrm{C_{12}H_{22}O_{11} + H_2O + 3\,O_2} \rightarrow \mathrm{2\,C_6H_8O_7 + 4\,H_2O} \tag{1.4.E.13}$$

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%?

1.4.E.5.11: Q4.4.8

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?

$$\mathrm{2\,C_6H_5CH_3 + 3\,O_2} \rightarrow \mathrm{2\,C_6H_5CO_2H + 2\,H_2O} \tag{1.4.E.14}$$

1.4.E.5.12: S4.4.8

$\text{percent yield} = 91.3\%$

1.4.E.5.13: Q4.4.9

In a laboratory experiment, the reaction of 3.0 mol of H_2 with 2.0 mol of I_2 produced 1.0 mol of HI. Determine the theoretical yield in grams and the percent yield for this reaction.

1.4.E.5.14: Q4.4.10

Outline the steps needed to solve the following problem, then do the calculations. Ether, $(C_2H_5)_2O$, which was originally used as an anesthetic but has been replaced by safer and more effective medications, is prepared by the reaction of ethanol with sulfuric acid.

$$2C_2H_5OH + H_2SO_4 \longrightarrow (C_2H_5)_2 + H_2SO_4{\cdot}H_2O$$

1.4.E.5.15: Q4.4.11

What is the percent yield of ether if 1.17 L (d = 0.7134 g/mL) is isolated from the reaction of 1.500 L of C_2H_5OH (d = 0.7894 g/mL)?

1.4.E.5.16: S4.4.11

Convert mass of ethanol to moles of ethanol; relate the moles of ethanol to the moles of ether produced using the stoichiometry of the balanced equation. Convert moles of ether to grams; divide the actual grams of ether (determined through the density) by the theoretical mass to determine the percent yield; 87.6%

1.4.E.5.17: Q4.4.12

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.

$$\text{percent yield} = \frac{0.8347 \ \cancel{\text{g}}}{0.9525 \ \cancel{\text{g}}} \times 100\% = 87.6\% \tag{1.4.E.15}$$

Determine the limiting reactant.

1.4.E.5.18: Q4.4.13

Outline the steps needed to determine the limiting reactant when 0.50 g of Cr and 0.75 g of H_3PO_4 react according to the following chemical equation?

$$2\,\mathrm{Cr} + 2\,\mathrm{H_3PO_4} \rightarrow 2\,\mathrm{CrPO_4} + 3\,\mathrm{H_2} \tag{1.4.E.16}$$

Determine the limiting reactant.

1.4.E.5.19: S4.4.13

The conversion needed is $\mathrm{mol\ Cr} \rightarrow \mathrm{mol\ H_2PO_4}$. Then compare the amount of Cr to the amount of acid present. Cr is the limiting reactant.

1.4.E.5.20: Q4.4.14

What is the limiting reactant when 1.50 g of lithium and 1.50 g of nitrogen combine to form lithium nitride, a component of advanced batteries, according to the following unbalanced equation?

$$\mathrm{Li} + \mathrm{N_2} \rightarrow \mathrm{Li_3N} \tag{1.4.E.17}$$

1.4.E.5.21: S4.4.14

$$6\,\mathrm{Li} + \mathrm{N_2} \rightarrow 2\,\mathrm{Li_3N} \tag{1.4.E.18}$$

$$1.50g\,\mathrm{Li} \times \frac{1\ mole\,\mathrm{Li}}{6.94g\,\mathrm{Li}} \times \frac{2\ mole\,\mathrm{Li_3N}}{6\ mole\,\mathrm{Li}} = 0.0720\ moles\,\mathrm{Li_3N} \tag{1.4.E.19}$$

$$1.50g\,\mathrm{N_2} \times \frac{1\ mole\,\mathrm{N_2}}{28.02g\,\mathrm{N_2}} \times \frac{2\ mole\,\mathrm{Li_3N}}{1\ mole\,\mathrm{N_2}} = 0.107\ moles\,\mathrm{Li_3N} \tag{1.4.E.20}$$

Li is the limiting reactant

1.4.E.5.22: Q4.4.15

Uranium can be isolated from its ores by dissolving it as $UO_2(NO_3)_2$, then separating it as solid $UO_2(C_2O_4){\cdot}3H_2O$. Addition of 0.4031 g of sodium oxalate, $Na_2C_2O_4$, to a solution containing 1.481 g of uranyl nitrate, $UO_2(NO_2)_2$, yields 1.073 g of solid $UO_2(C_2O_4){\cdot}3H_2O$.

$$\mathrm{Na_2C_2O_4} + \mathrm{UO_2(NO_3)_2} + 3\,\mathrm{H_2O} \longrightarrow \mathrm{UO_2(C_2O_4)\cdot 3\,H_2O} + 2\,\mathrm{NaNO_3} \tag{1.4.E.21}$$

Determine the limiting reactant and the percent yield of this reaction.

1.4.E.5.23: S4.4.15

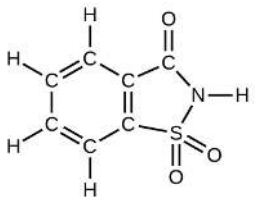
$Na_2C_2O_4$ is the limiting reactant. percent yield = 86.6%

1.4.E.5.24: Q4.4.16

How many molecules of $C_2H_4Cl_2$ can be prepared from 15 C_2H_4 molecules and 8 Cl_2 molecules?

1.4.E.5.25: Q4.4.17

How many molecules of the sweetener saccharin can be prepared from 30 C atoms, 25 H atoms, 12 O atoms, 8 S atoms, and 14 N atoms?



1.4.E.5.26: S4.4.17

Only four molecules can be made.

1.4.E.5.27: Q4.4.18

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

$$\mathrm{P_4 + 5\,O_2 \rightarrow P_4O_{10}} \tag{1.4.E.22}$$

b. Calculate the percent yield if 10.0 g of P_4O_{10} is isolated from the reaction.

1.4.E.5.28: Q4.4.19

Would you agree to buy 1 trillion (1,000,000,000,000) gold atoms for $5? Explain why or why not. Find the current price of gold at http://money.cnn.com/data/commodities/ $(1\text{ troy ounce} = 31.1\text{ g})$

1.4.E.5.29: S4.4.19

This amount cannot be weighted by ordinary balances and is worthless.

1.4.E.6: 4.5: Quantitative Chemical Analysis

1.4.E.6.1: Q4.5.1

What volume of 0.0105-M HBr solution is be required to titrate 125 mL of a 0.0100-*M* $Ca(OH)_2$ solution?

$$\mathrm{Ca(OH)_2}(aq) + 2\,\mathrm{HBr}(aq) \rightarrow \mathrm{CaBr_2}(aq) + 2\,\mathrm{H_2O}(l) \tag{1.4.E.23}$$

1.4.E.6.2: Q4.5.2

Titration of a 20.0-mL sample of acid rain required 1.7 mL of 0.0811 *M* NaOH to reach the end point. If we assume that the acidity of the rain is due to the presence of sulfuric acid, what was the concentration of sulfuric acid in this sample of rain?

1.4.E.6.3: S4.5.2

3.4×10^{-3} *M* H_2SO_4

1.4.E.6.4: Q4.5.3

What is the concentration of NaCl in a solution if titration of 15.00 mL of the solution with 0.2503 *M* $AgNO_3$ requires 20.22 mL of the $AgNO_3$ solution to reach the end point?

$$\mathrm{AgNO_3}(aq) + \mathrm{NaCl}(aq) \rightarrow \mathrm{AgCl}(s) + \mathrm{NaNO_3}(aq) \tag{1.4.E.24}$$

1.4.E.6.5: Q4.5.4

In a common medical laboratory determination of the concentration of free chloride ion in blood serum, a serum sample is titrated with a $Hg(NO_3)_2$ solution.

$$2\,Cl^-(aq) + Hg(NO_3)_2(aq) \rightarrow 2\,NO_3^-(aq) + HgCl_2(s) \tag{1.4.E.25}$$

What is the Cl^- concentration in a 0.25-mL sample of normal serum that requires 1.46 mL of 5.25×10^{-4} *M* $Hg(NO_3)_2(aq)$ to reach the end point?

1.4.E.6.6: S4.5.4

9.6×10^{-3} *M* Cl^-

1.4.E.6.7: Q4.5.5

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?

1.4.E.6.8: Q4.5.6

A sample of gallium bromide, $GaBr_2$, weighing 0.165 g was dissolved in water and treated with silver nitrate, $AgNO_3$, resulting in the precipitation of 0.299 g AgBr. Use these data to compute the %Ga (by mass) $GaBr_2$.

1.4.E.6.9: S4.5.6

22.4%

1.4.E.6.10: Q4.5.7

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.

1.4.E.6.11: Q4.5.8

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.

1.4.E.6.12: S4.5.8

The empirical formula is BH_3. The molecular formula is B_2H_6.

1.4.E.6.13: Q4.5.9

Sodium bicarbonate (baking soda), $NaHCO_3$, can be purified by dissolving it in hot water (60 °C), filtering to remove insoluble impurities, cooling to 0 °C to precipitate solid $NaHCO_3$, and then filtering to remove the solid, leaving soluble impurities in solution. Any $NaHCO_3$ that remains in solution is not recovered. The solubility of $NaHCO_3$ in hot water of 60 °C is 164 g L. Its solubility in cold water of 0 °C is 69 g/L. What is the percent yield of $NaHCO_3$ when it is purified by this method?

1.4.E.6.14: Q4.5.10

What volume of 0.600 *M* HCl is required to react completely with 2.50 g of sodium hydrogen carbonate?

$$NaHCO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O(l) \tag{1.4.E.26}$$

1.4.E.6.15: S4.5.10

49.6 mL

1.4.E.6.16: Q4.5.11

What volume of 0.08892 *M* HNO_3 is required to react completely with 0.2352 g of potassium hydrogen phosphate?

$$2\,HNO_3(aq) + K_2HPO_4(aq) \rightarrow H_2PO_4(aq) + 2\,KNO_3(aq) \tag{1.4.E.27}$$

1.4.E.6.17: Q4.5.12

What volume of a 0.3300-*M* solution of sodium hydroxide would be required to titrate 15.00 mL of 0.1500 *M* oxalic acid?

$$C_2O_4H_2(aq) + 2\,NaOH(aq) \rightarrow Na_2C_2O_4(aq) + 2\,H_2O(l) \tag{1.4.E.28}$$

1.4.E.6.18: S4.5.12

13.64 mL

1.4.E.6.19: Q4.5.13

What volume of a 0.00945-*M* solution of potassium hydroxide would be required to titrate 50.00 mL of a sample of acid rain with a H_2SO_4 concentration of 1.23×10^{-4} *M*.

$$H_2SO_4(aq) + 2\,KOH(aq) \rightarrow K_2SO_4(aq) + 2\,H_2O(l) \tag{1.4.E.29}$$

1.4.E.6.20: S4.5.13

1.30 mL

1.4.E.6.21: Q4.5.14

A sample of solid calcium hydroxide, $Ca(OH)_2$, is allowed to stand in water until a saturated solution is formed. A titration of 75.00 mL of this solution with 5.00×10^{-2} *M* HCl requires 36.6 mL of the acid to reach the end point.

$$Ca(OH)_2(aq) + 2\,HCl(aq) \rightarrow CaCl_2(aq) + 2\,H_2O(l) \tag{1.4.E.30}$$

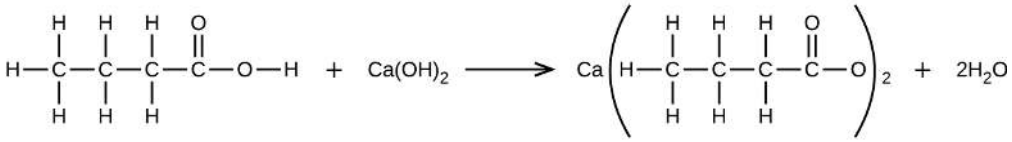
What is the molarity?

1.4.E.6.22: S4.5.14

1.22 *M*

1.4.E.6.23: Q4.5.15

What mass of $Ca(OH)_2$ will react with 25.0 g of propionic acid to form the preservative calcium propionate according to the equation?



1.4.E.6.24: Q4.5.16

How many milliliters of a 0.1500-*M* solution of KOH will be required to titrate 40.00 mL of a 0.0656-*M* solution of H_3PO_4?

$$H_3PO_4(aq) + 2\,KOH(aq) \rightarrow K_2HPO_4(aq) + 2\,H_2O(l) \tag{1.4.E.31}$$

1.4.E.6.25: S4.5.16

34.99 mL KOH

1.4.E.6.26: Q4.5.17

Potassium acid phthalate, $KHC_6H_4O_4$, or KHP, is used in many laboratories, including general chemistry laboratories, to standardize solutions of base. KHP is one of only a few stable solid acids that can be dried by warming and weighed. A 0.3420-g sample of $KHC_6H_4O_4$ reacts with 35.73 mL of a NaOH solution in a titration. What is the molar concentration of the NaOH?

$$KHC_6H_4O_4(aq) + NaOH(aq) \rightarrow KNaC_6H_4O_4(aq) + H_2O(aq) \tag{1.4.E.32}$$

1.4.E.6.27: Q4.5.18

The reaction of WCl_6 with Al at ~400 °C gives black crystals of a compound containing only tungsten and chlorine. A sample of this compound, when reduced with hydrogen, gives 0.2232 g of tungsten metal and hydrogen chloride, which is absorbed in water. Titration of the hydrochloric acid thus produced requires 46.2 mL of 0.1051 *M* NaOH to reach the end point. What is the empirical formula of the black tungsten chloride?

1.4.E.6.28: S4.5.19

The empirical formula is WCl_4.

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1.4.S: Stoichiometry of Chemical Reactions (Summary)

- atoms are neither created nor destroyed during any chemical reaction
- **stoichiometry** – quantitative nature of chemical formulas and chemical reactions

3.1: Chemical Equations

A chemical reaction is described by a chemical equation that gives the identities and quantities of the reactants and the products. In a chemical reaction, one or more substances are transformed to new substances. A chemical reaction is described by a chemical equation, an expression that gives the identities and quantities of the substances involved in a reaction. A chemical equation shows the starting compound(s)—the reactants—on the left and the final compound(s)—the products—on the right.

- chemical equations – the way chemical reactions are represented
- **reactants** – starting substances
- **products** – substances produced from a reaction
- **balanced equation** – equation with equal atoms on both sides of the equation
- subscripts should never be changed in balancing an equation
- coefficients changes only the amount and not identity of the substance

3.2: Some Simple Patterns of Chemical Reactivity

By recognizing general patterns of chemical reactivity, you will be able to successfully predict the products formed by a given combination of reactants We can often predict a reaction if we have seen a similar reaction before.

3.2.1 Using the Periodic Table

- periodic table can be used to determine reactivity of substances
- all alkali metals react with water to form their hydroxide compounds and hydrogen

3.2.2 Combustion in Air

- rapid reaction that produces a flame
- most combustion reactions in air involve oxygen
- hydrocarbons and related compounds produce CO_2 and H_2O during combustion

3.2.3 Combination and Decomposition Reactions

- combination reactions two or more substances react to form one product
- decomposition reaction one substance produces two or more substances

3.3: Formula Masses

The empirical formula of a substance can be calculated from its percent composition, and the molecular formula can be determined from the empirical formula and the compound's molar mass. The empirical formula of a substance can be calculated from the experimentally determined percent composition, the percentage of each element present in a pure substance by mass. In many cases, these percentages can be determined by combustion analysis.

3.3.1 The Atomic Mass Scale

- **atomic mass unit (amu)** – unit in measuring mass of atoms
- 1 amu = $1.66054*10^{-24}$g and 1 amu = $6.02214*10^{24}$amu

3.3.2 Average Atomic Masses

- **atomic weight –** average atomic mass

3.3.3 Formula and Molecular Weights

- **formula weight** – sum of the atomic weights of each atom in its chemical formula
- **molecular weight** – same as formula weight

3.3.4 Percentage composition from Formulas

- ((atoms of element)(AW)/(FW of compound) * 100

3.3.5 The Mole

- **avogadro's number** – $6.02*10^{23}$ atoms
- **molar mass** – numerically equal to its formula weight
- grams <use molar mass> moles <use avogadro's number> molecules

3.5: Empirical Formulas from Analysis

Molecular formulas tell you how many atoms of each element are in a compound, and empirical formulas tell you the simplest or most reduced ratio of elements in a compound. If a compound's molecular formula cannot be reduced any more, then the empirical formula is the same as the molecular formula. Combustion analysis can determine the empirical formula of a compound, but cannot determine the molecular formula (other techniques can though).

- empirical formula gives relative number of atoms in each element
- **mass % elements** >>> assume 100g sample >>> **grams of each element** >>> use atomic weights >>> **moles of each element** >>> calculate mole ratio >>> **empirical formula**
- "percent to mass, mass to mol, divide by small, multiply 'til whole/"

3.5.1 Molecular Formula from Empirical Formula

- the subscripts in the molecular formula of a substance are always a whole-number multiple of the corresponding subscripts in its empirical formula

3.5.2 Combustion Analysis

3.6: Quantitative Information from Balanced Equations

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

- the coefficients in a balanced chemical equation can be interpreted both as the relative numbers of molecules involved in the reaction and as the relative numbers of moles
- stoichiometrically equivalent quantities
- grams reactant >> moles reactant >> moles product >> grams product
- grams of substance A >> use molar mass of A >> moles of substance A >> use coefficients of A and B from balanced equation >> moles of substance B >> use molar mass of B >> grams of substance B

3.7: Limiting Reactants

The stoichiometry of a balanced chemical equation identifies the maximum amount of product that can be obtained. The stoichiometry of a reaction describes the relative amounts of reactants and products in a balanced chemical equation. A stoichiometric quantity of a reactant is the amount necessary to react completely with the other reactant(s). If a reactant remains unconsumed after complete reaction has occurred, it is in excess. The reactant that is consumed first is the limiting reagent.

- **limiting reactant** – limits the amount of product formed

3.7.1 Theoretical Yields

- theoretical yield – the amount of product that is calculated to form
- actual yield – the amount of product actually formed

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

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CHAPTER OVERVIEW

2: Gases

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General Chemistry

In this chapter, we examine the relationships between gas temperature, pressure, amount, and volume. We will study a simple theoretical model and use it to analyze the experimental behavior of gases. The results of these analyses will show us the limitations of the theory and how to improve on it.

2.1: Characteristics of Gases
2.2: Gas Pressure
2.3: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law
2.4: Stoichiometry of Gaseous Substances, Mixtures, and Reactions
2.5: The Kinetic-Molecular Theory
2.6: Effusion and Diffusion of Gases
2.7: Non-Ideal Gas Behavior
2.E: Gases (Exercises)
2.S: Gases (Study Guide)

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- Thumbnail: As long as black-body radiation (not shown) doesn't escape a system, atoms in thermal agitation undergo essentially elastic collisions. On average, two atoms rebound from each other with the same kinetic energy as before a collision. Five atoms are colored red so their paths of motion are easier to see. (Public Domain; Greg L via Wikipedia)

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2.1: Characteristics of Gases

Learning Objectives

- To describe the characteristics of a gas.

The three common phases (or states) of matter are gases, liquids, and solids. Gases have the lowest density of the three, are highly compressible, and completely fill any container in which they are placed. Gases behave this way because their intermolecular forces are relatively weak, so their molecules are constantly moving independently of the other molecules present. Solids, in contrast, are relatively dense, rigid, and incompressible because their intermolecular forces are so strong that the molecules are essentially locked in place. Liquids are relatively dense and incompressible, like solids, but they flow readily to adapt to the shape of their containers, like gases. We can therefore conclude that the sum of the intermolecular forces in liquids are between those of gases and solids. Figure 2.1.1 compares the three states of matter and illustrates the differences at the molecular level.

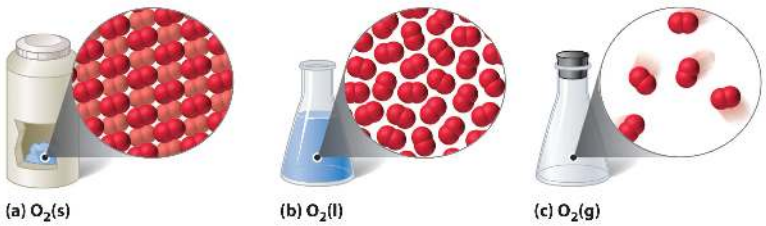


Figure 2.1.1: A Diatomic Substance (O_2) in the Solid, Liquid, and Gaseous States: (a) Solid O_2 has a fixed volume and shape, and the molecules are packed tightly together. (b) Liquid O_2 conforms to the shape of its container but has a fixed volume; it contains relatively densely packed molecules. (c) Gaseous O_2 fills its container completely—regardless of the container's size or shape—and consists of widely separated molecules.

The state of a given substance depends strongly on conditions. For example, H_2O is commonly found in all three states: solid ice, liquid water, and water vapor (its gaseous form). Under most conditions, we encounter water as the liquid that is essential for life; we drink it, cook with it, and bathe in it. When the temperature is cold enough to transform the liquid to ice, we can ski or skate on it, pack it into a snowball or snow cone, and even build dwellings with it. Water vapor (the term *vapor* refers to the gaseous form of a substance that is a liquid or a solid under normal conditions so nitrogen (N_2) and oxygen (O_2) are referred to as gases, but gaseous water in the atmosphere is called water vapor) is a component of the air we breathe, and it is produced whenever we heat water for cooking food or making coffee or tea. Water vapor at temperatures greater than 100°C is called steam. Steam is used to drive large machinery, including turbines that generate electricity. The properties of the three states of water are summarized in Table 10.1.

Table 2.1.1: Properties of Water at 1.0 atm

Temperature	State	Density (g/cm3)
≤0°C	solid (ice)	0.9167 (at 0.0°C)
0°C–100°C	liquid (water)	0.9997 (at 4.0°C)
≥100°C	vapor (steam)	0.005476 (at 127°C)

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

Figure 2.1.2 shows the locations in the periodic table of those elements that are commonly found in the gaseous, liquid, and solid states. Except for hydrogen, the elements that occur naturally as gases are on the right side of the periodic table. Of these, all the noble gases (group 18) are monatomic gases, whereas the other gaseous elements are diatomic molecules (**H_2, N_2, O_2, F_2, and Cl_2**). Oxygen can also form a second allotrope, the highly reactive triatomic molecule ozone (**O_3**), which is also a gas. In contrast, bromine (as Br_2) and mercury (Hg) are liquids under normal conditions (25°C and 1.0 atm, commonly referred to as "room temperature and pressure"). Gallium (Ga), which melts at only 29.76°C, can be converted to a liquid simply by holding a container

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

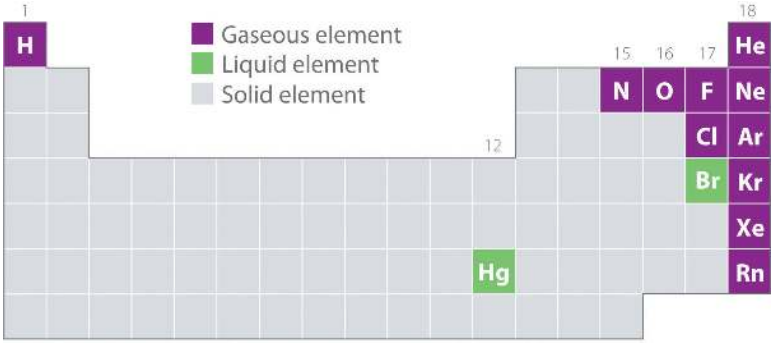


Figure 2.1.2: Elements That Occur Naturally as Gases, Liquids, and Solids at 25°C and 1 atm. The noble gases and mercury occur as monatomic species, whereas all other gases and bromine are diatomic molecules.

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

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

Summary

Bulk matter can exist in three states: gas, liquid, and solid. Gases have the lowest density of the three, are highly compressible, and fill their containers completely. Elements that exist as gases at room temperature and pressure are clustered on the right side of the periodic table; they occur as either monatomic gases (the noble gases) or diatomic molecules (some halogens, N_2, O_2).



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2.2: Gas Pressure

Learning Objectives

- Define the property of pressure
- Define and convert among the units of pressure measurements
- Describe the operation of common tools for measuring gas pressure
- Calculate pressure from manometer data

The earth's atmosphere exerts a pressure, as does any other gas. Although we do not normally notice atmospheric pressure, we are sensitive to pressure changes—for example, when your ears "pop" during take-off and landing while flying, or when you dive underwater. Gas pressure is caused by the force exerted by gas molecules colliding with the surfaces of objects (Figure 2.2.1). Although the force of each collision is very small, any surface of appreciable area experiences a large number of collisions in a short time, which can result in a high pressure. In fact, normal air pressure is strong enough to crush a metal container when not balanced by equal pressure from inside the container.

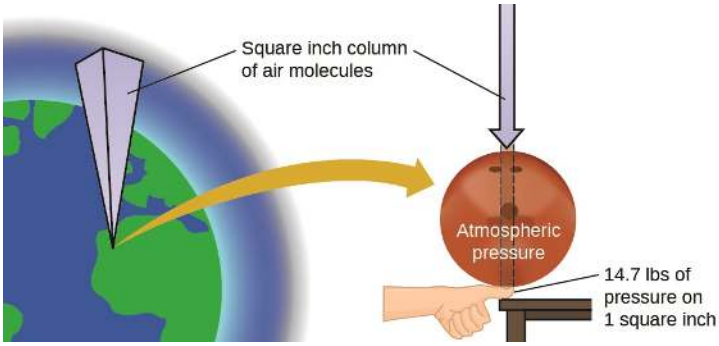


Figure 2.2.1: The atmosphere above us exerts a large pressure on objects at the surface of the earth, roughly equal to the weight of a bowling ball pressing on an area the size of a human thumbnail.

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



A dramatic illustration of atmospheric pressure is provided in this brief video, which shows a railway tanker car imploding when its internal pressure is decreased.

Pressure is defined as the force exerted on a given area:

$$P = \frac{F}{A} \tag{2.2.1}$$

Since pressure is directly proportional to force and inversely proportional to area (Equation 2.2.1), pressure can be increased either by either **increasing** the amount of force or by **decreasing** the area over which it is applied. Correspondingly, pressure

can be decreased by either **decreasing** the force or **increasing** the area.

Let's apply the definition of pressure (Equation 2.2.1) to determine which would be more likely to fall through thin ice in Figure 2.2.2—the elephant or the figure skater?



Figure 2.2.2: Although (a) an elephant's weight is large, creating a very large force on the ground, (b) the figure skater exerts a much higher pressure on the ice due to the small surface area of her skates. (credit a: modification of work by Guido da Rozze; credit b: modification of work by Ryosuke Yagi).

A large African elephant can weigh 7 tons, supported on four feet, each with a diameter of about 1.5 ft (footprint area of 250 in^2), so the pressure exerted by each foot is about 14 lb/in^2:

$$\text{pressure per elephant foot} = 14,000 \frac{\text{lb}}{\text{elephant}} \times \frac{1 \text{ elephant}}{4 \text{ feet}} \times \frac{1 \text{ foot}}{250 \text{ in}^2} = 14 \text{ lb/in}^2 \tag{2.2.2}$$

The figure skater weighs about 120 lbs, supported on two skate blades, each with an area of about 2 in^2, so the pressure exerted by each blade is about 30 lb/in^2:

$$\text{pressure per skate blade} = 120 \frac{\text{lb}}{\text{skater}} \times \frac{1 \text{ skater}}{2 \text{ blades}} \times \frac{1 \text{ blade}}{2 \text{ in}^2} = 30 \text{ lb/in}^2 \tag{2.2.3}$$

Even though the elephant is more than one hundred times heavier than the skater, it exerts less than one-half of the pressure and would therefore be less likely to fall through thin ice. On the other hand, if the skater removes her skates and stands with bare feet (or regular footwear) on the ice, the larger area over which her weight is applied greatly reduces the pressure exerted:

$$\text{pressure per human foot} = 120 \frac{\text{lb}}{\text{skater}} \times \frac{1 \text{ skater}}{2 \text{ feet}} \times \frac{1 \text{ foot}}{30 \text{ in}^2} = 2 \text{ lb/in}^2 \tag{2.2.4}$$

The SI unit of pressure is the pascal (Pa), with 1 Pa = 1 N/m^2, where N is the newton, a unit of force defined as 1 kg m/s^2. One pascal is a small pressure; in many cases, it is more convenient to use units of kilopascal (1 kPa = 1000 Pa) or bar (1 bar = 100,000 Pa). In the United States, pressure is often measured in pounds of force on an area of one square inch—pounds per square inch (psi)—for example, in car tires. Pressure can also be measured using the unit atmosphere (atm), which originally represented the average sea level air pressure at the approximate latitude of Paris (45°). Table 2.2.1 provides some information on these and a few other common units for pressure measurements

Table 2.2.1: Pressure Units

Unit Name and Abbreviation	Definition or Relation to Other Unit	Comment
pascal (Pa)	1 Pa = 1 N/m^2	recommended IUPAC unit
kilopascal (kPa)	1 kPa = 1000 Pa	
pounds per square inch (psi)	air pressure at sea level is ~14.7 psi	
atmosphere (atm)	1 atm = 101,325 Pa	air pressure at sea level is ~1 atm
bar (bar, or b)	1 bar = 100,000 Pa (exactly)	commonly used in meteorology
millibar (mbar, or mb)	1000 mbar = 1 bar	

Unit Name and Abbreviation	Definition or Relation to Other Unit	Comment
inches of mercury (in. Hg)	1 in. Hg = 3386 Pa	used by aviation industry, also some weather reports
torr	$1 \text{ torr} = \frac{1}{760} \text{ atm}$	named after Evangelista Torricelli, inventor of the barometer
millimeters of mercury (mm Hg)	1 mm Hg ~1 torr	

Example 2.2.1: Conversion of Pressure Units

The United States National Weather Service reports pressure in both inches of Hg and millibars. Convert a pressure of 29.2 in. Hg into:

a. torr
b. atm
c. kPa
d. mbar

Solution

This is a unit conversion problem. The relationships between the various pressure units are given in Table 9.2.1.

a. $29.2 \text{ in Hg} \times \frac{25.4 \text{ mm}}{1 \text{ in}} \times \frac{1 \text{ torr}}{1 \text{ mm Hg}} = 742 \text{ torr}$

b. $742 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.976 \text{ atm}$

c. $742 \text{ torr} \times \frac{101.325 \text{ kPa}}{760 \text{ torr}} = 98.9 \text{ kPa}$

d. $98.9 \text{ kPa} \times \frac{1000 \text{ Pa}}{1 \text{ kPa}} \times \frac{1 \text{ bar}}{100,000 \text{ Pa}} \times \frac{1000 \text{ mbar}}{1 \text{ bar}} = 989 \text{ mbar}$

Exercise 2.2.1

A typical barometric pressure in Kansas City is 740 torr. What is this pressure in atmospheres, in millimeters of mercury, in kilopascals, and in bar?

Answer

0.974 atm; 740 mm Hg; 98.7 kPa; 0.987 bar

We can measure atmospheric pressure, the force exerted by the atmosphere on the earth's surface, with a barometer (Figure 2.2.3). A barometer is a glass tube that is closed at one end, filled with a nonvolatile liquid such as mercury, and then inverted and immersed in a container of that liquid. The atmosphere exerts pressure on the liquid outside the tube, the column of liquid exerts pressure inside the tube, and the pressure at the liquid surface is the same inside and outside the tube. The height of the liquid in the tube is therefore proportional to the pressure exerted by the atmosphere.

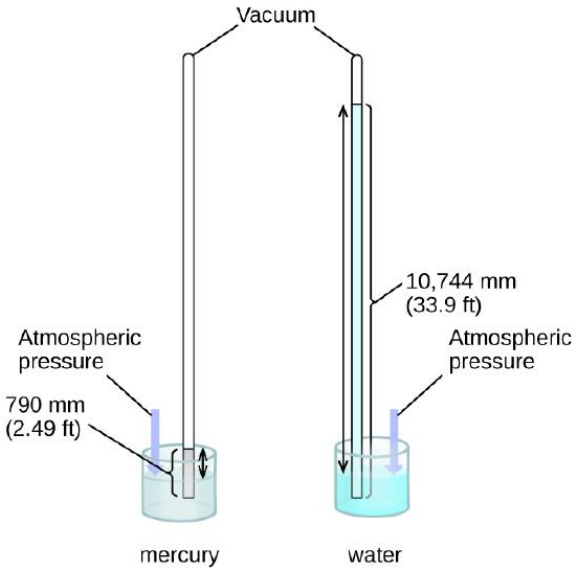


Figure 2.2.3: In a barometer, the height, h, of the column of liquid is used as a measurement of the air pressure. Using very dense liquid mercury (left) permits the construction of reasonably sized barometers, whereas using water (right) would require a barometer more than 30 feet tall.

If the liquid is water, normal atmospheric pressure will support a column of water over 10 meters high, which is rather inconvenient for making (and reading) a barometer. Because mercury (Hg) is about 13.6-times denser than water, a mercury barometer only needs to be $\frac{1}{13.6}$ as tall as a water barometer—a more suitable size. Standard atmospheric pressure of 1 atm at sea level (101,325 Pa) corresponds to a column of mercury that is about 760 mm (29.92 in.) high. The torr was originally intended to be a unit equal to one millimeter of mercury, but it no longer corresponds exactly. The pressure exerted by a fluid due to gravity is known as hydrostatic pressure, p:

$$p = h\rho g \tag{2.2.5}$$

where

- h is the height of the fluid,
- ρ is the density of the fluid, and
- g is acceleration due to gravity.

Example 2.2.2: Calculation of Barometric Pressure

Show the calculation supporting the claim that atmospheric pressure near sea level corresponds to the pressure exerted by a column of mercury that is about 760 mm high. The density of mercury = $13.6\ g/cm^3$.

Solution

The hydrostatic pressure is given by Equation 2.2.5, with $h = 760\ mm$, $\rho = 13.6\ g/cm^3$, and $g = 9.81\ m/s^2$. Plugging these values into the Equation 2.2.5 and doing the necessary unit conversions will give us the value we seek. (Note: We are expecting to find a pressure of ~101,325 Pa:)

$$101,325\ N/\text{m}^2 = 101,325\ \frac{\text{kg}\cdot\text{m/s}^2}{\text{m}^2} = 101,325\ \frac{\text{kg}}{\text{m}\cdot\text{s}^2}$$

$$p = \left(760\ \text{mm} \times \frac{1\ \text{m}}{1000\ \text{mm}}\right) \times \left(\frac{13.6\ \text{g}}{1\ \text{cm}^3} \times \frac{1\ \text{kg}}{1000\ \text{g}} \times \frac{(100\ \text{cm})^3}{(1\ \text{m})^3}\right) \times \left(\frac{9.81\ \text{m}}{1\ \text{s}^2}\right)$$

$$= (0.760\ \text{m})(13,600\ \text{kg/m}^3)(9.81\ \text{m/s}^2) = 1.01 \times 10^5\ \text{kg/ms}^2 = 1.01 \times 10^5 N/\text{m}^2$$

$$= 1.01 \times 10^5\ \text{Pa}$$

Exercise 2.2.2

Calculate the height of a column of water at 25 °C that corresponds to normal atmospheric pressure. The density of water at this temperature is 1.0 g/cm^3.

Answer

10.3 m

A manometer is a device similar to a barometer that can be used to measure the pressure of a gas trapped in a container. A closed-end manometer is a U-shaped tube with one closed arm, one arm that connects to the gas to be measured, and a nonvolatile liquid (usually mercury) in between. As with a barometer, the distance between the liquid levels in the two arms of the tube (*h* in the diagram) is proportional to the pressure of the gas in the container. An open-end manometer (Figure 2.2.3) is the same as a closed-end manometer, but one of its arms is open to the atmosphere. In this case, the distance between the liquid levels corresponds to the difference in pressure between the gas in the container and the atmosphere.

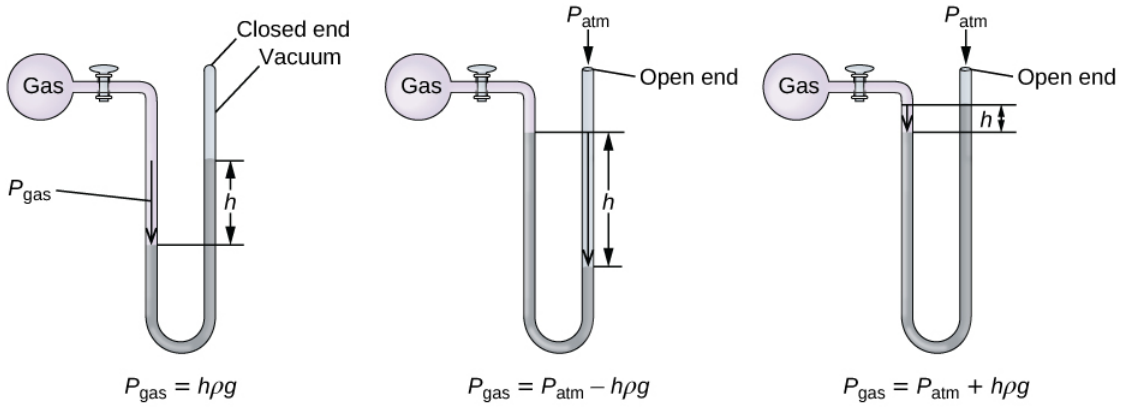
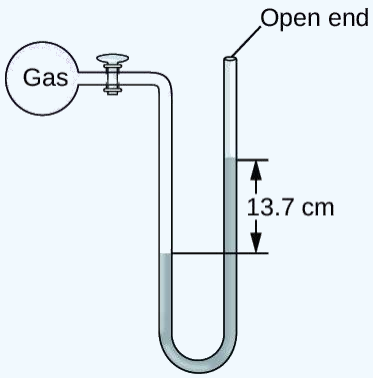


Figure 2.2.4: A manometer can be used to measure the pressure of a gas. The (difference in) height between the liquid levels (h) is a measure of the pressure. Mercury is usually used because of its large density.

Example 2.2.3: Calculation of Pressure Using an Open-End Manometer

The pressure of a sample of gas is measured at sea level with an open-end Hg (mercury) manometer, as shown below. Determine the pressure of the gas in:

a. mm Hg
b. atm
c. kPa



The height is the difference between the two levels of mercury on each side of the U tube and has a value of 13.7 centimeters. The level on the right side is higher than the left.

Solution

The pressure of the gas equals the hydrostatic pressure due to a column of mercury of height 13.7 cm plus the pressure of the atmosphere at sea level. (The pressure at the bottom horizontal line is equal on both sides of the tube. The pressure on the left is due to the gas and the pressure on the right is due to 13.7 cm of Hg plus atmospheric pressure.)

a. In mm Hg, this is: 137 mm Hg + 760 mm Hg = 897 mm Hg

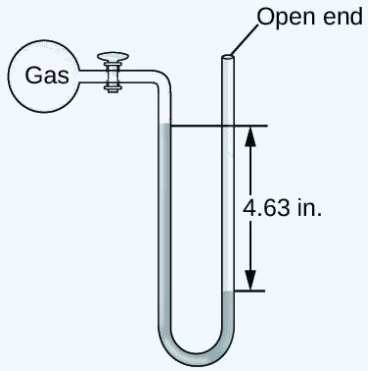
b. $897\ \cancel{\text{mmHg}} \times \dfrac{1\ \text{atm}}{760\ \cancel{\text{mmHg}}} = 1.18\ \text{atm}$

c. $1.18\ \cancel{\text{atm}} \times \dfrac{101.325\ \text{kPa}}{1\ \cancel{\text{atm}}} = 1.20 \times 10^2\ \text{kPa}$

Exercise 2.2.3

The pressure of a sample of gas is measured at sea level with an open-end Hg manometer, as shown below Determine the pressure of the gas in:

a. mm Hg
b. atm
c. kPa



The height is the difference between the two levels of mercury on each side of the U tube and has a value of 4.63 inches. The level on the left side is higher than the right.

Answer a

642 mm Hg

Answer b

0.845 atm

Answer c

85.6 kPa

Application: Measuring Blood Pressure

Blood pressure is measured using a device called a sphygmomanometer (Greek *sphygmos* = “pulse”). It consists of an inflatable cuff to restrict blood flow, a manometer to measure the pressure, and a method of determining when blood flow begins and when it becomes impeded (Figure 2.2.5). Since its invention in 1881, it has been an essential medical device. There are many types of sphygmomanometers: manual ones that require a stethoscope and are used by medical professionals; mercury ones, used when the most accuracy is required; less accurate mechanical ones; and digital ones that can be used with little training but that have limitations. When using a sphygmomanometer, the cuff is placed around the upper arm and inflated until blood flow is completely blocked, then slowly released. As the heart beats, blood forced through the arteries causes a rise in pressure. This rise in pressure at which blood flow begins is the *systolic pressure*—the peak pressure in the cardiac cycle. When the cuff’s pressure equals the arterial systolic pressure, blood flows past the cuff, creating audible sounds that can be heard using a stethoscope. This is followed by a decrease in pressure as the heart’s ventricles prepare for another beat. As cuff

pressure continues to decrease, eventually sound is no longer heard; this is the *diastolic pressure*—the lowest pressure (resting phase) in the cardiac cycle. Blood pressure units from a sphygmomanometer are in terms of millimeters of mercury (mm Hg).



Figure 2.2.5: (a) A medical technician prepares to measure a patient's blood pressure with a sphygmomanometer. (b) A typical sphygmomanometer uses a valved rubber bulb to inflate the cuff and a diaphragm gauge to measure pressure. (credit a: modification of work by Master Sgt. Jeffrey Allen)

2.2.1: Meteorology, Climatology, and Atmospheric Science

Throughout the ages, people have observed clouds, winds, and precipitation, trying to discern patterns and make predictions: when it is best to plant and harvest; whether it is safe to set out on a sea voyage; and much more. We now face complex weather and atmosphere-related challenges that will have a major impact on our civilization and the ecosystem. Several different scientific disciplines use chemical principles to help us better understand weather, the atmosphere, and climate. These are meteorology, climatology, and atmospheric science. Meteorology is the study of the atmosphere, atmospheric phenomena, and atmospheric effects on earth's weather. Meteorologists seek to understand and predict the weather in the short term, which can save lives and benefit the economy. Weather forecasts (Figure 2.2.6) are the result of thousands of measurements of air pressure, temperature, and the like, which are compiled, modeled, and analyzed in weather centers worldwide.

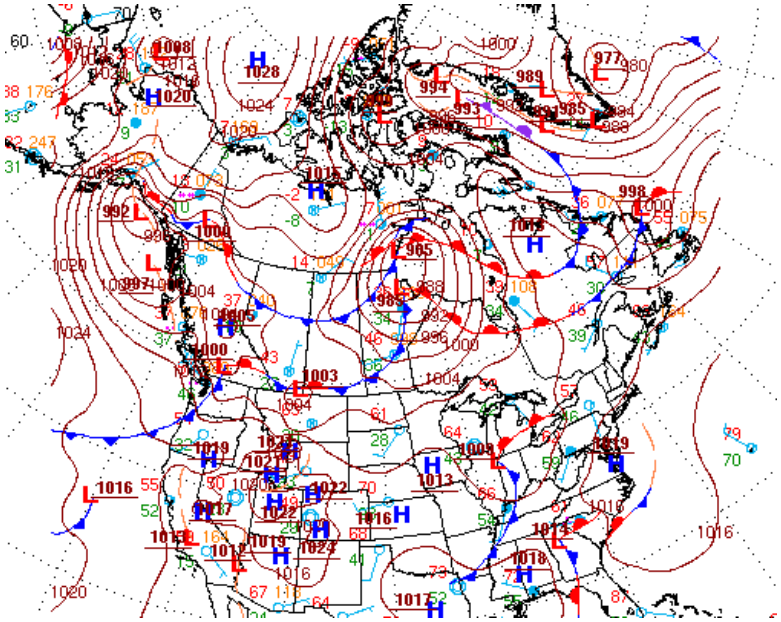


Figure 2.2.6: Meteorologists use weather maps to describe and predict weather. Regions of high (H) and low (L) pressure have large effects on weather conditions. The connected lines represent locations of constant pressure known as isobars. Pressure is in millibar. (credit: modification of work by National Oceanic and Atmospheric Administration, Oct. 31, 2022 data for North America)

In terms of weather, low-pressure systems occur when the earth's surface atmospheric pressure is lower than the surrounding environment: Moist air rises and condenses, producing clouds. Movement of moisture and air within various weather fronts instigates most weather events.

The atmosphere is the gaseous layer that surrounds a planet. Earth's atmosphere, which is roughly 100–125 km thick, consists of roughly 78.1% nitrogen and 21.0% oxygen, and can be subdivided further into the regions shown in Figure 2.2.7: the exosphere

(furthest from earth, > 700 km above sea level), the thermosphere (80–700 km), the mesosphere (50–80 km), the stratosphere (second lowest level of our atmosphere, 12–50 km above sea level), and the troposphere (up to 12 km above sea level, roughly 80% of the earth's atmosphere by mass and the layer where most weather events originate). As you go higher in the troposphere, air density and temperature both decrease.

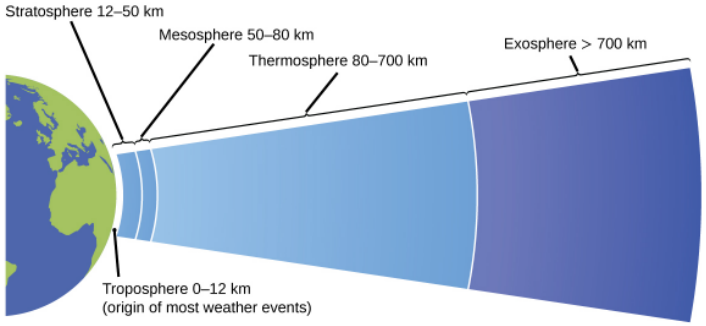


Figure 2.2.7: Earth's atmosphere has five layers: the troposphere, the stratosphere, the mesosphere, the thermosphere, and the exosphere.

The different layers of the atmosphere is illustrated as a cross sectional slice of the Earth's atmosphere. The different thickness of each layer is shown. The thermosphere has the largest portion, followed by the exosphere, stratosphere, mesosphere, and troposphere.

Climatology is the study of the climate, averaged weather conditions over long time periods, using atmospheric data. However, climatologists study patterns and effects that occur over decades, centuries, and millennia, rather than shorter time frames of hours, days, and weeks like meteorologists. Atmospheric science is an even broader field, combining meteorology, climatology, and other scientific disciplines that study the atmosphere.

Summary

Gases exert pressure, which is force per unit area. The pressure of a gas may be expressed in the SI unit of pascal or kilopascal, as well as in many other units including torr, atmosphere, and bar. Atmospheric pressure is measured using a barometer; other gas pressures can be measured using one of several types of manometers.

2.2.2: Key Equations

- $P = \frac{F}{A}$
- $p = h\rho g$

Glossary

atmosphere (atm)
unit of pressure; 1 atm = 101,325 Pa

bar
(bar or b) unit of pressure; 1 bar = 100,000 Pa

barometer
device used to measure atmospheric pressure

hydrostatic pressure
pressure exerted by a fluid due to gravity

manometer
device used to measure the pressure of a gas trapped in a container

pascal (Pa)
SI unit of pressure; 1 Pa = 1 N/m^2

pounds per square inch (psi)

unit of pressure common in the US

pressure

force exerted per unit area

torr

unit of pressure; $1\ \text{torr} = \frac{1}{760}\ \text{atm}$

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2.3: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law

Learning Objectives

- Identify the mathematical relationships between the various properties of gases
- Use the ideal gas law, and related gas laws, to compute the values of various gas properties under specified conditions

During the seventeenth and especially eighteenth centuries, driven both by a desire to understand nature and a quest to make balloons in which they could fly (Figure 2.3.1), a number of scientists established the relationships between the macroscopic physical properties of gases, that is, pressure, volume, temperature, and amount of gas. Although their measurements were not precise by today's standards, they were able to determine the mathematical relationships between pairs of these variables (e.g., pressure and temperature, pressure and volume) that hold for an *ideal* gas—a hypothetical construct that real gases approximate under certain conditions. Eventually, these individual laws were combined into a single equation—the *ideal gas law*—that relates gas quantities for gases and is quite accurate for low pressures and moderate temperatures. We will consider the key developments in individual relationships (for pedagogical reasons not quite in historical order), then put them together in the ideal gas law.



Figure 2.3.1: In 1783, the first (a) hydrogen-filled balloon flight, (b) manned hot air balloon flight, and (c) manned hydrogen-filled balloon flight occurred. When the hydrogen-filled balloon depicted in (a) landed, the frightened villagers of Gonesse reportedly destroyed it with pitchforks and knives. The launch of the latter was reportedly viewed by 400,000 people in Paris.

2.3.1: Pressure and Temperature: Amontons's Law

Imagine filling a rigid container attached to a pressure gauge with gas and then sealing the container so that no gas may escape. If the container is cooled, the gas inside likewise gets colder and its pressure is observed to decrease. Since the container is rigid and tightly sealed, both the volume and number of moles of gas remain constant. If we heat the sphere, the gas inside gets hotter (Figure 2.3.2) and the pressure increases.

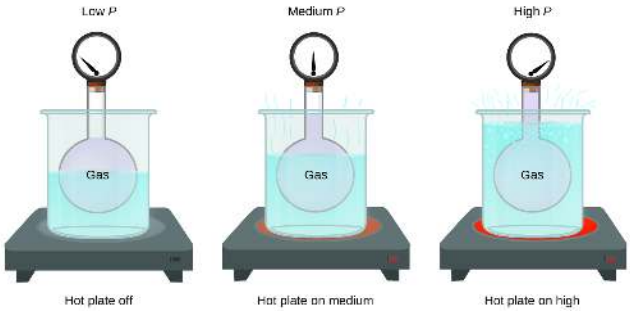


Figure 2.3.2: The effect of temperature on gas pressure: When the hot plate is off, the pressure of the gas in the sphere is relatively low. As the gas is heated, the pressure of the gas in the sphere increases.

This relationship between temperature and pressure is observed for any sample of gas confined to a constant volume. An example of experimental pressure-temperature data is shown for a sample of air under these conditions in Figure 2.3.3. We find that temperature and pressure are linearly related, and if the temperature is on the kelvin scale, then *P* and *T* are directly proportional (again, when *volume and moles of gas are held constant*); if the temperature on the kelvin scale increases by a certain factor, the gas pressure increases by the same factor.

Temperature (°C)	Temperature (K)	Pressure (kPa)
–150	173	36.0
–100	223	46.4
–50	273	56.7
0	323	67.1
50	373	77.5
100	423	88.0

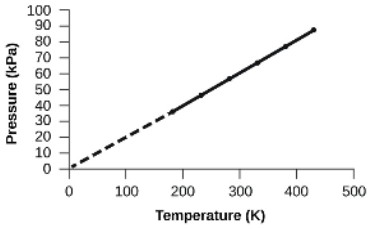


Figure 2.3.3: For a constant volume and amount of air, the pressure and temperature are directly proportional, provided the temperature is in kelvin. (Measurements cannot be made at lower temperatures because of the condensation of the gas.) When this line is extrapolated to lower pressures, it reaches a pressure of 0 at –273 °C, which is 0 on the kelvin scale and the lowest possible temperature, called absolute zero.

Guillaume Amontons was the first to empirically establish the relationship between the pressure and the temperature of a gas (~1700), and Joseph Louis Gay-Lussac determined the relationship more precisely (~1800). Because of this, the *P*-*T* relationship for gases is known as either Amontons's law or Gay-Lussac's law. Under either name, it states that *the pressure of a given amount of gas is directly proportional to its temperature on the kelvin scale when the volume is held constant.* Mathematically, this can be written:

$$P \propto T \text{ or } P = \text{constant} \times T \text{ or } P = k \times T$$

where ∝ means "is proportional to," and *k* is a proportionality constant that depends on the identity, amount, and volume of the gas.

For a confined, constant volume of gas, the ratio $\frac{P}{T}$ is therefore constant (i.e., $\frac{P}{T} = k$). If the gas is initially in "Condition 1" (with $P = P_1$ and $T = T_1$), and then changes to "Condition 2" (with $P = P_2$ and $T = T_2$), we have that $\frac{P_1}{T_1} = k$ and $\frac{P_2}{T_2} = k$, which reduces to $\frac{P_1}{T_1} = \frac{P_2}{T_2}$. This equation is useful for pressure-temperature calculations for a confined gas at constant volume. Note that temperatures must be on the kelvin scale for any gas law calculations (0 on the kelvin scale and the lowest possible temperature is called absolute zero). (Also note that there are at least three ways we can describe how the pressure of a gas changes as its temperature changes: We can use a table of values, a graph, or a mathematical equation.)

Example 2.3.1: Predicting Change in Pressure with Temperature

A can of hair spray is used until it is empty except for the propellant, isobutane gas.

a. On the can is the warning "Store only at temperatures below 120 °F (48.8 °C). Do not incinerate." Why?
b. The gas in the can is initially at 24 °C and 360 kPa, and the can has a volume of 350 mL. If the can is left in a car that reaches 50 °C on a hot day, what is the new pressure in the can?

Solution

a. The can contains an amount of isobutane gas at a constant volume, so if the temperature is increased by heating, the pressure will increase proportionately. High temperature could lead to high pressure, causing the can to burst. (Also, isobutane is combustible, so incineration could cause the can to explode.)
b. We are looking for a pressure change due to a temperature change at constant volume, so we will use Amontons's/Gay-Lussac's law. Taking P_1 and T_1 as the initial values, T_2 as the temperature where the pressure is unknown and P_2 as the unknown pressure, and converting °C to K, we have:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ which means that } \frac{360 \text{ kPa}}{297 \text{ K}} = \frac{P_2}{323 \text{ K}}$$

Rearranging and solving gives:

$$P_2 = \frac{360 \text{ kPa} \times 323 \cancel{\text{ K}}}{297 \cancel{\text{ K}}} = 390 \text{ kPa}$$

Exercise 2.3.1

A sample of nitrogen, N_2, occupies 45.0 mL at 27 °C and 600 torr. What pressure will it have if cooled to –73 °C while the volume remains constant?

Answer

400 torr

2.3.2: Volume and Temperature: Charles's Law

If we fill a balloon with air and seal it, the balloon contains a specific amount of air at atmospheric pressure, let's say 1 atm. If we put the balloon in a refrigerator, the gas inside gets cold and the balloon shrinks (although both the amount of gas and its pressure remain constant). If we make the balloon very cold, it will shrink a great deal, and it expands again when it warms up.



Video 2.3.1: This video shows how cooling and heating a gas causes its volume to decrease or increase, respectively.



Figure 2.3.4: When the amount of gas and the pressure are held constant, the volume increases when temperature is increased. (CC BY-SA-NC; anonymous).

These examples of the effect of temperature on the volume of a given amount of a confined gas at constant pressure are true in general: The volume increases as the temperature increases, and decreases as the temperature decreases. Volume-temperature data for a 1-mole sample of methane gas at 1 atm are listed and graphed in Figure 2.3.2.

Temperature (°C)	Temperature (K)	Volume (L)
−3	270	22
−23	250	21
−53	220	18
−162	111	9

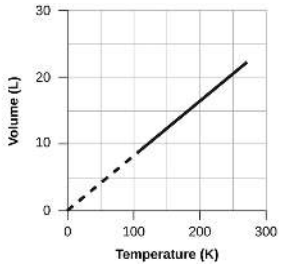


Figure 2.3.5: The volume and temperature are linearly related for 1 mole of methane gas at a constant pressure of 1 atm. If the temperature is in kelvin, volume and temperature are directly proportional. The line stops at 111 K because methane liquefies at this temperature; when extrapolated, it intersects the graph's origin, representing a temperature of absolute zero.

The relationship between the volume and temperature of a given amount of gas at constant pressure is known as Charles's law in recognition of the French scientist and balloon flight pioneer Jacques Alexandre César Charles. Charles's law states that *the volume of a given amount of gas is directly proportional to its temperature on the kelvin scale when the pressure is held constant*.

Mathematically, this can be written as:

$$V \alpha T \text{ or } V = \text{constant} \cdot T \text{ or } V = k \cdot T$$

with *k* being a proportionality constant that depends on the amount and pressure of the gas.

For a confined, constant pressure gas sample, $\frac{V}{T}$ is constant (i.e., the ratio = *k*), and as seen with the *P*-*T* relationship, this leads to another form of Charles's law: $\frac{V_1}{T_1} = \frac{V_2}{T_2}$.

Example 2.3.2: Predicting Change in Volume with Temperature

A sample of carbon dioxide, CO_2, occupies 0.300 L at 10 °C and 750 torr. What volume will the gas have at 30 °C and 750 torr?

Solution

Because we are looking for the volume change caused by a temperature change at constant pressure, this is a job for Charles's law. Taking V_1 and T_1 as the initial values, T_2 as the temperature at which the volume is unknown and V_2 as the unknown volume, and converting °C into K we have:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ which means that } \frac{0.300 \text{ L}}{283 \text{ K}} = \frac{V_2}{303 \text{ K}}$$

Rearranging and solving gives: $V_2 = \frac{0.300 \text{ L} \times 303 \cancel{\text{ K}}}{283 \cancel{\text{ K}}} = 0.321 \text{ L}$

This answer supports our expectation from Charles's law, namely, that raising the gas temperature (from 283 K to 303 K) at a constant pressure will yield an increase in its volume (from 0.300 L to 0.321 L).

Exercise 2.3.2

A sample of oxygen, O_2, occupies 32.2 mL at 30 °C and 452 torr. What volume will it occupy at –70 °C and the same pressure?

Answer

21.6 mL

Example 2.3.3: Measuring Temperature with a Volume

Change Temperature is sometimes measured with a gas thermometer by observing the change in the volume of the gas as the temperature changes at constant pressure. The hydrogen in a particular hydrogen gas thermometer has a volume of 150.0 cm^3 when immersed in a mixture of ice and water (0.00 °C). When immersed in boiling liquid ammonia, the volume of the hydrogen, at the same pressure, is 131.7 cm^3. Find the temperature of boiling ammonia on the kelvin and Celsius scales.

Solution

A volume change caused by a temperature change at constant pressure means we should use Charles's law. Taking V_1 and T_1 as the initial values, T_2 as the temperature at which the volume is unknown and V_2 as the unknown volume, and converting °C into K we have:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ which means that } \frac{150.0 \text{ cm}^3}{273.15 \text{ K}} = \frac{131.7 \text{ cm}^3}{T_2}$$

Rearrangement gives $T_2 = \frac{131.7 \cancel{\text{ cm}^3} \times 273.15 \text{ K}}{150.0 \text{ cm}^3} = 239.8 \text{ K}$

Subtracting 273.15 from 239.8 K, we find that the temperature of the boiling ammonia on the Celsius scale is –33.4 °C.

Exercise 2.3.3

What is the volume of a sample of ethane at 467 K and 1.1 atm if it occupies 405 mL at 298 K and 1.1 atm?

Answer

635 mL

2.3.2.0.1: Volume and Pressure: Boyle's Law

If we partially fill an airtight syringe with air, the syringe contains a specific amount of air at constant temperature, say 25 °C. If we slowly push in the plunger while keeping temperature constant, the gas in the syringe is compressed into a smaller volume and its pressure increases; if we pull out the plunger, the volume increases and the pressure decreases. This example of the effect of volume on the pressure of a given amount of a confined gas is true in general. Decreasing the volume of a contained gas will increase its pressure, and increasing its volume will decrease its pressure. In fact, if the volume increases by a certain factor, the pressure decreases by the same factor, and vice versa. Volume-pressure data for an air sample at room temperature are graphed in Figure 2.3.5.

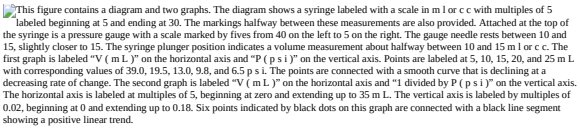


Figure 2.3.6: When a gas occupies a smaller volume, it exerts a higher pressure; when it occupies a larger volume, it exerts a lower pressure (assuming the amount of gas and the temperature do not change). Since P and V are inversely proportional, a graph of $\frac{1}{P}$ vs. V is linear.

Unlike the *P*-*T* and *V*-*T* relationships, pressure and volume are not directly proportional to each other. Instead, P and V exhibit inverse proportionality: Increasing the pressure results in a decrease of the volume of the gas. Mathematically this can be written:

$$P \propto \frac{1}{V}$$

or

$$P = k \cdot \frac{1}{V}$$

or

$$PV = k$$

or

$$P_1V_1 = P_2V_2$$

with k being a constant. Graphically, this relationship is shown by the straight line that results when plotting the inverse of the pressure $\left(\frac{1}{P}\right)$ versus the volume (V), or the inverse of volume $\left(\frac{1}{V}\right)$ versus the pressure (P). Graphs with curved lines are difficult to read accurately at low or high values of the variables, and they are more difficult to use in fitting theoretical equations and parameters to experimental data. For those reasons, scientists often try to find a way to "linearize" their data. If we plot *P* versus *V*, we obtain a hyperbola (Figure 2.3.6).

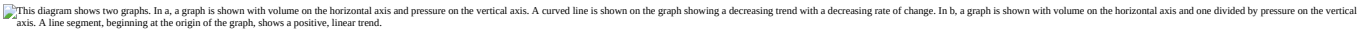


Figure 2.3.7: The relationship between pressure and volume is inversely proportional. (a) The graph of P vs. V is a hyperbola, whereas (b) the graph of $\left(\frac{1}{P}\right)$ vs. V is linear.

The relationship between the volume and pressure of a given amount of gas at constant temperature was first published by the English natural philosopher Robert Boyle over 300 years ago. It is summarized in the statement now known as **Boyle's law**: *The volume of a given amount of gas held at constant temperature is inversely proportional to the pressure under which it is measured.*

Example 2.3.4: Volume of a Gas Sample

The sample of gas has a volume of 15.0 mL at a pressure of 13.0 psi. Determine the pressure of the gas at a volume of 7.5 mL, using:

a. the *P*-*V* graph in Figure 2.3.6*a*
b. the $\frac{1}{P}$ vs. *V* graph in Figure 2.3.6*b*
c. the Boyle's law equation

Comment on the likely accuracy of each method.

Solution

a. Estimating from the *P*-*V* graph gives a value for *P* somewhere around 27 psi.
b. Estimating from the $\frac{1}{P}$ versus *V* graph give a value of about 26 psi.
c. From Boyle's law, we know that the product of pressure and volume (*PV*) for a given sample of gas at a constant temperature is always equal to the same value. Therefore we have $P_1V_1 = k$ and $P_2V_2 = k$ which means that $P_1V_1 = P_2V_2$.

Using P_1 and V_1 as the known values 13.0 psi and 15.0 mL, P_2 as the pressure at which the volume is unknown, and V_2 as the unknown volume, we have:

$$P_1V_1 = P_2V_2 \text{ or } 13.0 \text{ psi} \times 15.0 \text{ mL} = P_2 \times 7.5 \text{ mL}$$

Solving:

$$P_2 = \frac{13.0 \text{ psi} \times 15.0 \cancel{\text{mL}}}{7.5 \cancel{\text{mL}}} = 26 \text{ psi}$$

It was more difficult to estimate well from the *P*-*V* graph, so (a) is likely more inaccurate than (b) or (c). The calculation will be as accurate as the equation and measurements allow.

? Exercise 2.3.4

The sample of gas has a volume of 30.0 mL at a pressure of 6.5 psi. Determine the volume of the gas at a pressure of 11.0 psi, using:

a. the *P*-*V* graph in Figure 2.3.6*a*
b. the $\frac{1}{P}$ vs. *V* graph in Figure 2.3.6*b*
c. the Boyle's law equation

Comment on the likely accuracy of each method.

Answer a

about 17–18 mL

Answer b

~18 mL

Answer c

17.7 mL; it was more difficult to estimate well from the *P*-*V* graph, so (a) is likely more inaccurate than (b); the calculation will be as accurate as the equation and measurements allow

Breathing and Boyle's Law

What do you do about 20 times per minute for your whole life, without break, and often without even being aware of it? The answer, of course, is respiration, or breathing. How does it work? It turns out that the gas laws apply here. Your lungs take in gas that your body needs (oxygen) and get rid of waste gas (carbon dioxide). Lungs are made of spongy, stretchy tissue that expands and contracts while you breathe. When you inhale, your diaphragm and intercostal muscles (the muscles between your ribs) contract, expanding your chest cavity and making your lung volume larger. The increase in volume leads to a decrease in pressure (Boyle's law). This causes air to flow into the lungs (from high pressure to low pressure). When you exhale, the process reverses: Your diaphragm and rib muscles relax, your chest cavity contracts, and your lung volume decreases, causing the pressure to increase (Boyle's law again), and air flows out of the lungs (from high pressure to low pressure). You then breathe in and out again, and again, repeating this Boyle's law cycle for the rest of your life (Figure 2.3.7).

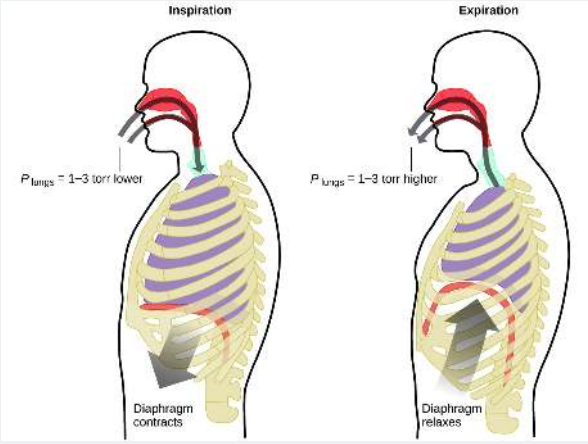


Figure 2.3.8: Breathing occurs because expanding and contracting lung volume creates small pressure differences between your lungs and your surroundings, causing air to be drawn into and forced out of your lungs.

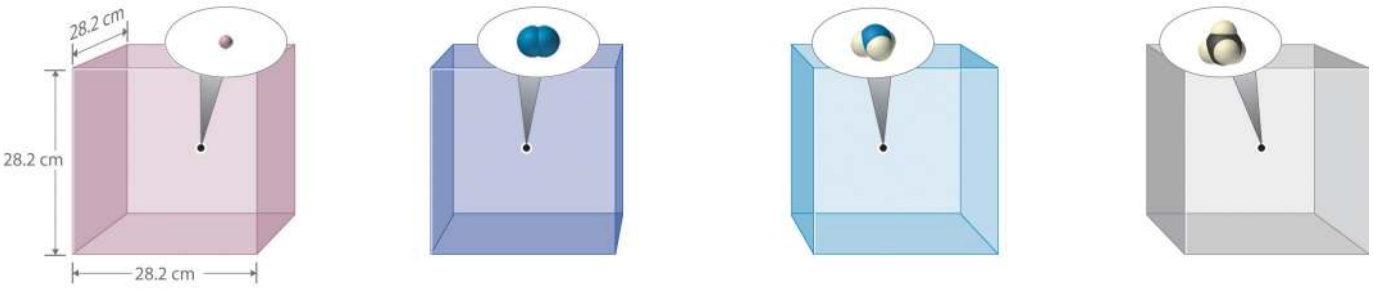
2.3.3: Moles of Gas and Volume: Avogadro's Law

The Italian scientist Amedeo Avogadro advanced a hypothesis in 1811 to account for the behavior of gases, stating that equal volumes of all gases, measured under the same conditions of temperature and pressure, contain the same number of molecules. Over time, this relationship was supported by many experimental observations as expressed by Avogadro's law: *For a confined gas, the volume (V) and number of moles (n) are directly proportional if the pressure and temperature both remain constant.*

In equation form, this is written as:

$$V \propto n \text{ or } V = k \times n \text{ or } \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Mathematical relationships can also be determined for the other variable pairs, such as *P* versus *n*, and *n* versus *T*.



He
V = 22.4 L
P = 1 atm
T = 0°C
Mass: 4.003 g/mol
n = 1 mol

N_2
V = 22.4 L
P = 1 atm
T = 0°C
Mass: 28.013 g/mol
n = 1 mol

NH_3
V = 22.4 L
P = 1 atm
T = 0°C
Mass: 17.031 g/mol
n = 1 mol

CH_4
V = 22.4 L
P = 1 atm
T = 0°C
Mass: 16.043 g/mol
n = 1 mol

Figure 2.3.9: Avogadro's Hypothesis. Equal volumes of four different gases at the same temperature and pressure contain the same number of gaseous particles. Because the molar mass of each gas is different, the *mass* of each gas sample is different even though all contain 1 mol of gas (CC BY-SA-NC; anonymous).

> *Visit this interactive PhET simulation to investigate the relationships between pressure, volume, temperature, and amount of gas. Use the simulation to examine the effect of changing one parameter on another while holding the other parameters constant (as described in the preceding sections on the various gas laws).*

2.3.4: The Ideal Gas Law

To this point, four separate laws have been discussed that relate pressure, volume, temperature, and the number of moles of the gas:

- Boyle's law: PV = constant at constant T and n
- Amontons's law: $\frac{P}{T}$ = constant at constant V and n
- Charles's law: $\frac{V}{T}$ = constant at constant P and n
- Avogadro's law: $\frac{V}{n}$ = constant at constant P and T

Combining these four laws yields the ideal gas law, a relation between the pressure, volume, temperature, and number of moles of a gas:

$$PV = nRT$$

where P is the pressure of a gas, V is its volume, n is the number of moles of the gas, T is its temperature on the kelvin scale, and R is a constant called the ideal gas constant or the universal gas constant. The units used to express pressure, volume, and temperature will determine the proper form of the gas constant as required by dimensional analysis, the most commonly encountered values being 0.08206 L atm mol^{-1} K^{-1} and 8.3145 kPa L mol^{-1} K^{-1}.

> *The ideal gas law is easy to remember and apply in solving problems, as long as you use the **proper values** and units for the gas constant, R. You can always obtain the ideal gas law from the units of R, and rearrange it to give the reaationship you need.*

Gases whose properties of P, V, and T are accurately described by the ideal gas law (or the other gas laws) are said to exhibit *ideal behavior* or to approximate the traits of an ideal gas. An ideal gas is a hypothetical construct that may be used along with *kinetic molecular theory* to effectively explain the gas laws as will be described in a later module of this chapter. Although all the calculations presented in this module assume ideal behavior, this assumption is only reasonable for gases under conditions of relatively low pressure and high temperature. In the final module of this chapter, a modified gas law will be introduced that accounts for the *non-ideal* behavior observed for many gases at relatively high pressures and low temperatures.

The ideal gas equation contains five terms, the gas constant R and the variable properties P, V, n, and T. Specifying any four of these terms will permit use of the ideal gas law to calculate the fifth term as demonstrated in the following example exercises.

Example 2.3.5: Using the Ideal Gas Law

Methane, CH_4, is being considered for use as an alternative automotive fuel to replace gasoline. One gallon of gasoline could be replaced by 655 g of CH_4. What is the volume of this much methane at 25 °C and 745 torr?

Solution

Exercise 2.3.5

Calculate the pressure in bar of 2520 moles of hydrogen gas stored at 27 °C in the 180-L storage tank of a modern hydrogen-powered car.

Answer

350 bar

If the number of moles of an ideal gas are kept constant under two different sets of conditions, a useful mathematical relationship called the combined gas law is obtained: $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ using units of atm, L, and K. Both sets of conditions are equal to the product of $n \times R$ (where n = the number of moles of the gas and R is the ideal gas law constant).

Example 2.3.6: Using the Combined Gas Law

When filled with air, a typical scuba tank with a volume of 13.2 L has a pressure of 153 atm (Figure 2.3.8). If the water temperature is 27 °C, how many liters of air will such a tank provide to a diver's lungs at a depth of approximately 70 feet in the ocean where the pressure is 3.13 atm?



Figure 2.3.10: Scuba divers use compressed air to breathe while underwater. (credit: modification of work by Mark Goodchild)
This photograph shows a scuba diver underwater with a tank on his or her back and bubbles ascending from the breathing apparatus.

Letting *1* represent the air in the scuba tank and *2* represent the air in the lungs, and noting that body temperature (the temperature the air will be in the lungs) is 37 °C, we have:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \longrightarrow \frac{(153\ \text{atm})(13.2\ \text{L})}{(300\ \text{K})} = \frac{(3.13\ \text{atm})(V_2)}{(310\ \text{K})}$$

Solving for V_2:

$$V_2 = \frac{(153\ \cancel{\text{atm}})(13.2\ \text{L})(310\ \cancel{\text{K}})}{(300\ \cancel{\text{K}})(3.13\ \cancel{\text{atm}})} = 667\ \text{L}$$

(Note: Be advised that this particular example is one in which the assumption of ideal gas behavior is not very reasonable, since it involves gases at relatively high pressures and low temperatures. Despite this limitation, the calculated volume can be viewed as a good "ballpark" estimate.)

Exercise 2.3.6

A sample of ammonia is found to occupy 0.250 L under laboratory conditions of 27 °C and 0.850 atm. Find the volume of this sample at 0 °C and 1.00 atm.

Answer

0.193 L

The Interdependence between Ocean Depth and Pressure in Scuba Diving

Whether scuba diving at the Great Barrier Reef in Australia (shown in Figure 2.3.9) or in the Caribbean, divers must understand how pressure affects a number of issues related to their comfort and safety.



Figure 2.3.11: Scuba divers, whether at the Great Barrier Reef or in the Caribbean, must be aware of buoyancy, pressure equalization, and the amount of time they spend underwater, to avoid the risks associated with pressurized gases in the body. (credit: Kyle Taylor).

Pressure increases with ocean depth, and the pressure changes most rapidly as divers reach the surface. The pressure a diver experiences is the sum of all pressures above the diver (from the water and the air). Most pressure measurements are given in units of atmospheres, expressed as "atmospheres absolute" or ATA in the diving community: Every 33 feet of salt water represents 1 ATA of pressure in addition to 1 ATA of pressure from the atmosphere at sea level. As a diver descends, the increase in pressure causes the body's air pockets in the ears and lungs to compress; on the ascent, the decrease in pressure causes these air pockets to expand, potentially rupturing eardrums or bursting the lungs. Divers must therefore undergo equalization by adding air to body airspaces on the descent by breathing normally and adding air to the mask by breathing out of the nose or adding air to the ears and sinuses by equalization techniques; the corollary is also true on ascent, divers must release air from the body to maintain equalization. Buoyancy, or the ability to control whether a diver sinks or floats, is controlled by the buoyancy compensator (BCD). If a diver is ascending, the air in his BCD expands because of lower pressure according to Boyle's law (decreasing the pressure of gases increases the volume). The expanding air increases the buoyancy of the diver, and she or he begins to ascend. The diver must vent air from the BCD or risk an uncontrolled ascent that could rupture the lungs. In descending, the increased pressure causes the air in the BCD to compress and the diver sinks much more quickly; the diver must add air to the BCD or risk an uncontrolled descent, facing much higher pressures near the ocean floor. The pressure also impacts how long a diver can stay underwater before ascending. The deeper a diver dives, the more compressed the air that is breathed because of increased pressure: If a diver dives 33 feet, the pressure is 2 ATA and the air would be compressed to one-half of its original volume. The diver uses up available air twice as fast as at the surface.

2.3.5: Standard Conditions of Temperature and Pressure

We have seen that the volume of a given quantity of gas and the number of molecules (moles) in a given volume of gas vary with changes in pressure and temperature. Chemists sometimes make comparisons against a standard temperature and pressure (STP) for reporting properties of gases. STP is cuurently defined as 273.15 K (0.00 °C) and 1 bar (100 kPa). At STP, one mole of an ideal gas has a volume of about 22.7 L, which is referred to as the standard molar volume. Chemists often work at 1 atm pressure which was used in an older definition of STP, where one mole of any ideal gas gas has a volume of about 22.4 L. Standard ambient temperature is often used as 25 ^{o}C (298.15K). The same amount of any ideal gas at the same temperature and pressure conditions will have the same volume (Figure 2.3.12).

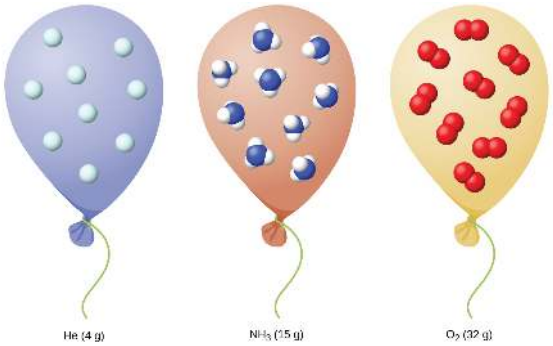


Figure 2.3.12: Each of these balloons contains one mole of a different ideal gas at the same conditions of temperature and pressure, so the balloons have the same volume.

Summary

The behavior of gases can be described by several laws based on experimental observations of their properties. The pressure of a given amount of gas is directly proportional to its absolute temperature, provided that the volume does not change (Amontons's law). The volume of a given gas sample is directly proportional to its absolute temperature at constant pressure (Charles's law). The volume of a given amount of gas is inversely proportional to its pressure when temperature is held constant (Boyle's law). Under the same conditions of temperature and pressure, equal volumes of all gases contain the same number of molecules (Avogadro's law).

The equations describing these laws are special cases of the ideal gas law, $PV = nRT$, where P is the pressure of the gas, V is its volume, n is the number of moles of the gas, T is its kelvin temperature, and R is the ideal (universal) gas constant.

2.3.6: Key Equations

- $PV = nRT$

Summary

absolute zero

temperature at which the volume of a gas would be zero according to Charles's law.

Amontons's law

(also, Gay-Lussac's law) pressure of a given number of moles of gas is directly proportional to its kelvin temperature when the volume is held constant

Avogadro's law
volume of a gas at constant temperature and pressure is proportional to the number of gas molecules

Boyle's law
volume of a given number of moles of gas held at constant temperature is inversely proportional to the pressure under which it is measured

Charles's law
volume of a given number of moles of gas is directly proportional to its kelvin temperature when the pressure is held constant

ideal gas
hypothetical gas whose physical properties are perfectly described by the gas laws

ideal gas constant (*R*)
constant derived from the ideal gas equation $R = 0.08226$ L atm mol^{-1} K^{-1} or 8.314 L kPa mol^{-1} K^{-1}

ideal gas law
relation between the pressure, volume, amount, and temperature of a gas under conditions derived by combination of the simple gas laws

standard conditions of temperature and pressure (STP)
273.15 K (0 °C) and 1 bar (100 kPa)

standard molar volume
volume of 1 mole of gas at STP, approximately 22.7 L for gases behaving ideally

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2.4: Stoichiometry of Gaseous Substances, Mixtures, and Reactions

Learning Objectives

- Use the ideal gas law to compute gas densities and molar masses
- Perform stoichiometric calculations involving gaseous substances
- State Dalton's law of partial pressures and use it in calculations involving gaseous mixtures

The study of the chemical behavior of gases was part of the basis of perhaps the most fundamental chemical revolution in history. French nobleman Antoine Lavoisier, widely regarded as the "father of modern chemistry," changed chemistry from a qualitative to a quantitative science through his work with gases. He discovered the law of conservation of matter, discovered the role of oxygen in combustion reactions, determined the composition of air, explained respiration in terms of chemical reactions, and more. He was a casualty of the French Revolution, guillotined in 1794. Of his death, mathematician and astronomer Joseph-Louis Lagrange said, "It took the mob only a moment to remove his head; a century will not suffice to reproduce it."

As described in an earlier chapter of this text, we can turn to chemical stoichiometry for answers to many of the questions that ask "How much?" We can answer the question with masses of substances or volumes of solutions. However, we can also answer this question another way: with volumes of gases. We can use the ideal gas equation to relate the pressure, volume, temperature, and number of moles of a gas. Here we will combine the ideal gas equation with other equations to find gas density and molar mass. We will deal with mixtures of different gases, and calculate amounts of substances in reactions involving gases. This section will not introduce any new material or ideas, but will provide examples of applications and ways to integrate concepts we have already discussed.

2.4.1: Density of a Gas

Recall that the density of a gas is its mass to volume ratio, $\rho = \frac{m}{V}$. Therefore, if we can determine the mass of some volume of a gas, we will get its density. The density of an unknown gas can used to determine its molar mass and thereby assist in its identification. The ideal gas law, *PV* = *nRT*, provides us with a means of deriving such a mathematical formula to relate the density of a gas to its volume in the proof shown in Example 2.4.1.

Example 2.4.1: Derivation of a Density Formula from the Ideal Gas Law

Use *PV* = *nRT* to derive a formula for the density of gas in g/L

Solution

$$PV = nRT$$

Rearrange to get (mol/L):

$$\frac{n}{v} = \frac{P}{RT}$$

Multiply each side of the equation by the molar mass, $\mathcal{M}$. When moles are multiplied by $\mathcal{M}$ in g/mol, g are obtained:

$$(\mathcal{M})\left(\frac{n}{V}\right) = \left(\frac{P}{RT}\right)(\mathcal{M})$$

$$\mathcal{M}/V = \rho = \frac{P\mathcal{M}}{RT}$$

Exercise 2.4.1

A gas was found to have a density of 0.0847 g/L at 17.0 °C and a pressure of 760 torr. What is its molar mass? What is the gas?

Answer

$$\rho = \frac{P\mathcal{M}}{RT}$$

$$0.0847\ \text{g/L} = 760\ \cancel{\text{torr}} \times \frac{1\ \cancel{\text{atm}}}{760\ \cancel{\text{torr}}} \times \frac{\mathcal{M}}{0.0821\ \text{L}\ \cancel{\text{atm}}/\text{mol K}} \times 290\ \text{K}$$

$\mathcal{M}$ = 2.02 g/mol; therefore, the gas must be hydrogen (H_2, 2.02 g/mol)

We must specify both the temperature and the pressure of a gas when calculating its density because the number of moles of a gas (and thus the mass of the gas) in a liter changes with temperature or pressure. Gas densities are often reported at STP.

Example 2.4.2: Empirical/Molecular Formula Problems

Using the Ideal Gas Law and Density of a Gas Cyclopropane, a gas once used with oxygen as a general anesthetic, is composed of 85.7% carbon and 14.3% hydrogen by mass. Find the empirical formula. If 1.56 g of cyclopropane occupies a volume of 1.00 L at 0.984 atm and 50 °C, what is the molecular formula for cyclopropane?

Solution

Strategy:

First solve the empirical formula problem using methods discussed earlier. Assume 100 g and convert the percentage of each element into grams. Determine the number of moles of carbon and hydrogen in the 100-g sample of cyclopropane. Divide by the smallest number of moles to relate the number of moles of carbon to the number of moles of hydrogen. In the last step, realize that the smallest whole number ratio is the empirical formula:

$$85.7\ \text{g C} \times \frac{1\ \text{mol C}}{12.01\ \text{g C}} = 7.136\ \text{mol C} \qquad \frac{7.136}{7.136} = 1.00\ \text{mol C}$$

$$14.3\ \text{g H} \times \frac{1\ \text{mol H}}{1.01\ \text{g H}} = 14.158\ \text{mol H} \qquad \frac{14.158}{7.136} = 1.98\ \text{mol H}$$

Empirical formula is CH_2 [empirical mass (EM) of 14.03 g/empirical unit].

Next, use the density equation related to the ideal gas law to determine the molar mass:

$$d = \frac{P\mathcal{M}}{RT} \qquad \frac{1.56\ \text{g}}{1.00\ \text{L}} = 0.984\ \text{atm} \times \frac{\mathcal{M}}{0.0821\ \text{L atm/mol K}} \times 323\ \text{K}$$

$\mathcal{M}$ = 42.0 g/mol, $\frac{\mathcal{M}}{E\mathcal{M}} = \frac{42.0}{14.03} = 2.99$, so (3)($CH_2$) = C_3H_6 (molecular formula)

Exercise 2.4.2

Acetylene, a fuel used welding torches, is comprised of 92.3% C and 7.7% H by mass. Find the empirical formula. If 1.10 g of acetylene occupies of volume of 1.00 L at 1.15 atm and 59.5 °C, what is the molecular formula for acetylene?

Answer

Empirical formula, CH; Molecular formula, C_2H_2

2.4.2: Molar Mass of a Gas

Another useful application of the ideal gas law involves the determination of molar mass. By definition, the molar mass of a substance is the ratio of its mass in grams, *m*, to its amount in moles, *n*:

$$\mathcal{M} = \frac{\text{grams of substance}}{\text{moles of substance}} = \frac{m}{n}$$

The ideal gas equation can be rearranged to isolate n:

$$n = \frac{PV}{RT}$$

and then combined with the molar mass equation to yield:

$$\mathcal{M} = \frac{mRT}{PV}$$

This equation can be used to derive the molar mass of a gas from measurements of its pressure, volume, temperature, and mass.

Example 2.4.3: Determining the Molar Mass of a Volatile Liquid

The approximate molar mass of a volatile liquid can be determined by:

1. Heating a sample of the liquid in a flask with a tiny hole at the top, which converts the liquid into gas that may escape through the hole
2. Removing the flask from heat at the instant when the last bit of liquid becomes gas, at which time the flask will be filled with only gaseous sample at ambient pressure
3. Sealing the flask and permitting the gaseous sample to condense to liquid, and then weighing the flask to determine the sample's mass (Figure 2.4.1)

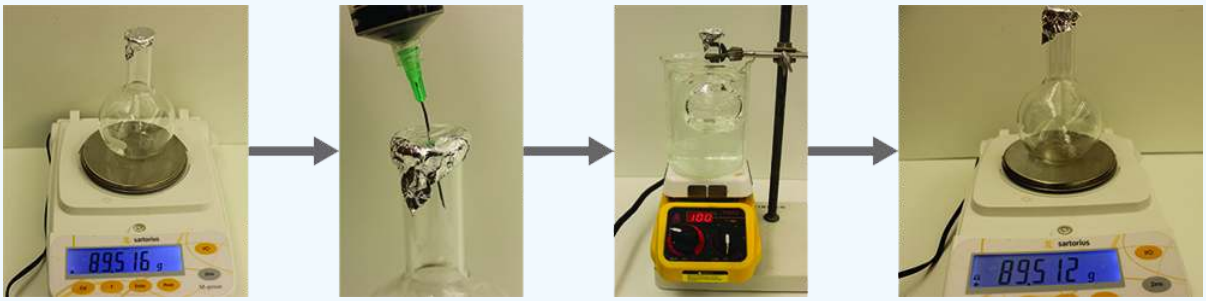


Figure 2.4.1: When the volatile liquid in the flask is heated past its boiling point, it becomes gas and drives air out of the flask. At $t_{l \longrightarrow g}$, *the flask is filled with volatile liquid gas at the same pressure as the atmosphere. If the flask is then cooled to room temperature, the gas condenses and the mass of the gas that filled the flask, and is now liquid, can be measured. (credit: modification of work by Mark Ott)*

Using this procedure, a sample of chloroform gas weighing 0.494 g is collected in a flask with a volume of 129 cm^3 at 99.6 °C when the atmospheric pressure is 742.1 mm Hg. What is the approximate molar mass of chloroform?

Solution

Since

$$\mathcal{M} = \frac{m}{n}$$

and

$$n = \frac{PV}{RT}$$

substituting and rearranging gives

$$\mathcal{M} = \frac{mRT}{PV}$$

then

$$\mathcal{M} = \frac{mRT}{PV} = \frac{(0.494\ \text{g}) \times 0.08206\ \text{L} \cdot \text{atm/mol K} \times 372.8\ \text{K}}{0.976\ \text{atm} \times 0.129\ \text{L}} = 120\ \text{g/mol}$$

Exercise 2.4.3

A sample of phosphorus that weighs 3.243×10^{-2} g exerts a pressure of 31.89 kPa in a 56.0-mL bulb at 550 °C. What are the molar mass and molecular formula of phosphorus vapor?

Answer

124 g/mol P_4

2.4.3: The Pressure of a Mixture of Gases: Dalton's Law

Unless they chemically react with each other, the individual gases in a mixture of gases do not affect each other's pressure. Each individual gas in a mixture exerts the same pressure that it would exert if it were present alone in the container (Figure 2.4.2). The pressure exerted by each individual gas in a mixture is called its partial pressure. This observation is summarized by Dalton's law of partial pressures: *The total pressure of a mixture of ideal gases is equal to the sum of the partial pressures of the component gases*:

$$P_{Total} = P_A + P_B + P_C + \ldots = \sum_i P_i$$

In the equation P_{Total} is the total pressure of a mixture of gases, P_A is the partial pressure of gas A; P_B is the partial pressure of gas B; P_C is the partial pressure of gas C; and so on.

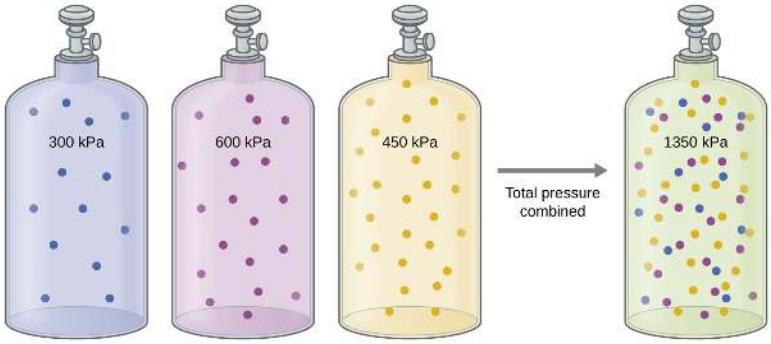


Figure 2.4.2: If equal-volume cylinders containing gas A at a pressure of 300 kPa, gas B at a pressure of 600 kPa, and gas C at a pressure of 450 kPa are all combined in the same-size cylinder, the total pressure of the mixture is 1350 kPa.

The partial pressure of gas A is related to the total pressure of the gas mixture via its mole fraction (X), a unit of concentration defined as the number of moles of a component of a solution divided by the total number of moles of all components:

$$P_A = X_A \times P_{Total} \quad \text{where} \quad X_A = \frac{n_A}{n_{Total}}$$

where P_A, X_A, and n_A are the partial pressure, mole fraction, and number of moles of gas A, respectively, and n_{Total} is the number of moles of all components in the mixture.

Example 2.4.2: The Pressure of a Mixture of Gases

A 10.0-L vessel contains 2.50×10^{-3} mol of H_2, 1.00×10^{-3} mol of He, and 3.00×10^{-4} mol of Ne at 35 °C.

a. What are the partial pressures of each of the gases?
b. What is the total pressure in atmospheres?

Solution

The gases behave independently, so the partial pressure of each gas can be determined from the ideal gas equation, using $P = \frac{nRT}{V}$:

$$P_{H_2} = \frac{(2.50 \times 10^{-3}\ \text{mol})(0.08206\ \cancel{\text{L}}\cancel{\text{atm mol}^{-1}\ \text{K}^{-1}})(308\ \cancel{\text{K}})}{10.0\ \cancel{\text{L}}} = 6.32 \times 10^{-3}\ \text{atm}$$

$$P_{He} = \frac{(1.00 \times 10^{-3}\ \cancel{\text{mol}})(0.08206\ \cancel{\text{L}}\cancel{\text{atm mol}^{-1}\ \text{K}^{-1}})(308\ \cancel{\text{K}})}{10.0\ \cancel{\text{L}}} = 2.53 \times 10^{-3}\ \text{atm}$$

$$P_{Ne} = \frac{(3.00 \times 10^{-4}\ \cancel{\text{mol}})(0.08206\ \cancel{\text{L}}\cancel{\text{atm mol}^{-1}\ \text{K}^{-1}})(308\ \cancel{\text{K}})}{10.0\ \cancel{\text{L}}} = 7.58 \times 10^{-4}\ \text{atm}$$

The total pressure is given by the sum of the partial pressures:

$$P_T = P_{H_2} + P_{He} + P_{Ne} = (0.00632 + 0.00253 + 0.00076)\ \text{atm} = 9.61 \times 10^{-3}\ \text{atm}$$

Exercise 2.4.2

A 5.73-L flask at 25 °C contains 0.0388 mol of N_2, 0.147 mol of CO, and 0.0803 mol of H_2. What is the total pressure in the flask in atmospheres?

Answer

1.137 atm

Here is another example of this concept, but dealing with mole fraction calculations.

Example 2.4.3: The Pressure of a Mixture of Gases

A gas mixture used for anesthesia contains 2.83 mol oxygen, O_2, and 8.41 mol nitrous oxide, N_2O. The total pressure of the mixture is 192 kPa.

a. What are the mole fractions of O_2 and N_2O?
b. What are the partial pressures of O_2 and N_2O?

Solution

The mole fraction is given by

$$X_A = \frac{n_A}{n_{Total}}$$

and the partial pressure is

$$P_A = X_A \times P_{Total}$$

For O_2,

$$X_{O_2} = \frac{n_{O_2}}{n_{Total}} = \frac{2.83\text{mol}}{(2.83 + 8.41)\ \text{mol}} = 0.252$$

and

$$P_{O_2} = X_{O_2} \times P_{Total} = 0.252 \times 192\ \text{kPa} = 48.4\ \text{kPa}$$

For N_2O,

$$X_{N_2O} = \frac{n_{N_2O}}{n_{Total}} = \frac{8.41\ \text{mol}}{(2.83 + 8.41)\ \text{mol}} = 0.748$$

and

$$P_{N_2O} = X_{N_2O} \times P_{Total} = (0.748) \times 192\ \text{kPa} = 143.6\ \text{kPa}$$

Exercise 2.4.3

What is the pressure of a mixture of 0.200 g of H_2, 1.00 g of N_2, and 0.820 g of Ar in a container with a volume of 2.00 L at 20 °C?

Answer

1.87 atm

2.4.3.1: Collection of Gases over Water

A simple way to collect gases that do not react with water is to capture them in a bottle that has been filled with water and inverted into a dish filled with water. The pressure of the gas inside the bottle can be made equal to the air pressure outside by raising or lowering the bottle. When the water level is the same both inside and outside the bottle (Figure 2.4.3), the pressure of the gas is equal to the atmospheric pressure, which can be measured with a barometer.

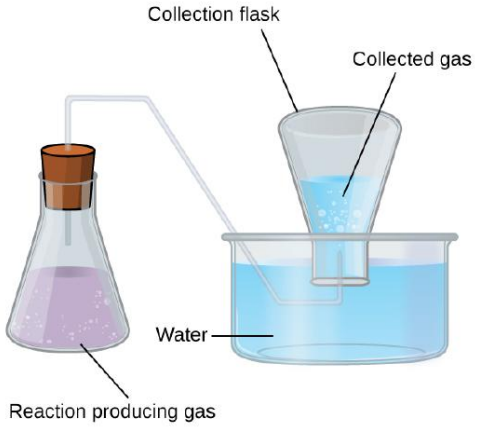


Figure 2.4.3: When a reaction produces a gas that is collected above water, the trapped gas is a mixture of the gas produced by the reaction and water vapor. If the collection flask is appropriately positioned to equalize the water levels both within and outside the flask, the pressure of the trapped gas mixture will equal the atmospheric pressure outside the flask (see the earlier discussion of manometers).

However, there is another factor we must consider when we measure the pressure of the gas by this method. Water evaporates and there is always gaseous water (water vapor) above a sample of liquid water. As a gas is collected over water, it becomes saturated with water vapor and the total pressure of the mixture equals the partial pressure of the gas plus the partial pressure of the water vapor. The pressure of the pure gas is therefore equal to the total pressure minus the pressure of the water vapor—this is referred to as the “dry” gas pressure, that is, the pressure of the gas only, without water vapor.

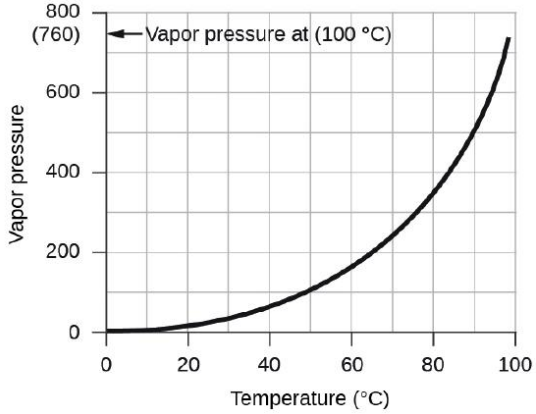


Figure 2.4.4: This graph shows the vapor pressure of water at sea level as a function of temperature.

The vapor pressure of water, which is the pressure exerted by water vapor in equilibrium with liquid water in a closed container, depends on the temperature (Figure 2.4.4); more detailed information on the temperature dependence of water vapor can be found in Table 2.4.1, and vapor pressure will be discussed in more detail in the next chapter on liquids.

Table 2.4.1: *Vapor Pressure of Ice and Water in Various Temperatures at Sea Level*

Temperature (°C)	Pressure (torr)		Temperature (°C)	Pressure (torr)		Temperature (°C)	Pressure (torr)
–10	1.95		18	15.5		30	31.8

Temperature (°C)	Pressure (torr)	Temperature (°C)	Pressure (torr)	Temperature (°C)	Pressure (torr)
–5	3.0	19	16.5	35	42.2
–2	3.9	20	17.5	40	55.3
0	4.6	21	18.7	50	92.5
2	5.3	22	19.8	60	149.4
4	6.1	23	21.1	70	233.7
6	7.0	24	22.4	80	355.1
8	8.0	25	23.8	90	525.8
10	9.2	26	25.2	95	633.9
12	10.5	27	26.7	99	733.2
14	12.0	28	28.3	100.0	760.0
16	13.6	29	30.0	101.0	787.6

Example 2.4.4: Pressure of a Gas Collected Over Water

If 0.200 L of argon is collected over water at a temperature of 26 °C and a pressure of 750 torr in a system like that shown in Figure 2.4.3, what is the partial pressure of argon?

Solution

According to Dalton's law, the total pressure in the bottle (750 torr) is the sum of the partial pressure of argon and the partial pressure of gaseous water:

$$P_{\mathrm{T}} = P_{\mathrm{Ar}} + P_{\mathrm{H_2O}}$$

Rearranging this equation to solve for the pressure of argon gives:

$$P_{\mathrm{Ar}} = P_{\mathrm{T}} - P_{\mathrm{H_2O}}$$

The pressure of water vapor above a sample of liquid water at 26 °C is 25.2 torr (Appendix E), so:

$$P_{\mathrm{Ar}} = 750 \text{ torr} - 25.2 \text{ torr} = 725 \text{ torr}$$

Exercise 2.4.4

A sample of oxygen collected over water at a temperature of 29.0 °C and a pressure of 764 torr has a volume of 0.560 L. What volume would the dry oxygen have under the same conditions of temperature and pressure?

Answer

0.583 L

2.4.4: Chemical Stoichiometry and Gases

Chemical stoichiometry describes the quantitative relationships between reactants and products in chemical reactions. We have previously measured quantities of reactants and products using masses for solids and volumes in conjunction with the molarity for solutions; now we can also use gas volumes to indicate quantities. If we know the volume, pressure, and temperature of a gas, we can use the ideal gas equation to calculate how many moles of the gas are present. If we know how many moles of a gas are involved, we can calculate the volume of a gas at any temperature and pressure.

2.4.4.1: Avogadro's Law Revisited

Sometimes we can take advantage of a simplifying feature of the stoichiometry of gases that solids and solutions do not exhibit: All gases that show ideal behavior contain the same number of molecules in the same volume (at the same temperature and pressure). Thus, the ratios of volumes of gases involved in a chemical reaction are given by the coefficients in the equation for the reaction, provided that the gas volumes are measured at the same temperature and pressure.

We can extend Avogadro's law (that the volume of a gas is directly proportional to the number of moles of the gas) to chemical reactions with gases: Gases combine, or react, in definite and simple proportions by volume, provided that all gas volumes are measured at the same temperature and pressure. For example, since nitrogen and hydrogen gases react to produce ammonia gas according to

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \longrightarrow 2\,\mathrm{NH_3}(g)$$

a given volume of nitrogen gas reacts with three times that volume of hydrogen gas to produce two times that volume of ammonia gas, if pressure and temperature remain constant.

The explanation for this is illustrated in Figure 2.4.4. According to Avogadro's law, equal volumes of gaseous N_2, H_2, and NH_3, at the same temperature and pressure, contain the same number of molecules. Because one molecule of N_2 reacts with three molecules of H_2 to produce two molecules of NH_3, the volume of H_2 required is three times the volume of N_2, and the volume of NH_3 produced is two times the volume of N_2.

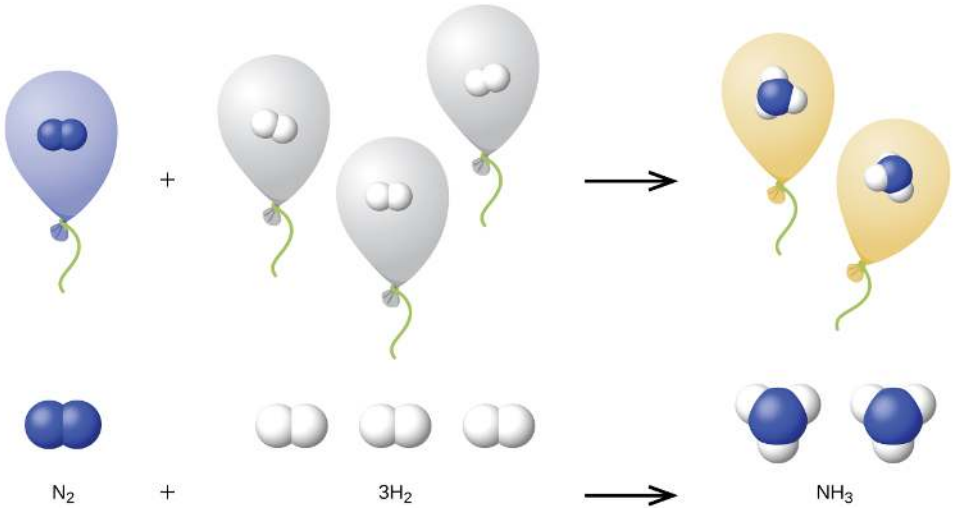


Figure 2.4.5: *One volume of N_2 combines with three volumes of H_2 to form two volumes of NH_3.*

Example 2.4.5: Reaction of Gases

Propane, $C_3H_8(g)$, is used in gas grills to provide the heat for cooking. What volume of $O_2(g)$ measured at 25 °C and 760 torr is required to react with 2.7 L of propane measured under the same conditions of temperature and pressure? Assume that the propane undergoes complete combustion.

Solution

The ratio of the volumes of C_3H_8 and O_2 will be equal to the ratio of their coefficients in the balanced equation for the reaction:

$$\begin{aligned} &\mathrm{C_3H_8}(g) + 5\,\mathrm{O_2}(g) \longrightarrow \quad 3\,\mathrm{CO_2}(g) + 4\,\mathrm{H_2O}(l) && (2.4.1)\\ &1\ \text{volume} + 5\ \text{volumes} \quad\ \ 3\ \text{volumes} + 4\ \text{volumes} && (2.4.2)\end{aligned}$$

From the equation, we see that one volume of C_3H_8 will react with five volumes of O_2:

$$2.7\ \mathrm{L}\ \cancel{\mathrm{C_3H_8}} \times \frac{5\ \mathrm{L}\ \mathrm{O_2}}{1\ \mathrm{L}\ \cancel{\mathrm{C_3H_8}}} = 13.5\ \mathrm{L}\ \mathrm{O_2}$$

A volume of 13.5 L of O_2 will be required to react with 2.7 L of C_3H_8.

Exercise 2.4.5

An acetylene tank for an oxyacetylene welding torch provides 9340 L of acetylene gas, C_2H_2, at 0 °C and 1 atm. How many tanks of oxygen, each providing 7.00×10^3 L of O_2 at 0 °C and 1 atm, will be required to burn the acetylene?

$$2\,C_2H_2 + 5\,O_2 \longrightarrow 4\,CO_2 + 2\,H_2O$$

Answer

3.34 tanks (2.34×10^4 L)

Example 2.4.6: Volumes of Reacting Gases

Ammonia is an important fertilizer and industrial chemical. Suppose that a volume of 683 billion cubic feet of gaseous ammonia, measured at 25 °C and 1 atm, was manufactured. What volume of $H_2(g)$, measured under the same conditions, was required to prepare this amount of ammonia by reaction with N_2?

$$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$$

Solution

Because equal volumes of H_2 and NH_3 contain equal numbers of molecules and each three molecules of H_2 that react produce two molecules of NH_3, the ratio of the volumes of H_2 and NH_3 will be equal to 3:2. Two volumes of NH_3, in this case in units of billion ft^3, will be formed from three volumes of H_2:

$$683\ \text{billion ft}^3\ \cancel{\text{NH}_3} \times \frac{3\ \text{billion ft}^3\ \text{H}_2}{2\ \text{billion ft}^3\ \cancel{\text{NH}_3}} = 1.02 \times 10^3\ \text{billion ft}^3\ \text{H}_2$$

The manufacture of 683 billion ft^3 of NH_3 required 1020 billion ft^3 of H_2. (At 25 °C and 1 atm, this is the volume of a cube with an edge length of approximately 1.9 miles.)

Exercise 2.4.6

What volume of $O_2(g)$ measured at 25 °C and 760 torr is required to react with 17.0 L of ethylene, $C_2H_4(g)$, measured under the same conditions of temperature and pressure? The products are CO_2 and water vapor.

Answer

51.0 L

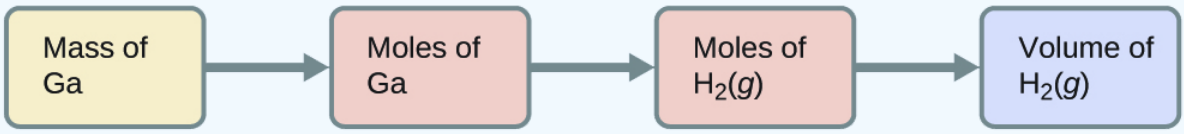
Example 2.4.7: Volume of Gaseous Product

What volume of hydrogen at 27 °C and 723 torr may be prepared by the reaction of 8.88 g of gallium with an excess of hydrochloric acid?

$$2\,Ga(s) + 6\,HCl(aq) \longrightarrow 2\,GaCl_3(aq) + 3\,H_2(g)$$

Solution

To convert from the mass of gallium to the volume of $H_2(g)$, we need to do something like this:



The first two conversions are:

https://chem.libretexts.org/@go/page/393477

$$8.88 \text{ g } \cancel{\text{Ga}} \times \frac{1 \text{ mol } \cancel{\text{Ga}}}{69.723 \text{ g } \cancel{\text{Ga}}} \times \frac{3 \text{ mol } \text{H}_2}{2 \text{ mol } \cancel{\text{Ga}}} = 0.191 \text{ mol } \text{H}_2$$

Finally, we can use the ideal gas law:

$$V_{\text{H}_2} = \left(\frac{nRT}{P}\right)_{\text{H}_2} = \frac{0.191 \text{ } \cancel{\text{mol}} \times 0.08206 \text{ L atm } \cancel{\text{mol}^{-1}\text{ K}^{-1}} \times 300 \text{ K}}{0.951 \text{ atm}} = 4.94 \text{ L}$$

Exercise 2.4.7

Sulfur dioxide is an intermediate in the preparation of sulfuric acid. What volume of SO_2 at 343 °C and 1.21 atm is produced by burning l.00 kg of sulfur in oxygen?

Answer

1.30×10^3 L

Greenhouse Gases and Climate Change

The thin skin of our atmosphere keeps the earth from being an ice planet and makes it habitable. In fact, this is due to less than 0.5% of the air molecules. Of the energy from the sun that reaches the earth, almost $\frac{1}{3}$ is reflected back into space, with the rest absorbed by the atmosphere and the surface of the earth. Some of the energy that the earth absorbs is re-emitted as infrared (IR) radiation, a portion of which passes back out through the atmosphere into space. However, most of this IR radiation is absorbed by certain substances in the atmosphere, known as greenhouse gases, which re-emit this energy in all directions, trapping some of the heat. This maintains favorable living conditions—without atmosphere, the average global average temperature of 14 °C (57 °F) would be about –19 °C (–2 °F). The major greenhouse gases (GHGs) are water vapor, carbon dioxide, methane, and ozone. Since the Industrial Revolution, human activity has been increasing the concentrations of GHGs, which have changed the energy balance and are significantly altering the earth's climate (Figure 2.4.6).

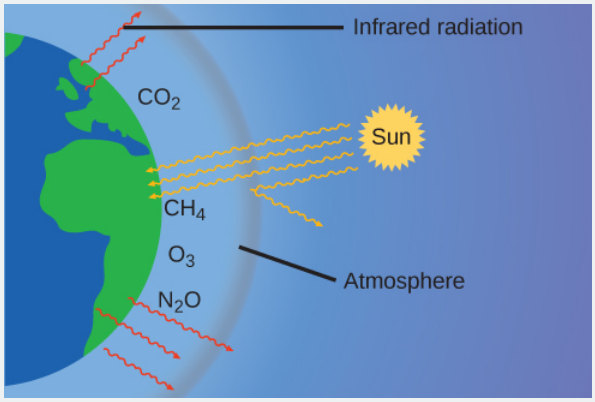


Figure 2.4.6: Greenhouse gases trap enough of the sun's energy to make the planet habitable—this is known as the greenhouse effect. Human activities are increasing greenhouse gas levels, warming the planet and causing more extreme weather events.

There is strong evidence from multiple sources that higher atmospheric levels of CO_2 are caused by human activity, with fossil fuel burning accounting for about $\frac{3}{4}$ of the recent increase in CO_2. Reliable data from ice cores reveals that CO_2 concentration in the atmosphere is at the highest level in the past 800,000 years; other evidence indicates that it may be at its highest level in 20 million years. In recent years, the CO_2 concentration has increased from historical levels of below 300 ppm to almost 400 ppm today (Figure 2.4.7).

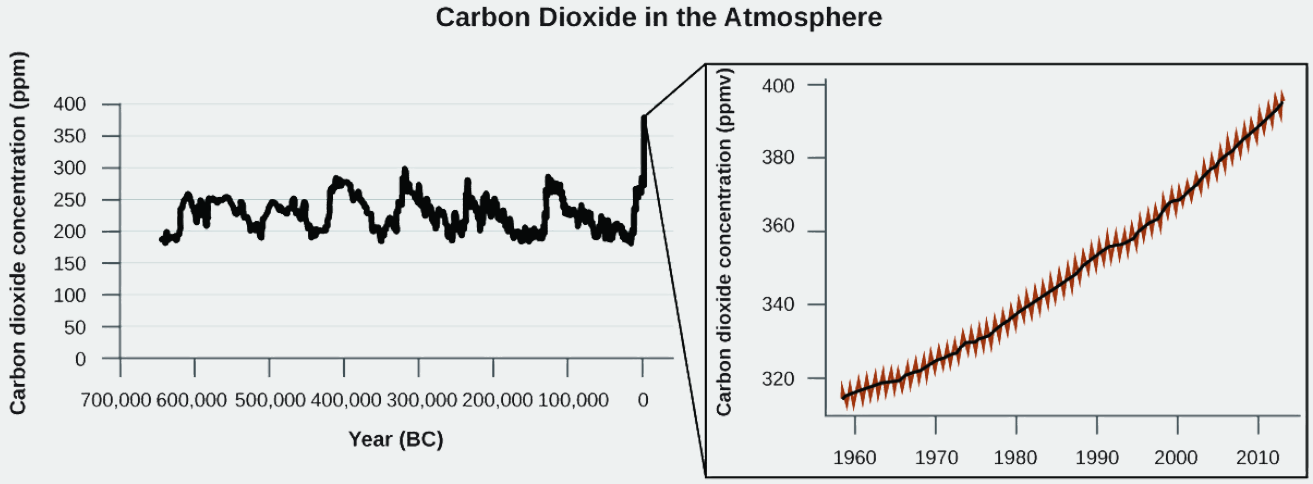


Figure 2.4.7: Figure CO_2 levels over the past 700,000 years were typically from 200–300 ppm, with a steep, unprecedented increase over the past 50 years.

Summary

The ideal gas law can be used to derive a number of convenient equations relating directly measured quantities to properties of interest for gaseous substances and mixtures. Appropriate rearrangement of the ideal gas equation may be made to permit the calculation of gas densities and molar masses. Dalton's law of partial pressures may be used to relate measured gas pressures for gaseous mixtures to their compositions. Avogadro's law may be used in stoichiometric computations for chemical reactions involving gaseous reactants or products.

2.4.4.0.1: Key Equations

- $P_{Total} = P_A + P_B + P_C + \ldots = \Sigma_i P_i$
- $P_A = X_A P_{Total}$
- $X_A = \dfrac{n_A}{n_{Total}}$

2.4.4.0.1: Footnotes

1. "Quotations by Joseph-Louis Lagrange," last modified February 2006, accessed February 10, 2015, www-history.mcs.st-andrews.ac.../Lagrange.html

Summary

Dalton's law of partial pressures

total pressure of a mixture of ideal gases is equal to the sum of the partial pressures of the component gases.

mole fraction (*X*)

concentration unit defined as the ratio of the molar amount of a mixture component to the total number of moles of all mixture components

partial pressure

pressure exerted by an individual gas in a mixture

vapor pressure of water

pressure exerted by water vapor in equilibrium with liquid water in a closed container at a specific temperature

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2.5: The Kinetic-Molecular Theory

Learning Objectives

- State the postulates of the kinetic-molecular theory
- Use this theory's postulates to explain the gas laws

The gas laws that we have seen to this point, as well as the ideal gas equation, are empirical, that is, they have been derived from experimental observations. The mathematical forms of these laws closely describe the macroscopic behavior of most gases at pressures less than about 1 or 2 atm. Although the gas laws describe relationships that have been verified by many experiments, they do not tell us why gases follow these relationships.

The kinetic molecular theory (KMT) is a simple microscopic model that effectively explains the gas laws described in previous modules of this chapter. This theory is based on the following five postulates described here. (Note: The term "molecule" will be used to refer to the individual chemical species that compose the gas, although some gases are composed of atomic species, for example, the noble gases.)

1. Gases are composed of molecules that are in continuous motion, travelling in straight lines and changing direction only when they collide with other molecules or with the walls of a container.
2. The molecules composing the gas are negligibly small compared to the distances between them.
3. The pressure exerted by a gas in a container results from collisions between the gas molecules and the container walls.
4. Gas molecules exert no attractive or repulsive forces on each other or the container walls; therefore, their collisions are *elastic* (do not involve a loss of energy).
5. The average kinetic energy of the gas molecules is proportional to the kelvin temperature of the gas.

The test of the KMT and its postulates is its ability to explain and describe the behavior of a gas. The various gas laws can be derived from the assumptions of the KMT, which have led chemists to believe that the assumptions of the theory accurately represent the properties of gas molecules. We will first look at the individual gas laws (Boyle's, Charles's, Amontons's, Avogadro's, and Dalton's laws) conceptually to see how the KMT explains them. Then, we will more carefully consider the relationships between molecular masses, speeds, and kinetic energies with temperature, and explain Graham's law.

2.5.1: The Kinetic-Molecular Theory Explains the Behavior of Gases, Part I

Recalling that gas pressure is exerted by rapidly moving gas molecules and depends directly on the number of molecules hitting a unit area of the wall per unit of time, we see that the KMT conceptually explains the behavior of a gas as follows:

- *Amontons's law.* If the temperature is increased, the average speed and kinetic energy of the gas molecules increase. If the volume is held constant, the increased speed of the gas molecules results in more frequent and more forceful collisions with the walls of the container, therefore increasing the pressure (Figure $2.5.1a$).
- *Charles's law.* If the temperature of a gas is increased, a constant pressure may be maintained only if the volume occupied by the gas increases. This will result in greater average distances traveled by the molecules to reach the container walls, as well as increased wall surface area. These conditions will decrease both the frequency of molecule-wall collisions and the number of collisions per unit area, the combined effects of which balance the effect of increased collision forces due to the greater kinetic energy at the higher temperature.
- *Boyle's law.* If the gas volume is decreased, the container wall area decreases and the molecule-wall collision frequency increases, both of which increase the pressure exerted by the gas (Figure $2.5.1b$).
- *Avogadro's law.* At constant pressure and temperature, the frequency and force of molecule-wall collisions are constant. Under such conditions, increasing the number of gaseous molecules will require a proportional increase in the container volume in order to yield a decrease in the number of collisions per unit area to compensate for the increased frequency of collisions (Figure $2.5.1c$).
- *Dalton's Law.* Because of the large distances between them, the molecules of one gas in a mixture bombard the container walls with the same frequency whether other gases are present or not, and the total pressure of a gas mixture equals the sum of the (partial) pressures of the individual gases.

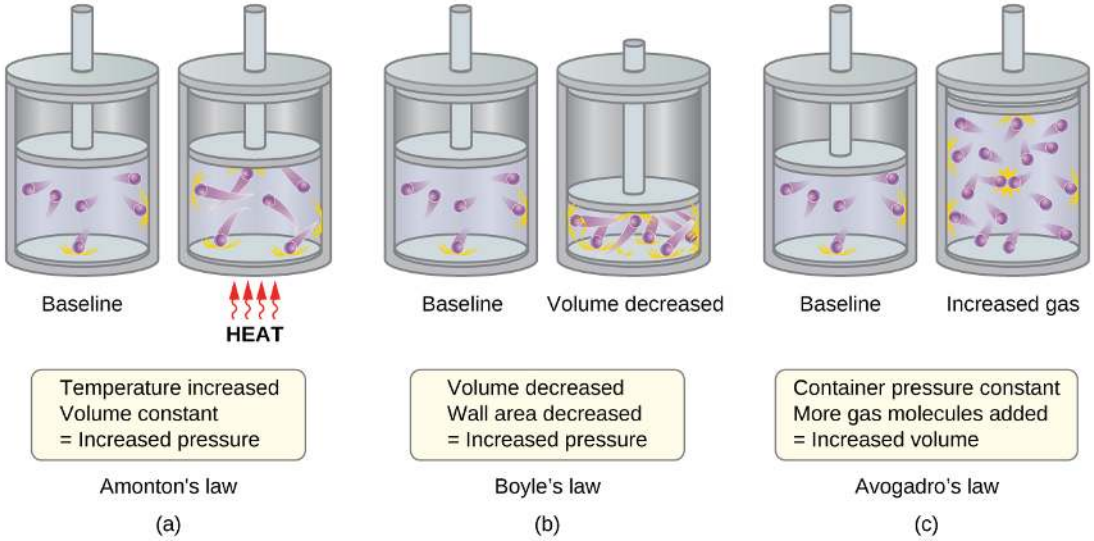


Figure 2.5.1: (a) When gas temperature increases, gas pressure increases due to increased force and frequency of molecular collisions. (b) When volume decreases, gas pressure increases due to increased frequency of molecular collisions. (c) When the amount of gas increases at a constant pressure, volume increases to yield a constant number of collisions per unit wall area per unit time.

2.5.2: Molecular Velocities and Kinetic Energy

The previous discussion showed that the KMT qualitatively explains the behaviors described by the various gas laws. The postulates of this theory may be applied in a more quantitative fashion to derive these individual laws. To do this, we must first look at velocities and kinetic energies of gas molecules, and the temperature of a gas sample.

In a gas sample, individual molecules have widely varying speeds; however, because of the *vast* number of molecules and collisions involved, the molecular speed distribution and average speed are constant. This molecular speed distribution is known as a Maxwell-Boltzmann distribution, and it depicts the relative numbers of molecules in a bulk sample of gas that possesses a given speed (Figure 2.5.2).

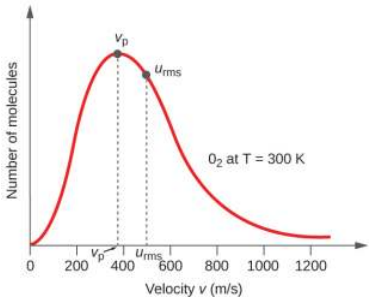


Figure 2.5.2: The molecular speed distribution for oxygen gas at 300 K is shown here. Very few molecules move at either very low or very high speeds. The number of molecules with intermediate speeds increases rapidly up to a maximum, which is the most probable speed, then drops off rapidly. Note that the most probable speed, v_p, is a little less than 400 m/s, while the root mean square speed, u_{rms}, is closer to 500 m/s.

The kinetic energy (KE) of a particle of mass (m) and speed (u) is given by:

$$\text{KE} = \frac{1}{2}mu^2$$

Expressing mass in kilograms and speed in meters per second will yield energy values in units of joules (J = kg m^2 s^{-2}). To deal with a large number of gas molecules, we use averages for both speed and kinetic energy. In the KMT, the root mean square velocity of a particle, u_{rms}, is defined as the square root of the average of the squares of the velocities with n = the number of particles:

$$u_{\text{rms}} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + u_4^2 + \ldots}{n}}$$

The average kinetic energy, KE_{avg}, is then equal to:

$$\text{KE}_{\text{avg}} = \frac{1}{2} m u_{\text{rms}}^2$$

The KE_{avg} of a collection of gas molecules is also directly proportional to the temperature of the gas and may be described by the equation:

$$\text{KE}_{\text{avg}} = \frac{3}{2} RT$$

where R is the gas constant and T is the kelvin temperature. When used in this equation, the appropriate form of the gas constant is 8.314 J $\text{mol}^{-1}\text{K}^{-1}$ (8.314 kg $\text{m}^2\text{s}^{-2}\text{mol}^{-1}\text{K}^{-1}$). These two separate equations for KE_{avg} may be combined and rearranged to yield a relation between molecular speed and temperature:

$$\frac{1}{2} m u_{\text{rms}}^2 = \frac{3}{2} RT$$

$$u_{\text{rms}} = \sqrt{\frac{3RT}{m}} \tag{2.5.1}$$

Example 2.5.1: Calculation of u_{rms}

Calculate the root-mean-square velocity for a nitrogen molecule at 30 °C.

Solution

Convert the temperature into Kelvin:

$$30^\circ C + 273 = 303\ K$$

Determine the mass of a nitrogen molecule in kilograms:

$$\frac{28.0\ \cancel{\text{g}}}{1\ \text{mol}} \times \frac{1\ \text{kg}}{1000\ \cancel{\text{g}}} = 0.028\ \text{kg/mol}$$

Replace the variables and constants in the root-mean-square velocity formula (Equation 2.5.1), replacing Joules with the equivalent kg m^2s^{-2}:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{m}}$$

$$u_{\text{rms}} = \sqrt{\frac{3(8.314\ J/mol\ K)(303\ K)}{(0.028\ kg/mol)}}$$

$$= \sqrt{2.70 \times 10^5\ m^2 s^{-2}}$$

$$= 519\ m/s$$

Exercise 2.5.1

Calculate the root-mean-square velocity for an oxygen molecule at –23 °C.

Answer

441 m/s

If the temperature of a gas increases, its KE_{avg} increases, more molecules have higher speeds and fewer molecules have lower speeds, and the distribution shifts toward higher speeds overall, that is, to the right. If temperature decreases, KE_{avg} decreases, more

molecules have lower speeds and fewer molecules have higher speeds, and the distribution shifts toward lower speeds overall, that is, to the left. This behavior is illustrated for nitrogen gas in Figure 2.5.3.

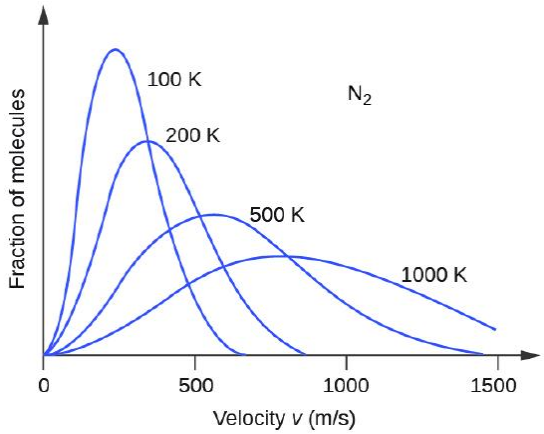


Figure 2.5.3: The molecular speed distribution for nitrogen gas (N_2) shifts to the right and flattens as the temperature increases; it shifts to the left and heightens as the temperature decreases.

At a given temperature, all gases have the same KE_{avg} for their molecules. Gases composed of lighter molecules have more high-speed particles and a higher u_{rms}, with a speed distribution that peaks at relatively higher velocities. Gases consisting of heavier molecules have more low-speed particles, a lower u_{rms}, and a speed distribution that peaks at relatively lower velocities. This trend is demonstrated by the data for a series of noble gases shown in Figure 2.5.4.

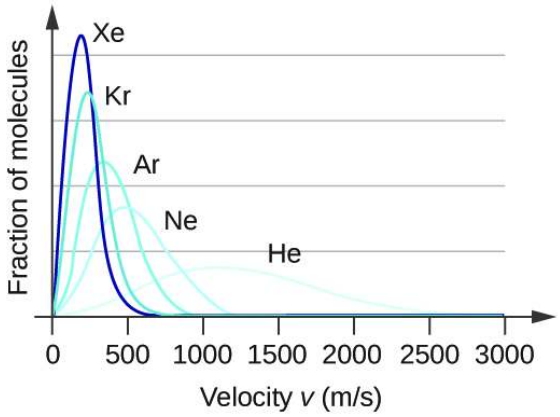


Figure 2.5.4: Molecular velocity is directly related to molecular mass. At a given temperature, lighter molecules move faster on average than heavier molecules.

> *The gas simulator may be used to examine the effect of temperature on molecular velocities. Examine the simulator's "energy histograms" (molecular speed distributions) and "species information" (which gives average speed values) for molecules of different masses at various temperatures.*

2.5.3: The Kinetic-Molecular Theory Explains the Behavior of Gases, Part II

According to Graham's law, the molecules of a gas are in rapid motion and the molecules themselves are small. The average distance between the molecules of a gas is large compared to the size of the molecules. As a consequence, gas molecules can move past each other easily and diffuse at relatively fast rates.

The rate of effusion of a gas depends directly on the (average) speed of its molecules:

$$\text{effusion rate} \propto u_{\text{rms}}$$

Using this relation, and the equation relating molecular speed to mass, Graham's law may be easily derived as shown here:

$$u_{\text{rms}} = \sqrt{\frac{3RT}{m}}$$

$$m = \frac{3RT}{u_{\text{rms}}^2} = \frac{3RT}{\overline{u}^2}$$

$$\frac{\text{effusion rate A}}{\text{effusion rate B}} = \frac{u_{\text{rms A}}}{u_{\text{rms B}}} = \frac{\sqrt{\frac{3RT}{m_{\text{A}}}}}{\sqrt{\frac{3RT}{m_{\text{B}}}}} = \sqrt{\frac{m_{\text{B}}}{m_{\text{A}}}}$$

The ratio of the rates of effusion is thus derived to be inversely proportional to the ratio of the square roots of their masses. This is the same relation observed experimentally and expressed as Graham's law.

Summary

The kinetic molecular theory is a simple but very effective model that effectively explains ideal gas behavior. The theory assumes that gases consist of widely separated molecules of negligible volume that are in constant motion, colliding elastically with one another and the walls of their container with average velocities determined by their absolute temperatures. The individual molecules of a gas exhibit a range of velocities, the distribution of these velocities being dependent on the temperature of the gas and the mass of its molecules.

2.5.4: Key Equations

- $u_{\text{rms}} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + u_4^2 + \ldots}{n}}$
- $\text{KE}_{\text{avg}} = \frac{3}{2}RT$
- $u_{\text{rms}} = \sqrt{\frac{3RT}{m}}$

Summary

kinetic molecular theory

theory based on simple principles and assumptions that effectively explains ideal gas behavior

root mean square velocity (u_{rms})

measure of average velocity for a group of particles calculated as the square root of the average squared velocity

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2.6: Effusion and Diffusion of Gases

Learning Objectives

- Define and explain effusion and diffusion
- State Graham's law and use it to compute relevant gas properties

If you have ever been in a room when a piping hot pizza was delivered, you have been made aware of the fact that gaseous molecules can quickly spread throughout a room, as evidenced by the pleasant aroma that soon reaches your nose. Although gaseous molecules travel at tremendous speeds (hundreds of meters per second), they collide with other gaseous molecules and travel in many different directions before reaching the desired target. At room temperature, a gaseous molecule will experience billions of collisions per second. The mean free path is the average distance a molecule travels between collisions. The mean free path increases with decreasing pressure; in general, the mean free path for a gaseous molecule will be hundreds of times the diameter of the molecule

In general, we know that when a sample of gas is introduced to one part of a closed container, its molecules very quickly disperse throughout the container; this process by which molecules disperse in space in response to differences in concentration is called diffusion (shown in Figure 2.6.1). The gaseous atoms or molecules are, of course, unaware of any concentration gradient, they simply move randomly—regions of higher concentration have more particles than regions of lower concentrations, and so a net movement of species from high to low concentration areas takes place. In a closed environment, diffusion will ultimately result in equal concentrations of gas throughout, as depicted in Figure 2.6.1. The gaseous atoms and molecules continue to move, but since their concentrations are the same in both bulbs, the rates of transfer between the bulbs are equal (no *net* transfer of molecules occurs).

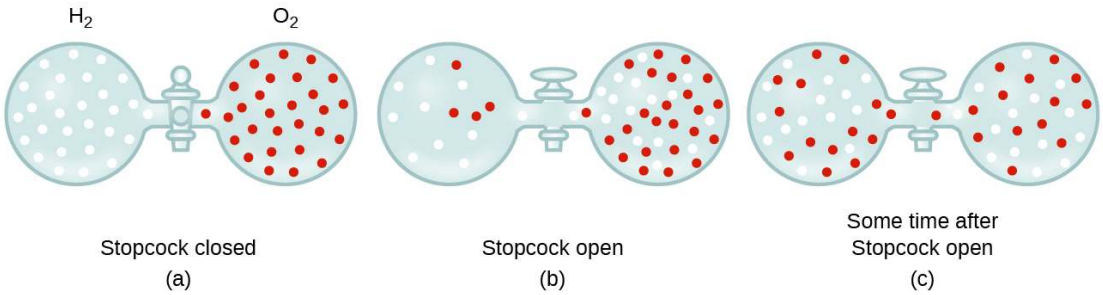


Figure 2.6.1: (a) Two gases, H_2 and O_2, are initially separated. (b) When the stopcock is opened, they mix together. The lighter gas, H_2, passes through the opening faster than O_2, so just after the stopcock is opened, more H_2 molecules move to the O_2 side than O_2 molecules move to the H_2 side. (c) After a short time, both the slower-moving O_2 molecules and the faster-moving H_2 molecules have distributed themselves evenly on both sides of the vessel.

We are often interested in the rate of diffusion, the amount of gas passing through some area per unit time:

$$\text{rate of diffusion} = \frac{\text{amount of gas passing through an area}}{\text{unit of time}}$$

The diffusion rate depends on several factors: the concentration gradient (the increase or decrease in concentration from one point to another); the amount of surface area available for diffusion; and the distance the gas particles must travel. Note also that the time required for diffusion to occur is inversely proportional to the rate of diffusion, as shown in the rate of diffusion equation.

A process involving movement of gaseous species similar to diffusion is effusion, the escape of gas molecules through a tiny hole such as a pinhole in a balloon into a vacuum (Figure 2.6.1). Although diffusion and effusion rates both depend on the molar mass of the gas involved, their rates are not equal; however, the ratios of their rates are the same.

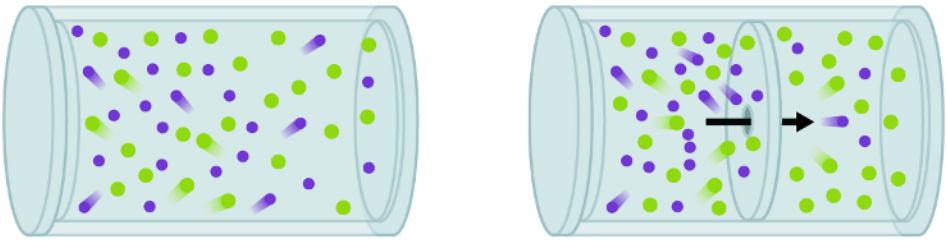


Figure 2.6.2: Diffusion occurs when gas molecules disperse throughout a container. Effusion occurs when a gas passes through an opening that is smaller than the mean free path of the particles, that is, the average distance traveled between collisions. Effectively, this means that only one particle passes through at a time.

If a mixture of gases is placed in a container with porous walls, the gases effuse through the small openings in the walls. The lighter gases pass through the small openings more rapidly (at a higher rate) than the heavier ones (Figure 2.6.2). In 1832, Thomas Graham studied the rates of effusion of different gases and formulated Graham's law of effusion: *The rate of effusion of a gas is inversely proportional to the square root of the mass of its particles*:

$$\text{rate of effusion} \propto \frac{1}{\sqrt{\mathcal{M}}}$$

This means that if two gases A and B are at the same temperature and pressure, the ratio of their effusion rates is inversely proportional to the ratio of the square roots of the masses of their particles:

$$\frac{\text{rate of effusion of B}}{\text{rate of effusion of A}} = \frac{\sqrt{\mathcal{M}_\text{A}}}{\sqrt{\mathcal{M}_\text{B}}}$$

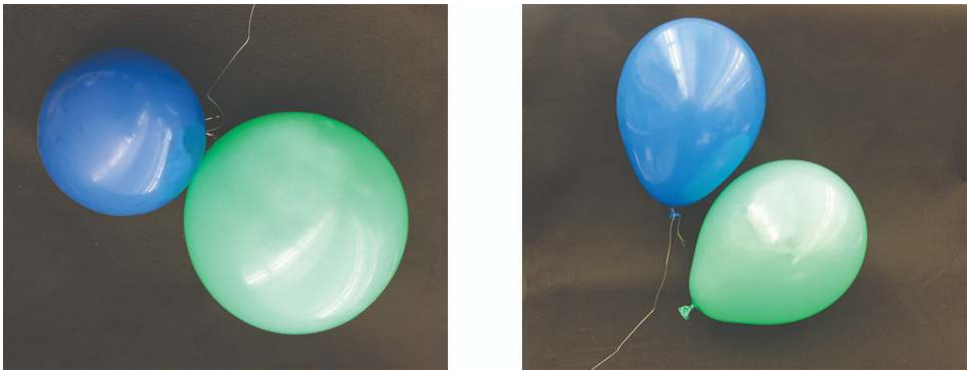


Figure 2.6.3: A balloon filled with air (the blue one) remains full overnight. A balloon filled with helium (the green one) partially deflates because the smaller, light helium atoms effuse through small holes in the rubber much more readily than the heavier molecules of nitrogen and oxygen found in air. (credit: modification of work by Mark Ott)

Example 2.6.1: Applying Graham's Law to Rates of Effusion

Calculate the ratio of the rate of effusion of hydrogen to the rate of effusion of oxygen.

Solution

From Graham's law, we have:

$$\frac{\text{rate of effusion of hydrogen}}{\text{rate of effusion of oxygen}} = \frac{\sqrt{1.43 \text{ g L}^{-1}}}{\sqrt{0.0899 \text{ g L}^{-1}}} = \frac{1.20}{0.300} = \frac{4}{1}$$

Using molar masses:

$$\frac{\text{rate of effusion of hydrogen}}{\text{rate of effusion of oxygen}} = \frac{32 \text{ g mol}^{-1}}{2 \text{ g mol}^{-1}} = \frac{\sqrt{16}}{\sqrt{1}} = \frac{4}{1}$$

Hydrogen effuses four times as rapidly as oxygen.

Exercise 2.6.1

At a particular pressure and temperature, nitrogen gas effuses at the rate of 79 mL/s. Using the same apparatus at the same temperature and pressure, at what rate will sulfur dioxide effuse?

Answer

52 mL/s

Here's another example, making the point about how determining times differs from determining rates.

Example 2.6.2: Effusion Time Calculations

It takes 243 s for 4.46×10^{-5} mol Xe to effuse through a tiny hole. Under the same conditions, how long will it take 4.46×10^{-5} mol Ne to effuse?

Solution

It is important to resist the temptation to use the times directly, and to remember how rate relates to time as well as how it relates to mass. Recall the definition of rate of effusion:

$$\text{rate of effusion} = \frac{\text{amount of gas transferred}}{\text{time}}$$

and combine it with Graham's law:

$$\frac{\text{rate of effusion of gas Xe}}{\text{rate of effusion of gas Ne}} = \frac{\sqrt{\mathcal{M}_{\text{Ne}}}}{\sqrt{\mathcal{M}_{\text{Xe}}}}$$

To get:

$$\frac{\dfrac{\text{amount of Xe transferred}}{\text{time for Xe}}}{\dfrac{\text{amount of Ne transferred}}{\text{time for Ne}}} = \frac{\sqrt{\mathcal{M}_{\text{Ne}}}}{\sqrt{\mathcal{M}_{\text{Xe}}}}$$

Noting that *amount of A* = *amount of B*, and solving for *time for Ne*:

$$\frac{\dfrac{\cancel{\text{amount of Xe}}}{\text{time for Xe}}}{\dfrac{\cancel{\text{amount of Ne}}}{\text{time for Ne}}} = \frac{\text{time for Ne}}{\text{time for Xe}} = \frac{\sqrt{\mathcal{M}_{\text{Ne}}}}{\sqrt{\mathcal{M}_{\text{Xe}}}} = \frac{\sqrt{\mathcal{M}_{\text{Ne}}}}{\sqrt{\mathcal{M}_{\text{Xe}}}}$$

and substitute values:

$$\frac{\text{time for Ne}}{243\ \text{s}} = \sqrt{\frac{20.2\ \cancel{\text{g mol}}}{131.3\ \cancel{\text{g mol}}}} = 0.392$$

Finally, solve for the desired quantity:

$$\text{time for Ne} = 0.392 \times 243\ \text{s} = 95.3\ \text{s}$$

Note that this answer is reasonable: Since Ne is lighter than Xe, the effusion rate for Ne will be larger than that for Xe, which means the time of effusion for Ne will be smaller than that for Xe.

Exercise 2.6.2

A party balloon filled with helium deflates to $\frac{2}{3}$ of its original volume in 8.0 hours. How long will it take an identical balloon filled with the same number of moles of air ($\mathcal{M}$ = 28.2 g/mol) to deflate to $\frac{1}{2}$ of its original volume?

Answer

32 h

Finally, here is one more example showing how to calculate molar mass from effusion rate data.

Example 2.6.3: Determining Molar Mass Using Graham's Law

An unknown gas effuses 1.66 times more rapidly than CO_2. What is the molar mass of the unknown gas? Can you make a reasonable guess as to its identity?

Solution

From Graham's law, we have:

$$\frac{\text{rate of effusion of Unknown}}{\text{rate of effusion of } CO_2} = \frac{\sqrt{\mathcal{M}_{CO_2}}}{\sqrt{\mathcal{M}_{Unknown}}}$$

Plug in known data:

$$\frac{1.66}{1} = \frac{\sqrt{44.0\ \text{g/mol}}}{\sqrt{\mathcal{M}_{Unknown}}}$$

Solve:

$$\mathcal{M}_{Unknown} = \frac{44.0\ \text{g/mol}}{(1.66)^2} = 16.0\ \text{g/mol}$$

The gas could well be CH_4, the only gas with this molar mass.

Exercise

Hydrogen gas effuses through a porous container 8.97-times faster than an unknown gas. Estimate the molar mass of the unknown gas.

Answer

163 g/mol

Application: Use of Diffusion for Uranium Enrichment

Gaseous diffusion has been used to produce enriched uranium for use in nuclear power plants and weapons. Naturally occurring uranium contains only 0.72% of ^{235}U, the kind of uranium that is "fissile," that is, capable of sustaining a nuclear fission chain reaction. Nuclear reactors require fuel that is 2–5% ^{235}U, and nuclear bombs need even higher concentrations. One way to enrich uranium to the desired levels is to take advantage of Graham's law. In a gaseous diffusion enrichment plant, uranium hexafluoride (UF_6, the only uranium compound that is volatile enough to work) is slowly pumped through large cylindrical vessels called diffusers, which contain porous barriers with microscopic openings. The process is one of diffusion because the other side of the barrier is not evacuated. The $^{235}UF_6$ molecules have a higher average speed and diffuse through the barrier a little faster than the heavier $^{238}UF_6$ molecules. The gas that has passed through the barrier is slightly enriched in $^{235}UF_6$ and the residual gas is slightly depleted. The small difference in molecular weights between $^{235}UF_6$ and $^{238}UF_6$ only about 0.4% enrichment, is achieved in one diffuser (Figure 2.6.4). But by connecting many diffusers in a sequence of stages (called a cascade), the desired level of enrichment can be attained.

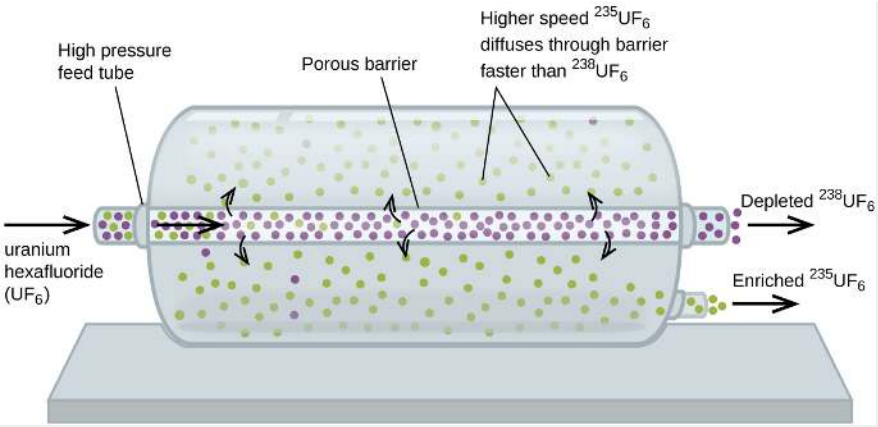


Figure 2.6.4: In a diffuser, gaseous UF_6 is pumped through a porous barrier, which partially separates $^{235}UF_6$ from $^{238}UF_6$ The UF_6 must pass through many large diffuser units to achieve sufficient enrichment in ^{235}U.

The large scale separation of gaseous $^{235}UF_6$ from $^{238}UF_6$ was first done during the World War II, at the atomic energy installation in Oak Ridge, Tennessee, as part of the Manhattan Project (the development of the first atomic bomb). Although the theory is simple, this required surmounting many daunting technical challenges to make it work in practice. The barrier must have tiny, uniform holes (about 10^{-6} cm in diameter) and be porous enough to produce high flow rates. All materials (the barrier, tubing, surface coatings, lubricants, and gaskets) need to be able to contain, but not react with, the highly reactive and corrosive UF_6.

Because gaseous diffusion plants require very large amounts of energy (to compress the gas to the high pressures required and drive it through the diffuser cascade, to remove the heat produced during compression, and so on), it is now being replaced by gas centrifuge technology, which requires far less energy. A current hot political issue is how to deny this technology to Iran, to prevent it from producing enough enriched uranium for them to use to make nuclear weapons.

Summary

Gaseous atoms and molecules move freely and randomly through space. Diffusion is the process whereby gaseous atoms and molecules are transferred from regions of relatively high concentration to regions of relatively low concentration. Effusion is a similar process in which gaseous species pass from a container to a vacuum through very small orifices. The rates of effusion of gases are inversely proportional to the square roots of their densities or to the square roots of their atoms/molecules' masses (Graham's law).

2.6.0.0.1: Key Equations

- $\text{rate of diffusion} = \dfrac{\text{amount of gas passing through an area}}{\text{unit of time}}$
- $\dfrac{\text{rate of effusion of gas A}}{\text{rate of effusion of gas B}} = \dfrac{\sqrt{m_B}}{\sqrt{m_A}} = \dfrac{\sqrt{\mathscr{M}_B}}{\sqrt{\mathscr{M}_A}}$

Summary

diffusion

movement of an atom or molecule from a region of relatively high concentration to one of relatively low concentration (discussed in this chapter with regard to gaseous species, but applicable to species in any phase)

effusion

transfer of gaseous atoms or molecules from a container to a vacuum through very small openings

Graham's law of effusion

rates of diffusion and effusion of gases are inversely proportional to the square roots of their molecular masses

mean free path

average distance a molecule travels between collisions

rate of diffusion

amount of gas diffusing through a given area over a given time

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2.7: Non-Ideal Gas Behavior

Learning Objectives

- Describe the physical factors that lead to deviations from ideal gas behavior
- Explain how these factors are represented in the van der Waals equation
- Define compressibility (Z) and describe how its variation with pressure reflects non-ideal behavior
- Quantify non-ideal behavior by comparing computations of gas properties using the ideal gas law and the van der Waals equation

Thus far, the ideal gas law, $PV = nRT$, has been applied to a variety of different types of problems, ranging from reaction stoichiometry and empirical and molecular formula problems to determining the density and molar mass of a gas. As mentioned in the previous modules of this chapter, however, the behavior of a gas is often non-ideal, meaning that the observed relationships between its pressure, volume, and temperature are not accurately described by the gas laws. In this section, the reasons for these deviations from ideal gas behavior are considered.

One way in which the accuracy of PV = nRT can be judged is by comparing the actual volume of 1 mole of gas (its molar volume, Vm) to the molar volume of an ideal gas at the same temperature and pressure. This ratio is called the compressibility factor (Z) with:

$$\mathrm{Z} = \frac{\text{molar volume of gas at same } T \text{ and } P}{\text{molar volume of ideal gas at same } T \text{ and } P} = \left(\frac{PV_m}{RT}\right)_{\text{measured}}$$

Ideal gas behavior is therefore indicated when this ratio is equal to 1, and any deviation from 1 is an indication of non-ideal behavior. Figure 2.7.1 shows plots of Z over a large pressure range for several common gases.

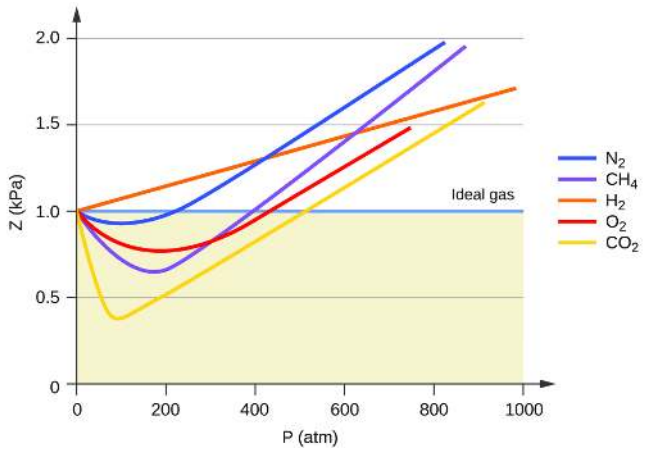


Figure 2.7.1: A graph of the compressibility factor (Z) vs. pressure shows that gases can exhibit significant deviations from the behavior predicted by the ideal gas law.

As is apparent from Figure 2.7.1, the ideal gas law does not describe gas behavior well at relatively high pressures. To determine why this is, consider the differences between real gas properties and what is expected of a hypothetical ideal gas.

Particles of a hypothetical ideal gas have **no significant volume** and **do not attract or repel each other**. In general, real gases approximate this behavior at relatively low pressures and high temperatures. However, at high pressures, the molecules of a gas are crowded closer together, and the amount of empty space between the molecules is reduced. At these higher pressures, the volume of the gas molecules themselves becomes appreciable relative to the total volume occupied by the gas (Figure 2.7.2). The gas therefore becomes less compressible at these high pressures, and although its volume continues to decrease with increasing pressure, this decrease is not *proportional* as predicted by Boyle's law.

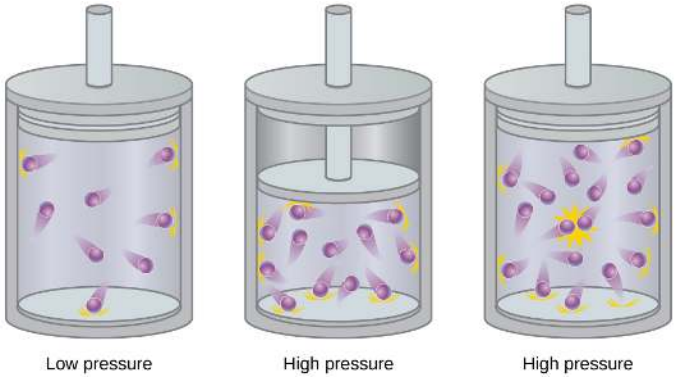


Figure 2.7.2: Raising the pressure of a gas increases the fraction of its volume that is occupied by the gas molecules and makes the gas less compressible.

At relatively low pressures, gas molecules have practically no attraction for one another because they are (on average) so far apart, and they behave almost like particles of an ideal gas. At higher pressures, however, the force of attraction is also no longer insignificant. This force pulls the molecules a little closer together, slightly decreasing the pressure (if the volume is constant) or decreasing the volume (at constant pressure) (Figure 2.7.3). This change is more pronounced at low temperatures because the molecules have lower KE relative to the attractive forces, and so they are less effective in overcoming these attractions after colliding with one another.

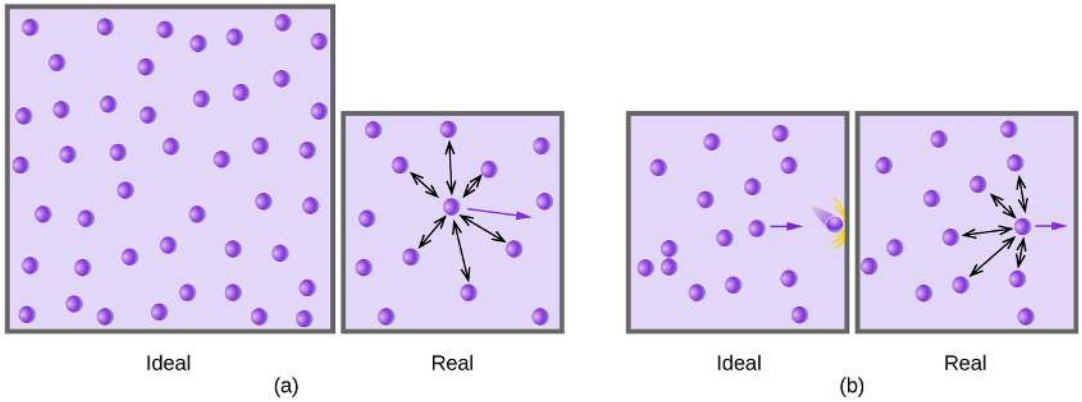


Figure 2.7.3: (a) Attractions between gas molecules serve to decrease the gas volume at constant pressure compared to an ideal gas whose molecules experience no attractive forces. (b) These attractive forces will decrease the force of collisions between the molecules and container walls, therefore reducing the pressure exerted compared to an ideal gas.

There are several different equations that better approximate gas behavior than does the ideal gas law. The first, and simplest, of these was developed by the Dutch scientist Johannes van der Waals in 1879. The van der Waals equation improves upon the ideal gas law by adding two terms: one to account for the volume of the gas molecules and another for the attractive forces between them.

$$PV = nRT \longrightarrow \left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

Correction for molecular attraction

Correction for volume of molecules

Figure \(\PageIndex{4}\): The changes from the ideal gas law to the van der Waals equation.

The constant *a* corresponds to the strength of the attraction between molecules of a particular gas, and the constant *b* corresponds to the size of the molecules of a particular gas. The "correction" to the pressure term in the ideal gas law is $\frac{n^2a}{V^2}$, and the "correction" to the volume is *nb*. Note that when *V* is relatively large and *n* is relatively small, both of these correction terms become negligible, and the van der Waals equation reduces to the ideal gas law, *PV* = *nRT*. Such a condition corresponds to a gas in which a relatively

low number of molecules is occupying a relatively large volume, that is, a gas at a relatively low pressure. Experimental values for the van der Waals constants of some common gases are given in Table 2.7.1.

Table 2.7.1: Values of van der Waals Constants for Some Common Gases

Gas	a (L^2 atm/mol^2)	b (L/mol)
N_2	1.39	0.0391
O_2	1.36	0.0318
CO_2	3.59	0.0427
H_2O	5.46	0.0305
He	0.0342	0.0237
CCl_4	20.4	0.1383

At low pressures, the correction for intermolecular attraction, *a*, is more important than the one for molecular volume, *b*. At high pressures and small volumes, the correction for the volume of the molecules becomes important because the molecules themselves are incompressible and constitute an appreciable fraction of the total volume. At some intermediate pressure, the two corrections have opposing influences and the gas appears to follow the relationship given by *PV* = *nRT* over a small range of pressures. This behavior is reflected by the "dips" in several of the compressibility curves shown in Figure 2.7.1. The attractive force between molecules initially makes the gas more compressible than an ideal gas, as pressure is raised (Z decreases with increasing *P*). At very high pressures, the gas becomes less compressible (Z increases with *P*), as the gas molecules begin to occupy an increasingly significant fraction of the total gas volume.

Strictly speaking, the ideal gas equation functions well when intermolecular attractions between gas molecules are negligible and the gas molecules themselves do not occupy an appreciable part of the whole volume. These criteria are satisfied under conditions of *low pressure and high temperature*. Under such conditions, the gas is said to behave ideally, and deviations from the gas laws are small enough that they may be disregarded—this is, however, very often not the case.

Example 2.7.1: Comparison of Ideal Gas Law and van der Waals Equation

A 4.25-L flask contains 3.46 mol CO_2 at 229 °C. Calculate the pressure of this sample of CO_2:

a. from the ideal gas law
b. from the van der Waals equation
c. Explain the reason(s) for the difference.

Solution

(a) From the ideal gas law:

$$P = \frac{nRT}{V} = \frac{3.46 \cancel{\text{ mol}} \times 0.08206 \cancel{\text{ L}}\,\text{atm}\,\cancel{\text{mol}^{-1}}\,\cancel{\text{K}^{-1}} \times 502 \cancel{\text{ K}}}{4.25 \cancel{\text{ L}}} = 33.5 \text{ atm}$$

(b) From the van der Waals equation:

$$\left(P + \frac{n^2 a}{V^2}\right) \times (V - nb) = nRT \longrightarrow P = \frac{nRT}{(V - nb)} - \frac{n^2 a}{V^2}$$

$$P = \frac{3.46 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 502 \text{ K}}{(4.25 \text{ L} - 3.46 \text{ mol} \times 0.0427 \text{ L mol}^{-1})} - \frac{(3.46 \text{ mol})^2 \times 3.59 \text{ L}^2 \text{ atm mol}^2}{(4.25 \text{ L})^2}$$

This finally yields *P* = 32.4 atm.

(c) This is not very different from the value from the ideal gas law because the pressure is not very high and the temperature is not very low. The value is somewhat different because CO_2 molecules do have some volume and attractions between molecules, and the ideal gas law assumes they do not have volume or attractions.

? Exercise 2.7.1

A 560-mL flask contains 21.3 g N_2 at 145 °C. Calculate the pressure of N_2:

a. from the ideal gas law
b. from the van der Waals equation
c. Explain the reason(s) for the difference.

Answer a

46.562 atm

Answer b

46.594 atm

Answer c

The van der Waals equation takes into account the volume of the gas molecules themselves as well as intermolecular attractions.

Summary

Gas molecules possess a finite volume and experience forces of attraction for one another. Consequently, gas behavior is not necessarily described well by the ideal gas law. Under conditions of low pressure and high temperature, these factors are negligible, the ideal gas equation is an accurate description of gas behavior, and the gas is said to exhibit ideal behavior. However, at lower temperatures and higher pressures, corrections for molecular volume and molecular attractions are required to account for finite molecular size and attractive forces. The van der Waals equation is a modified version of the ideal gas law that can be used to account for the non-ideal behavior of gases under these conditions.

2.7.1: Key Equations

- $\mathrm{Z} = \dfrac{\text{molar volume of gas at same } T \text{ and } P}{\text{molar volume of ideal gas at same } T \text{ and } P} = \left(\dfrac{P \times V_m}{R \times T}\right)_{\text{measured}}$
- $\left(P + \dfrac{n^2 a}{V^2}\right) \times (V - nb) = nRT$

Glossary

compressibility factor (Z)

ratio of the experimentally measured molar volume for a gas to its molar volume as computed from the ideal gas equation

van der Waals equation

modified version of the ideal gas equation containing additional terms to account for non-ideal gas behavior

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2.E: Gases (Exercises)

2.1 Characteristics of Gases

Exercise 2.E.1

For a substance that has gas, liquid, and solid phases, arrange these phases in order of

a) increasing density

b) strength of intermolecular interactions

c) compressibility

d) molecular motion.

Answer

a) gas < liquid < solid

b) gas < liquid < solid

d) solid < liquid < gas

d) solid < liquid < gas

2.2 Gas Pressure

Exercise 2.E.2

Why are sharp knives more effective than dull knives (Hint: think about the definition of pressure)?

Answer

The cutting edge of a knife that has been sharpened has a smaller surface area than a dull knife. Since pressure is force per unit area, a sharp knife will exert a higher pressure with the same amount of force and cut through material more effectively.

Exercise 2.E.3

Barometric pressure in Vancouver BC was 102.3 kPa. Calculate this barometric pressure in atm and mm Hg.

Answer

1.010 atm, 767.6 mmHg

Exercise 2.E.4

The barometric pressure at the top of Sun Peaks ski hill near Kamloops BC was 655 mm Hg. What is this pressure in atm and kPa?

Answer

0.861 atm, 87.2 kPa

Exercise 2.E.5

Canadian tire pressure gauges are marked in units of kilopascals. What reading on such a gauge corresponds to 32 psi?

Answer

2.2×10^2 kPa

Exercise 2.E.6

The pressure of the atmosphere on the surface of the planet Venus is about 88.8 atm. Compare that pressure in psi to the normal pressure on earth at sea level in psi.

Answer

Earth: 14.7 lb in^{-2}; Venus: 13.1×10^3 lb in^{-2}

Exercise 2.E.7

In November 2021 BC was hit by tremendous storms including an atmospheric river. Between Nov. 13 and Nov. 15 2021 219 mm of rain fell in Chilliwack BC and the barometric pressure dropped from 102.77 kPa to 99.21 kPa. What is the pressure drop in torr?

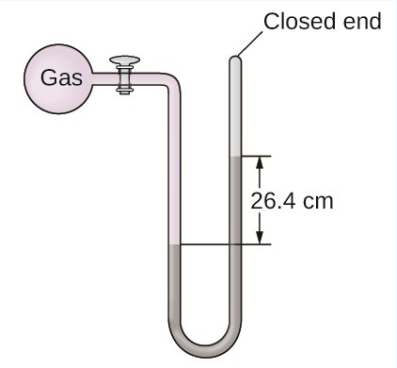
Answer

26.7 torr

Exercise 2.E.8

The pressure of a sample of gas is measured at sea level with a closed-end manometer as shown in the figure below. The liquid in the manometer is mercury. Determine the pressure of the gas in:

a. torr
b. Pa
c. bar



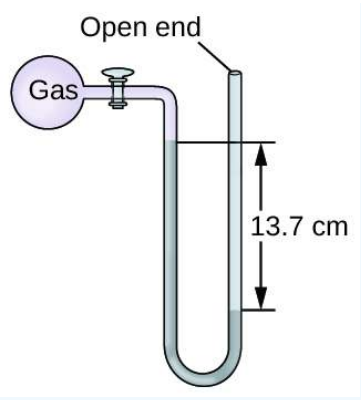
Answer

a. 264 torr; b. 35,200 Pa; c. 0.352 bar

Exercise 2.E.9

The pressure of a sample of gas is measured at sea level with an open-end mercury manometer. Assuming atmospheric pressure is 760.0 mm Hg, determine the pressure of the gas in:

a. mm Hg
b. atm
c. kPa



Answer

a. 623 mm Hg; b. 0.820 atm; c. 83.1 kPa

2.3: Relating Pressure, Volume, Amount, and Temperature: The Ideal Gas Law

Exercise 2.E.10

When a scuba diver exhales gas bubbles, the bubbles rise through the column of water going from higher to lower pressure. Explain how the volume of the bubbles change as they rise to the surface, assuming that they remain intact.

Answer

As the bubbles rise, the pressure decreases, so their volume increases as suggested by Boyle's law.

Exercise 2.E.11

An alternate way to state Avogadro's law is "All other things being equal, the number of molecules in a gas is directly proportional to the volume of the gas."

a. What is the meaning of the term "directly proportional?"
b. What are the "other things" that must be equal?

Answer

a. The number of particles in the gas increases as the volume increases. b. temperature, pressure

Exercise 2.E.12

A spray can which has a pressure of 1344 torr at 23°C is used until it is empty except for the propellant gas. If the can is thrown into a fire at 475°C, what will be the pressure in the hot can in atmospheres?

Answer

4.47 atm

Exercise 2.E.13

Calculate the volume of 1.00 mol of CH_4 gas at 150.0 K and 1.00 atm

Answer

12.3 L

Exercise 2.E.14

What is the temperature of an 11.2-L sample of carbon monoxide, CO, at 744 torr if it occupies 13.3 L at 55 °C and 744 torr?

Answer

276°K ; 3°C

Solution

we must use $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ and solve for T_1

$T_1 = \frac{P_1V_1T_2}{P_2V_2}$

Where:

$P_1 = 744\ torr$

$V_1 = 11.2\ L$

$P_2 = 744\ torr$

$V_2 = 13.3\ L$

$T_2 = 328.15^\circ\ K$

$\frac{(744\ torr)(11.2\ L)(328.15^\circ\ K)}{(744\ torr)(13.3\ L)} = 276^\circ\ K$

276°K ; 3°C

Exercise 2.E.15

A 2.50-L volume of hydrogen measured at –196 °C is warmed to 100 °C. Calculate the volume of the gas at the higher temperature, assuming no change in pressure.

Answer

12.1 L

Exercise 2.E.16

A weather balloon contains 8.80 moles of helium at a pressure of 0.992 atm and a temperature of 25 °C at ground level. What is the volume of the balloon under these conditions?



Answer

217 L

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Exercise 2.E.17

How many moles of gaseous boron trifluoride, BF_3, are contained in a 4.3410-L bulb at 788.0 K if the pressure is 1.220 atm? How many grams of BF_3?

Answer

8.190×10^{-2} mol; 5.553 g

Exercise 2.E.18

A balloon that is 100.21 L at 21 °C and 0.981 atm is released and just barely clears the top of Mount Crumpet in British Columbia. If the final volume of the balloon is 144.53 L at a temperature of 5.24 °C, what is the pressure experienced by the balloon as it clears Mount Crumpet?

Answer

0.644 atm

xercise 2.E.19

Iodine, I_2, is a solid at room temperature but sublimes (converts from a solid into a gas) when warmed. What is the temperature in a 73.3-mL bulb that contains 0.292 g of I_2 vapor at a pressure of 0.462 atm?

Answer

359°K ; 86°C

Solution

Use the equation $PV = nRT$ and solve for T

$$T = \frac{PV}{nR}$$

2.) convert grams of I_2 to moles of I_2 and convert mL to L

$$0.292 g\, I_2 \times \frac{1\ mole\, I_2}{253.8 g\, I_2} = 1.15 \times 10^{-3}\ moles\, I_2$$

$$73.3\ mL = 0.0733\ L$$

3.) Use these values along with $R = 0.08206\ \frac{atm\ L}{mole\ ^\circ K}$ to solve for T

$$T = \frac{(0.462\ \cancel{atm})(0.0733\ \cancel{L})}{(1.15 \times 10^{-3}\ \cancel{moles})(0.08206\ \frac{\cancel{atm}\ \cancel{L}}{\cancel{mole}\ ^\circ K})} = 359\ ^\circ K$$

359°K ; 86°C

Exercise 2.E.20

How many grams of gas are present in each of the following cases?

a. 0.100 L of CO_2 at 307 torr and 26 °C
b. 8.75 L of C_2H_4, at 378.3 kPa and 483 K
c. 221 mL of Ar at 0.23 torr and –54 °C

Answer

a. 7.24×10^{-2} g; b. 23.1 g; c. 1.5×10^{-4} g

Exercise 2.E.21

A cylinder of medical oxygen has a volume of 35.4 L, and contains O_2 at a pressure of 151 atm and a temperature of 25 °C. What volume of O_2 does this correspond to at normal body conditions, that is, 1 atm and 37 °C?

Answer

5561 L

Exercise 2.E.22

A 20.0-L cylinder containing 11.34 kg of butane, C_4H_{10}, was opened to the atmosphere. Calculate the mass of the gas remaining in the cylinder if it were opened and the gas escaped until the pressure in the cylinder was equal to the atmospheric pressure, 0.983 atm, and a temperature of 27 °C.

Answer

46.4 g

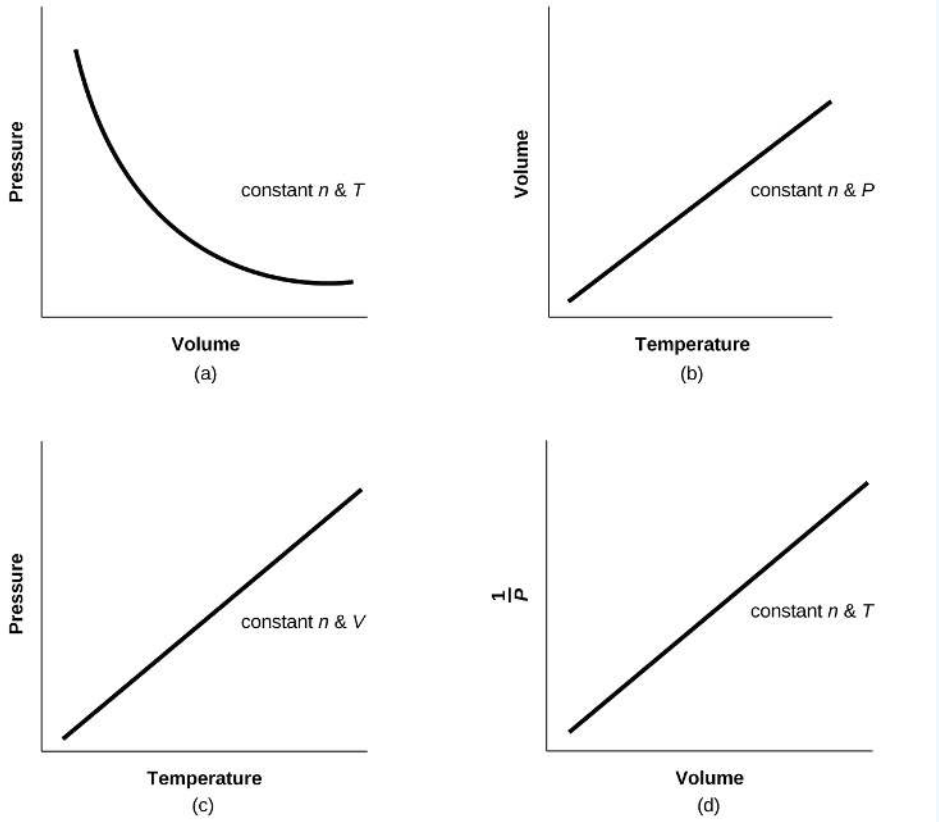
Exercise 2.E.23

For a given amount of gas showing ideal behavior, draw labeled graphs of:

a. the variation of P with V
b. the variation of V with T
c. the variation of P with T
d. the variation of $\frac{1}{P}$ with V

Answer

For a gas exhibiting ideal behavior:



Exercise 2.E.24

If the volume of a fixed amount of an ideal gas is tripled at constant temperature, what happens to the pressure?

Answer

The pressure decreases by a factor of 3.

Exercise 2.E.25

Your instructor blows up a balloon so that it is filled with 0.55 moles of Helium at 21.5 ºC and 1.00 atm pressure. The instructor adds an additional 0.050 moles of Helium. If the pressure in the balloon remains the same, do you expect the volume to increase or decrease? Explain your reasoning in clear and complete statements.

Answer

Volume is predicted to increase. (explain this answer in your own words)

Solution

under construction

Exercise 2.E.26

A balloon inflated with three breaths of air has a volume of 1.7 L. At the same temperature and pressure, what is the volume of the balloon if five more same-sized breaths are added to the balloon?

Answer

4.5 L

Solution

$$\frac{V1}{n1} = \frac{V2}{n2}$$

$$V2 = \frac{V2n2}{n1}$$

n1 = 3 breaths = 3x; n2 = (3+5) breaths = 8x

$$V2 = \frac{(1.7L)(8x)}{3x}$$

V2 = 4.5 L

Printable Worksheet

Link to worksheet with guided solution

Exercise $2.E.27$

Your Instructor blows up a balloon so that it is filled with 506 mL of Helium at 22.00 ^{o}C and 1.00 atm pressure. What volume (in mL) will the balloon have at 4.00 ^{o}C?

Answer

475 mL

Solution

under construction

2.4: Stoichiometry of Gaseous Substances, Mixtures, and Reactions

Exercise $2.E.28$

What is the density of laughing gas, dinitrogen monoxide, N_2O, at a temperature of 325 K and a pressure of 113.0 kPa?

Answer

1.84 g/L

Answer

First convert kPa to atm

$$113.0\ kPa \times \frac{1\ atm}{101.325\ kPa} = 1.115\ atm$$

2.) The use the equation $d = \frac{PM}{RT}$ where d = density in g L^{-1} and M = molar mass in g mol^{-1}

$$d = \frac{(1.115\ atm)(44.02 \frac{g}{\cancel{mol}})}{(0.08206 \frac{\cancel{atm}\ L}{\cancel{mole}\ \cancel{^\circ K}})(325\ \cancel{^\circ K})} = 1.84\ \frac{g}{L}$$

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Exercise 2.E.29

Calculate the density of Freon 12, CF_2Cl_2, at 30.0 °C and 0.954 atm.

Answer

4.64 g/L

Exercise 2.E.30

What is the molar mass of a gas if 0.0494 g of the gas occupies a volume of 0.100 L at a temperature 26 °C and a pressure of 307 torr?

Answer

30.0 g/mol

Solution

Convert torr to atm and °C to °K

$307\ torr = 0.404 atm$

$26^\circ C = 300.^\circ K$

2.) Use the equation $PV = nRT$ and solve for n

$$n = \frac{PV}{RT}$$

$$n = \frac{(0.404\ \cancel{atm})(0.100\ \cancel{L})}{(0.08206 \frac{\cancel{atm}\ \cancel{L}}{mol\ \cancel{^\circ K}})(300.\ \cancel{^\circ K})} = 0.00165\ moles$$

3.) Then divide grams by the number of moles to obtain the molar mass:

$$\frac{0.0494 g}{0.00165\ moles} = 30.0 \frac{g}{mole}$$

Exercise 2.E.31

What is the molar mass of a gas if 0.281 g of the gas occupies a volume of 125 mL at a temperature 126 °C and a pressure of 777 torr?

Answer

72.0 g/mol

Exercise 2.E.32

The density of a certain gaseous fluoride of phosphorus is 3.93 g/L at 0.00 °C and 1.00 atm. Calculate the molar mass of this fluoride and determine its molecular formula.

Answer

88.1 g mol^{-1}; PF_3

Exercise 2.E.33

A 36.0–L cylinder of a gas used for calibration of blood gas analyzers in medical laboratories contains 350 g CO_2, 805 g O_2, and 4,880 g N_2. At 25 degrees C, what is the pressure in the cylinder in atmospheres?

Answer

141 atm

Exercise 2.E.34

A sample of gas isolated from unrefined petroleum contains 90.0% CH_4, 8.9% C_2H_6, and 1.1% C_3H_8 at a total pressure of 307.2 kPa. What is the partial pressure of each component of this gas?

Hint

The percentages given indicate the percent of the total pressure that is due to each component.

Answer

CH_4: 276 kPa; C_2H_6: 27 kPa; C_3H_8: 3.4 kPa

Exercise 2.E.35

Most mixtures of hydrogen gas with oxygen gas are explosive. However, a mixture that contains less than 3.0 % O_2 is not. If enough O_2 is added to a cylinder of H_2 at 33.2 atm to bring the total pressure to 34.5 atm, is the mixture explosive?

Answer

Yes

Exercise 2.E.36

A sample of carbon monoxide was collected over water at a total pressure of 756 torr and a temperature of 18 °C. What is the pressure of the carbon monoxide? The vapour pressure of H_2O at 18 ºC is 15.5 torr.

Answer

$740._5$ torr or 741 torr

Exercise 2.E.37

Joseph Priestley first prepared pure oxygen by heating mercuric oxide, HgO:

$$2\,\mathrm{HgO}(s) \longrightarrow 2\,\mathrm{Hg}(l) + \mathrm{O_2}(g)$$

a. Outline the steps necessary to answer the following question: What volume of O_2 at 23 °C and 0.975 atm is produced by the decomposition of 5.36 g of HgO?
b. Answer the question.

Answer

a. Determine the moles of HgO that decompose; using the chemical equation, determine the moles of O_2 produced by decomposition of this amount of HgO; and determine the volume of O_2 from the moles of O_2, temperature, and pressure.

b. 0.308 L

Exercise 2.E.38

The chlorofluorocarbon CCl_2F_2 can be recycled into a different compound by reaction with hydrogen to produce $CH_2F_2(g)$, a compound useful in chemical manufacturing:

$$CCl_2F_2(g) + 4\,H_2(g) \longrightarrow CH_2F_2(g) + 2\,HCl(g) \tag{2.E.1}$$

a. Outline the steps necessary to answer the following question: What volume of hydrogen at 225 atm and 35.5 °C would be required to react with 1 ton (1.000×10^3 kg) of CCl_2F_2?
b. Answer the question.

Answer

a. Determine the molar mass of CCl_2F_2. From the balanced equation, calculate the moles of H_2 needed for the complete reaction. From the ideal gas law, convert moles of H_2 into volume.

b. 3.72×10^3 L

Exercise 2.E.39

Lime, CaO, is produced by heating calcium carbonate, $CaCO_3$; carbon dioxide is the other product.

a. Outline the steps necessary to answer the following question: What volume of carbon dioxide at 875° and 0.966 atm is produced by the decomposition of 1 ton (1.000×10^3 kg) of calcium carbonate?
b. Answer the question.

Answer

a. Balance the equation. Determine the grams of CO_2 produced and the number of moles. From the ideal gas law, determine the volume of gas.

b. 7.43×10^5 L

Exercise 2.E.40

Calculate the volume of oxygen required to burn 12.00 L of ethane gas, C_2H_6, to produce carbon dioxide and water, if the volumes of C_2H_6 and O_2 are measured under the same conditions of temperature and pressure.

Answer

42.00 L

Exercise 2.E.41

Consider the following questions:

a. What is the total volume of the $CO_2(g)$ and $H_2O(g)$ at 600 °C and 0.888 atm produced by the combustion of 1.00 L of $C_2H_6(g)$ measured at 0.00 °C and 1.00 atm?
b. What is the partial pressure of H_2O in the product gases?

Answer

a. 18.0 L

b. 0.533 atm

Exercise 2.E.42

What volume of oxygen at 423.0 K and a pressure of 127.4 kPa is produced by the decomposition of 129.7 g of BaO_2 to BaO and O_2?

Answer

10.57 L O_2

Exercise 2.E.43

Ethanol, C_2H_5OH, is produced industrially from ethylene, C_2H_4, by the following sequence of reactions:

$$3\,C_2H_4 + 2\,H_2SO_4 \longrightarrow C_2H_5HSO_4 + (C_2H_5)_2SO_4 \tag{2.E.2}$$

$$C_2H_5HSO_4 + (C_2H_5)_2SO_4 + 3\,H_2O \longrightarrow 3\,C_2H_5OH + 2\,H_2SO_4 \tag{2.E.3}$$

What volume of ethylene at 0.00 °C and 1.00 atm is required to produce 1.000 metric ton (1000 kg) of ethanol if the overall yield of ethanol is 90.1%?

Answer

5.40×10^5 L

Exercise 2.E.44

A sample of a compound of xenon and fluorine was confined in a bulb with a pressure of 18 torr. Hydrogen was added to the bulb until the pressure was 72 torr. Passage of an electric spark through the mixture produced Xe and HF. After the HF was removed by reaction with solid KOH, the final pressure of xenon and unreacted hydrogen in the bulb was 36 torr. What is the empirical formula of the xenon fluoride in the original sample? (Note: Xenon fluorides contain only one xenon atom per molecule.)

Answer

XeF_2

2.5: The Kinetic-Molecular Theory

Exercise 2.E.45

A 1-L sample of CO initially at 0 °C and 1 atm is heated to 546 K, and its volume is increased to 2 L.

a. What effect do these changes have on the number of collisions of the molecules of the gas per unit area of the container wall?
b. What is the effect on the average kinetic energy of the molecules?
c. What is the effect on the root mean square speed of the molecules?

Answer

a. The number of collisions per unit area of the container wall is constant.

b. The average kinetic energy doubles.

c. The root mean square speed increases to $\sqrt{2}$ times its initial value; u_{rms} is proportional to KE_{avg}.

Exercise 2.E.46

The distribution of molecular velocities in a sample of helium is shown in Figure 2.5.4. If the sample is cooled, will the distribution of velocities look more like that of H_2 or of H_2O? Explain your answer.

Answer

H_2O. Cooling slows the velocities of the He atoms, causing them to behave as though they were heavier.

Exercise 2.E.47

Calculate the root-mean-square speed of nitrogen, N_2, molecules in an air sample at 25 ^oC.

Answer

515 m/s

Exercise 2.E.48

What is the ratio of root-mean-square speed values for helium to xenon at 30 ^oC? Which has a higher root-mean-square speed and why?

Answer

0.18, so He has a higher root-mean-square speed

He has a higher root-mean-square speed than xenon, He should be faster as is has a smaller molar mass.

Hint

The temperature is the same so the ratio of root-mean-square speeds becomes the square root of the ratio of molar masses.

$$u_{rms}= \sqrt{\frac{3RT}{m}}$$

2.6: Effusion and Diffusion of Gases

Exercise 2.E.49

A balloon filled with helium gas is found to take 6 hours to deflate to 50% of its original volume. How long will it take for an identical balloon filled with the same volume of hydrogen gas (instead of helium) to decrease its volume by 50%?

Answer

4.2 hours

Exercise 2.E.50

Starting with the definition of rate of effusion and Graham's finding relating rate and molar mass, show how to derive the Graham's law equation, relating the relative rates of effusion for two gases to their molecular masses.

Answer

Effusion can be defined as the process by which a gas escapes through a pinhole into a vacuum. Graham's law states that with a mixture of two gases A and B: $\left(\frac{\text{rate A}}{\text{rate B}}\right) = \left(\frac{\text{molar mass of B}}{\text{molar mass of A}}\right)^{1/2}$. Both A and B are in the same container at the same temperature, and therefore will have the same kinetic energy:

$$\mathrm{KE_A} = \mathrm{KE_B KE} = \frac{1}{2}mv^2 \quad \text{Therefore, } \frac{1}{2}m_\mathrm{A}v_\mathrm{A}^2 = \frac{1}{2}m_\mathrm{B}v_\mathrm{B}^2 \; \frac{v_\mathrm{A}^2}{v_\mathrm{B}^2} = \frac{m_\mathrm{B}}{m_\mathrm{A}} \; \left(\frac{v_\mathrm{A}^2}{v_\mathrm{B}^2}\right)^{1/2} = \left(\frac{m_\mathrm{B}}{m_\mathrm{A}}\right)^{1/2} \; \frac{v_\mathrm{A}}{v_\mathrm{B}} = \left(\frac{m_\mathrm{B}}{m_\mathrm{A}}\right)^{1/2}$$

Exercise 2.E.51

Which of the following gases diffuse more slowly than oxygen? F_2, Ne, N_2O, C_2H_2, NO, Cl_2, H_2S

Answer

F_2, N_2O, Cl_2, H_2S

Exercise 2.E.52

Calculate the relative rate of diffusion of $^1H_2$ (molar mass 2.0 g/mol) compared to that of $^2H_2$ (molar mass 4.0 g/mol) and the relative rate of diffusion of O_2 (molar mass 32 g/mol) compared to that of O_3 (molar mass 48 g/mol).

Answer

1.4; 1.2

2.7: Non-Ideal Gas Behavior

Exercise 2.E.53

Under which of the following sets of conditions does a real gas behave most like an ideal gas, and for which conditions is a real gas expected to deviate from ideal behavior? Explain.

1. high pressure, small volume
2. high temperature, low pressure
3. low temperature, high pressure

Answer

The gas behavior most like an ideal gas will occur under the conditions in (b). Molecules have high speeds and move through greater distances between collision; they also have shorter contact times and interactions are less likely. Deviations occur with the conditions described in (a) and (c). Under conditions of (a), some gases may liquefy. Under conditions of (c), most gases will liquefy.

Exercise 2.E.54

For which of the following gases should the correction for the molecular volume be largest: CO, CO_2, H_2, He, NH_3, SF_6?

Answer

SF_6

Exercise 2.E.55

Answer the following questions:

a. If XX behaved as an ideal gas, what would its graph of Z vs. P look like?
b. For most of this chapter, we performed calculations treating gases as ideal. Was this justified?
c. What is the effect of the volume of gas molecules on Z? Under what conditions is this effect small? When is it large? Explain using an appropriate diagram.

d. What is the effect of intermolecular attractions on the value of Z? Under what conditions is this effect small? When is it large? Explain using an appropriate diagram.
e. In general, under what temperature conditions would you expect Z to have the largest deviations from the Z for an ideal gas?

Answer

a. A straight horizontal line at 1.0

b. When real gases are at low pressures and high temperatures they behave close enough to ideal gases that they are approximated as such, however, in some cases, we see that at a high pressure and temperature, the ideal gas approximation breaks down and is significantly different from the pressure calculated by the van der Waals equation

c. The greater the compressibility, the more the volume matters. At low pressures, the correction factor for intermolecular attractions is more significant, and the effect of the volume of the gas molecules on Z would be a small lowering compressibility. At higher pressures, the effect of the volume of the gas molecules themselves on Z would increase compressibility (see Figure 2.7.1)

d. Once again, at low pressures, the effect of intermolecular attractions on Z would be more important than the correction factor for the volume of the gas molecules themselves, though perhaps still small. At higher pressures and low temperatures, the effect of intermolecular attractions would be larger. (see Figure 2.7.1)

e. low temperatures

Exercise $2.E.56$

A 0.245-L flask contains 0.467 mol CO_2 at 159 °C. Calculate the pressure:

(a) using the ideal gas law

(b) using the van der Waals equation

(c) Explain the reason for the difference.

Answer

a. 67.6 atm

b. 60.5 atm

c. The van der Waals equation pressure is lower than the ideal gas pressure because at these conditions the molecules are attracted to each other so are applying less force on the walls of the flask and the molecules take up space so the volume available to the gas is less than the flask volume. The van der Waals equation corrects for the intermolecular attractions and the volume of gas molecules.

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2.S: Gases (Study Guide)

2.1: Characteristics of Gases

Bulk matter can exist in three states: gas, liquid, and solid. Gases have the lowest density of the three, are highly compressible, and fill their containers completely. Elements that exist as gases at room temperature and pressure are clustered on the right side of the periodic table; they occur as either monatomic gases (the noble gases) or diatomic molecules (some halogens, N_2, O_2).

- Gases expand spontaneously to fill containers in which they are held, equaling their volume. Consequently, they are highly compressible.
- Gases form homogeneous mixtures with each other *regardless* of the identities or relative proportions of the component gases
- The characteristic properties of gases arise because the individual molecules are relatively far apart, hence, acting largely as though they were alone.

2.2: Gas Pressure

Pressure is defined as the force exerted per unit area; it can be measured using a barometer or manometer. Four quantities must be known for a complete physical description of a sample of a gas: temperature, volume, amount, and pressure. Pressure is force per unit area of surface; the SI unit for pressure is the pascal (Pa), defined as 1 newton per square meter (N/m^2). The pressure exerted by an object is proportional to the force it exerts and inversely proportional to the area.

- Pressure, *P*, is the Force, *F*, that acts on a given Area, *A*:

$$P = F/A$$

Atmospheric Pressure and units

- The force, *F*, exerted by any object is the product of its mass, *m*, times its acceleration, *a*: *F* = *ma*
- SI unit for force is kg-m/s^2 and is called the *Newton* (N)
- SI unit of pressure is N/m^2, called a Pascal
- **Standard atmospheric pressure**: defined as 760 torr (760 mm Hg), or, in SI units, 101.325 kPa
- **Atmosphere**: unit of pressure equal to 760 torr; 1 atm = 101.325 kPa
- To convert between pressures of different units use our dimensional analysis approach and write down all units including those on conversion factors.

Barometer

A barometer is used to measure atmospheric pressure, which is the force exerted by the atmosphere on the earth's surface.

Manometer

A manometer can be used to measure the pressure of a gas trapped in a container. An open end manometer has one arm open to the atmosphere and a non-liquid such as mercury between the open arm and the gas. A closed-end manometer has a vacuum in the closed end.

2.3: Relating Pressure, Volume, Amount, and Temperature - The Ideal Gas Law

The volume of a gas is inversely proportional to its pressure and directly proportional to its temperature and the amount of gas. Boyle showed that the volume of a sample of a gas is inversely proportional to pressure (Boyle's law), Charles and Gay-Lussac demonstrated that the volume of a gas is directly proportional to its temperature at constant pressure (Charles's law), and Avogadro showed that the volume of a gas is directly proportional to the number of moles of gas (Avogadro's law).

The Pressure-Volume Relationship: Boyle's Law

- Boyle's law states that the volume of a fixed quantity of gas maintained at constant temperature is inversely proportional to the pressure. When two measurements are inversely proportional, one gets smaller as the other one gets larger.

$$PV = constant$$

where P = pressure, V = volume

The Temperature-Volume Relationship: Charles's Law

- **Charles's law**: states that the volume of a fixed amount of gas maintained at constant pressure is directly proportional to its absolute temperature. Thus, as the pressure gets higher, so does the temperature.

$$\frac{V}{T} = constant$$

where V = volume, T = Temperature

The Quantity-Volume Relationship: Avogadro's Law

- **Law of combining volumes**: at a given pressure and temperature, the volumes of gases that react with one another are in the ratios of small whole numbers. (ie: $2H_2 + O_2 = 2H_2O$)
- **Avogadro's hypothesis**: equal volumes of gases at the same temperature and pressure contain equal number of molecules
- **Avogadro's law**: The volume of a gas maintained at constant temperature and pressure is directly proportional to the number of moles of the gas

$$V = constant \times n$$

where V = volume, *n* = number of moles

Ideal-gas equation

The empirical relationships among the volume, the temperature, the pressure, and the amount of a gas can be combined into the ideal gas law, PV = nRT. The proportionality constant, R, is called the gas constant. The ideal gas law describes the behavior of an ideal gas, a hypothetical substance whose behavior can be explained quantitatively by the ideal gas law and the kinetic molecular theory of gases. Standard temperature and pressure (STP) is 0°C and 1 atm.

$$PV = nRT$$

where P = pressure, V = volume, n = number of moles, R = gas constant, T = Temperature (always expressed on absolute-temperature scale, usually Kelvin)

The *Gas constant* (R) is the constant of proportionality in the ideal-gas equation. Some values of R are given below

Some values of R

Units	Numerical value
L-atm/mol-K	0.08206
Cal/mol-K	1.987
J/mol-K	8.314
M^3-Pa/mol-K	8.314
L-torr/mol-K	62.36

Standard temperature and pressure (STP): 0°C and 1 bar. Older version of STP was 0°C and 1 atm. 1 mol of gas at STP has a volume of 22.7 L (*molar volume*), and at 0°C and 1 atm 1 mol of gas has a volume of 22.4 L.

2.4: Stoichiometry of Gaseous Substances, Mixtures, and Reactions

The relationship between the amounts of products and reactants in a chemical reaction can be expressed in units of moles or masses of pure substances, of volumes of solutions, or of volumes of gaseous substances. The ideal gas law can be used to calculate the volume of gaseous products or reactants as needed. In the laboratory, gases produced in a reaction are often collected by the displacement of water from filled vessels; the amount of gas can be calculated from the volume of water displaced.

Density of a gas (*\rho\) = density, M = molar mass):

\[\rho = \dfrac{PM}{ RT} \nonumber \]

Molar mass of a gas:

$$M = \frac{\rho RT}{P}$$

Gas Mixtures and Partial Pressures

The pressure exerted by each gas in a gas mixture is independent of the pressure exerted by all other gases present. Consequently, the total pressure exerted by a mixture of gases is the sum of the partial pressures of the components (Dalton's law of partial pressures). The amount of gas in a mixture may be described by its partial pressure or its mole fraction. In a mixture, the partial pressure of each gas is the product of the total pressure and the mole fraction.

- **Partial pressure**: the pressure exerted by a particular gas in a mixture
- **Dalton's law of partial pressures**: law stating that the total pressure of a mixture of gases equals the sum of the pressures that each would exert if it were present alone

The total pressure at constant temperature and volume is determined by the total number of moles of gas present, whether that total represents just one substance or a mixture

Partial Pressures and Mole Fractions

- **Mole fraction**: the ratio of the number of one component of a mixture to the total moles of all components; abbreviated χ, with a subscript to identify the components.

The partial pressure of a gas in a mixture is its mole fraction times the total pressure

2.5: Kinetic-Molecular Theory

The behavior of ideal gases is explained by the kinetic molecular theory of gases. Molecular motion, which leads to collisions between molecules and the container walls, explains pressure, and the large intermolecular distances in gases explain their high compressibility. Although all gases have the same average kinetic energy at a given temperature, they do not all possess the same root mean square speed. The actual values of speed and kinetic energy are not the same for all gas particles.

Kinetic-molecular theory: set of assumptions about the nature of gases. These assumptions, when translated into mathematical form, yield the ideal-gas equation

1. Gases consist of large numbers of molecules that are in continuous, random motion
2. The volume of all the molecules of the gas is negligible compared to the total volume in which the gas is contained
3. Attractive and repulsive forces between gas molecules are negligible
4. Energy can be transferred between molecules during collisions, but the *average* kinetic energy of the molecules does *not* change with time, as long as the temperature of the gas remains constant
5. The average kinetic energy of the molecules is proportional to absolute temperature. At any given temperature, the molecules of all gases have the same average kinetic energy

The pressure of a gas is caused by collisions of molecules with the walls of the container. The magnitude of the pressure is determined by how often and how "hard" the molecules strike the walls.

If two different gases are at the same temperature, they have the same average kinetic energy. If the temperature of a gas is doubled, its kinetic energy also doubles. Hence, molecular motion increases with increasing temperature.

- **Root-mean-square (rms) speed**: the square root of the squared speeds of the gas molecules in a gas sample. This quantity is the speed of a molecule possessing average kinetic energy.

The rms speed is important because the average kinetic energy of the gas molecules, ε, is related directly to u^2:

$$\varepsilon = \frac{1}{2}mu^2$$

where m is the mass of the molecule

Because mass doesn't change with temperature, the rms speed (and also the average speed) of molecules must increase as temperature increases

Applications to the Gas Laws

1. *Effect of a volume increase at constant temperature*: If the volume is increased, the molecules must move a longer distance between collisions. Consequently, there are fewer collisions per unit time with the container walls, and pressure decreases.
2. *Effect of a temperature increase at constant volume*: An increases in temperature means an increase in the average kinetic energy of the molecules. If there is no change in volume, there will be more collisions with the walls per unit time. Furthermore,

the molecules strike harder, hence explaining how the observed pressure increases.

2.6: Effusion and Diffusion of Gases

Diffusion is the gradual mixing of gases to form a sample of uniform composition even in the absence of mechanical agitation. In contrast, effusion is the escape of a gas from a container through a tiny opening into an evacuated space. The rate of effusion of a gas is inversely proportional to the square root of its molar mass (Graham's law), a relationship that closely approximates the rate of diffusion. As a result, light gases tend to diffuse and effuse much more rapidly than heavier gases.

A gas composed of light gas particles will have the same average kinetic energy as one composed of much heavier particles, provided that the two gases are at the same temperature. The mass, m, of the particles in the lighter gas is smaller that that in the heavier gas. Consequently, the particles of the lighter gas must have a higher rms speed, u, than the heavier one:

$$u = \sqrt{\frac{3RT}{M}}$$

Since M is in the denominator, the less massive the gas molecules, the higher the rms speed

- **Effusion**: the escape of a gas through an orifice or hole. The rate of effusion depends on the molecular mass of the gas.
- **Diffusion**: the spreading of one substance through a space or through another substance

Graham's Law of Effusion

- **Graham's law**: law stating that the rate of effusion of a gas is inversely proportional to the square root of its molecular weight

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

where r is the rate of effusion

- The rate of effusion is also directly proportional to the rms speed of the molecules. This is because the only way for the molecule to escape is to "collide" with the opening. Hence, the faster the molecules are moving, the greater the likelihood that a molecule will hit the opening and effuse.

Diffusion and Mean Free Path

- Diffusion, like effusion, is faster for light molecules than for heavy ones. The diffusion of gases is much slower than molecular speeds because of molecular collisions. Because of these collisions, the direction of motion of a gas molecule is constantly changing, making this a slow process.
- **Mean free path**: average distance traveled by a molecule between collisions. The higher the density of a gas, the smaller the mean free path

2.7: Non-Ideal Gas Behavior

No real gas exhibits ideal gas behavior, although many real gases approximate it over a range of conditions. Gases most closely approximate ideal gas behavior at high temperatures and low pressures. Deviations from ideal gas law behavior can be described by the van der Waals equation, which includes empirical constants to correct for the actual volume of the gaseous molecules and quantify the reduction in pressure due to intermolecular attractive forces.

The ideal gas equation may be rearranged as follows to understand deviations from ideal-gas behavior:

$$\frac{PV}{RT} = n$$

- For a mole of ideal gas (n = 1), the quantity PV / RT = 1 at all pressures. However, real gases do not behave in such a way. At high pressures, the deviation is very high, however it is less with lower pressures. In general, the deviations from idea behavior increase as temperature decreases, becoming significant near the temperature at which the gas is converted into a liquid.
- Basic assumptions in the kinetic molecular theory suggest that molecules of an ideal gas occupy no space and have no attraction for each other. *Real molecules, however, do have finite volumes, and they do attract one another*.
- Also, if the volume of the container in which the gas is contained is large, the molecules have plenty of free space, and do not take much of the container's volume itself. However, as pressure increases, the gas molecules occupy a much larger fraction of the container's volume.

- In addition, the attractive forces between molecules come into play at short distances, as when molecules are crowded together at high pressures. Because of these attractive forces, the impact of a given molecule with the wall of the container is lessened.
- Temperature determines how effective attractive forces between gas molecules are. As the gas is cooled, the average kinetic energy decreases, while intermolecular attractions remain constant.

The Van der Waals Equation

According to the ideal gas equation:

$$\underbrace{P = \frac{nRT}{V}}_{\text{ideal gas}}$$

According to Van der Waals:

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

Correction for volume of molecules – Correction for molecular attractions

- The Van der Waals constant *b* is a measure of the actual volume occupied by a mole of gas molecules; *b* has units of L/mol.
- The Van der Walls constant *a* has units of L^2-atm/mol^2. The magnitude of *a* reflects how strongly the gas molecules attract each other

Van der Waals equation

$$\left[P + \left(\frac{n^2 a}{V^2}\right)\right](V - nb) = nRT$$

The Van der Waals constants *a* and *b* are different for each gas. The values of these constants generally increase with an increase in mass of the molecule and with an increase in the complexity of its structures.

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CHAPTER OVERVIEW

3: Thermochemistry

This chapter introduces you to **thermochemistry**, a branch of chemistry that describes the energy changes that occur during chemical reactions. In some situations, the energy produced by chemical reactions is actually of greater interest to chemists than the material products of the reaction. For example, the controlled combustion of organic molecules, primarily sugars and fats, within our cells provides the energy for physical activity, thought, and other complex chemical transformations that occur in our bodies. Similarly, our energy-intensive society extracts energy from the combustion of fossil fuels, such as coal, petroleum, and natural gas, to manufacture clothing and furniture, heat your home in winter and cool it in summer, and power the car or bus that gets you to class and to the movies. By the end of this chapter, you will know enough about thermochemistry to explain why ice cubes cool a glass of soda, how instant cold packs and hot packs work, and why swimming pools and waterbeds are heated. You will also understand what factors determine the caloric content of your diet and why even “nonpolluting” uses of fossil fuels may be affecting the environment.

3.1: The Nature of Energy
3.2: The First Law of Thermodynamics
3.3: Enthalpy
3.4: Enthalpy of Reaction
3.5: Calorimetry
3.6: Hess's Law
3.7: Enthalpies of Formation
3.8: Types of Solutions and Solubility
3.9: Foods and Fuels
3.E: Thermochemistry (Exercises)
3.S: Thermochemistry (Study Guide)

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3.1: The Nature of Energy

Learning Objectives

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

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

Forms of Energy

The forms of energy include thermal energy, radiant energy, electrical energy, nuclear energy, and chemical energy (Figure 3.1.1). Thermal energy results from atomic and molecular motion; the faster the motion, the greater the thermal energy. The temperature of an object is a measure of its thermal energy content. Radiant energy is the energy carried by light, microwaves, and radio waves. Objects left in bright sunshine or exposed to microwaves become warm because much of the radiant energy they absorb is converted to thermal energy. Electrical energy results from the flow of electrically charged particles. When the ground and a cloud develop a separation of charge, for example, the resulting flow of electrons from one to the other produces lightning, a natural form of electrical energy. Nuclear energy is stored in the nucleus of an atom, and chemical energy is stored within a chemical compound because of a particular arrangement of atoms.

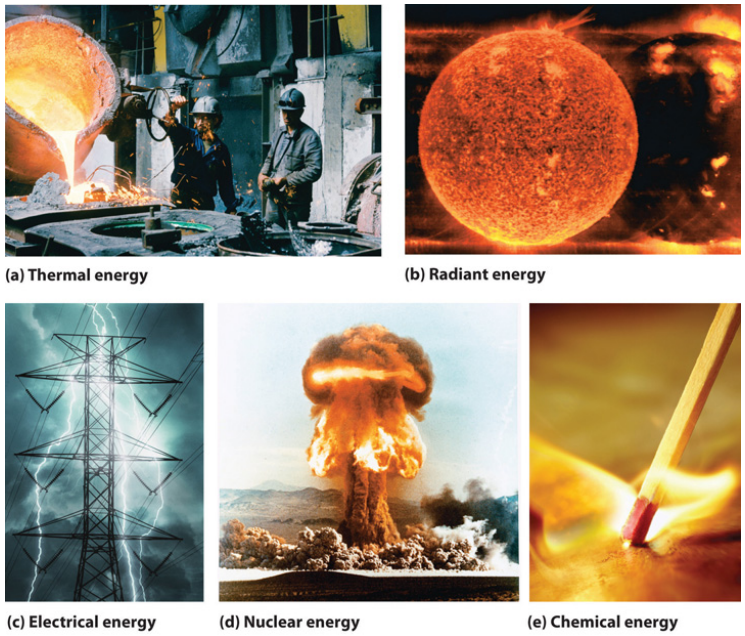


Figure 3.1.1: Forms of Energy. (a) *Thermal energy* results from atomic and molecular motion; molten steel at 2000°C has a very high thermal energy content. (b) *Radiant energy* (e.g., from the sun) is the energy in light, microwaves, and radio waves. (c) Lightning is an example of *electrical energy*, which is due to the flow of electrically charged particles. (d) *Nuclear energy* is released when particles in the nucleus of the atom are rearranged. (e) *Chemical energy* results from the particular arrangement of atoms in a chemical compound; the heat and light produced in this reaction are due to energy released during the breaking and reforming of chemical bonds.

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

Energy can be converted from one form to another (Figure 3.1.2) or, as we saw with the brick, transferred from one object to another. For example, when you climb a ladder to a high diving board, your body uses chemical energy produced by the combustion of organic molecules. As you climb, the chemical energy is converted to *mechanical work* to overcome the force of gravity. When you stand on the end of the diving board, your potential energy is greater than it was before you climbed the ladder: the greater the distance from the water, the greater the potential energy. When you then dive into the water, your potential energy is converted to kinetic energy as you fall, and when you hit the surface, some of that energy is transferred to the water, causing it to splash into the air. Chemical energy can also be converted to radiant energy; one common example is the light emitted by fireflies, which is produced from a chemical reaction.

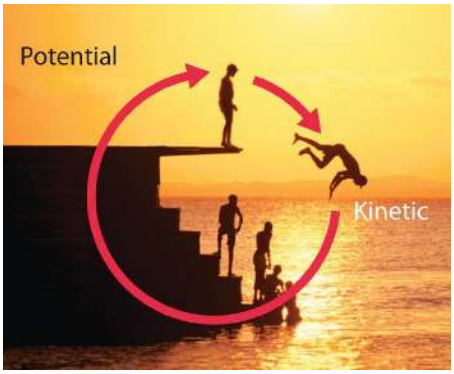


Figure 3.1.2: Interconversion of Forms of Energy. When a swimmer steps off the platform to dive into the water, potential energy is converted to kinetic energy. As the swimmer climbs back up to the top of the diving platform, chemical energy is converted to mechanical work.

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

Energy, Heat, and Work

One definition of energy is the capacity to do work. The easiest form of work to visualize is mechanical work (Figure 3.1.3), which is the energy required to move an object a distance d when opposed by a force F, such as gravity:

work = force x distance

$$w = F\,d \tag{3.1.1}$$

Because the force (F) that opposes the action is equal to the mass (m) of the object times its acceleration (a), we can also write Equation 3.1.1 as follows:

work= mass x acceleration x distance

$$w = m\,a\,d \tag{3.1.2}$$

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

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

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

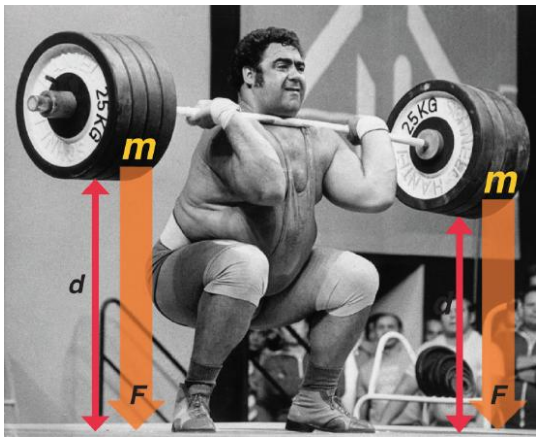


Figure 3.1.2: An Example of Mechanical Work. One form of energy is mechanical work, the energy required to move an object of mass *m* a distance *d* when opposed by a force *F*, such as gravity.

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

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

Kinetic and Potential Energy

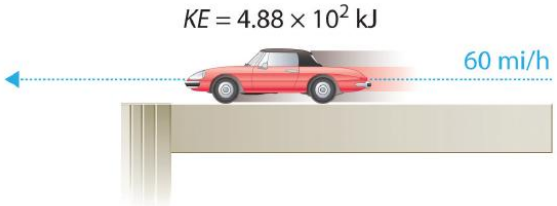
The kinetic energy of an object is related to its mass m and velocity v:

$$KE = \frac{1}{2}mv^2 \tag{3.1.3}$$

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

$$KE = \frac{1}{2}(1360kg)(26.8ms)^2 = 4.88 \times 10^5 g \cdot m^2 \tag{3.1.4}$$

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



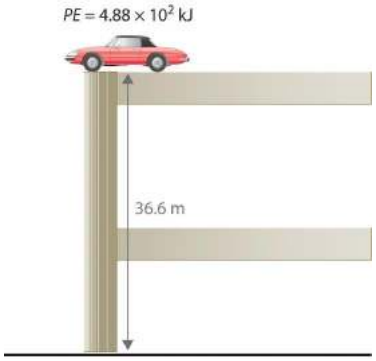
To demonstrate, let's calculate the potential energy of the same 1360 kg automobile if it were parked on the top level of a parking garage 36.6 m (120 ft) high. Its potential energy is equivalent to the amount of work required to raise the vehicle from street level to the top level of the parking garage, which is *w* = *Fd*. According to Equation 3.1.2, the force (*F*) exerted by gravity on any object is equal to its mass (*m*, in this case, 1360 kg) times the acceleration (*a*) due to gravity (*g*, 9.81 m/s^2 at Earth's surface). The distance (*d*) is the height (*h*) above street level (in this case, 36.6 m). Thus the potential energy of the car is as follows:

$$PE = F\ d = m\ a\ d = m\ g\ h \tag{3.1.5}$$

$$PE = (1360, Kg)\left(\frac{9.81\, m}{s^2}\right)(36.6\ m) = 4.88 \times 10^5\ \frac{Kg \cdot m}{s^2} \tag{3.1.6}$$

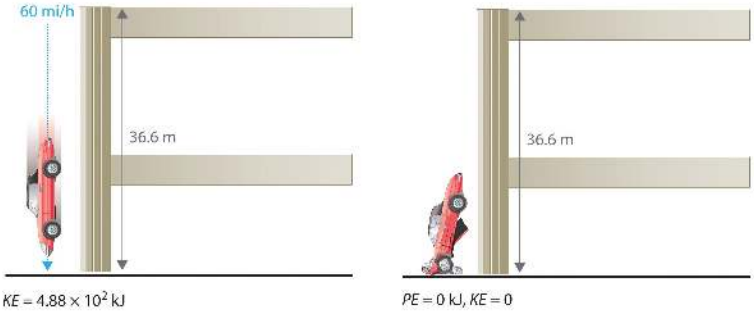
$$= 4.88 \times 10^5 J = 488\ kJ \tag{3.1.7}$$

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



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

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



When the car is falling from the top of the parking structure it has a kinetic energy of 488 kilojoules. When the car hits the floor is has a potential and kinetic energy of zero.

Units of Energy

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

$$1\ cal = 4.184\ J \text{ exactly} \tag{3.1.8}$$

$$1\ J = 0.2390\ cal \tag{3.1.9}$$

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

Example 3.1.1

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

Given: mass and velocity or height

Asked for: kinetic and potential energy

Strategy:

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

Solution:

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

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

The kinetic energy of the baseball is therefore

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

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

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

Exercise 3.1.1

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

Answer a

3.10×10^2 J

Answer b

65 J

Summary

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

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3.2: The First Law of Thermodynamics

Learning Objectives

- To calculate changes in internal energy

To study the flow of energy during a chemical reaction, we need to distinguish between a system, the small, well-defined part of the universe in which we are interested (such as a chemical reaction), and its surroundings, the rest of the universe, including the container in which the reaction is carried out (Figure 3.2.1). In the discussion that follows, the mixture of chemical substances that undergoes a reaction is always the system, and the flow of heat can be from the system to the surroundings or vice versa.

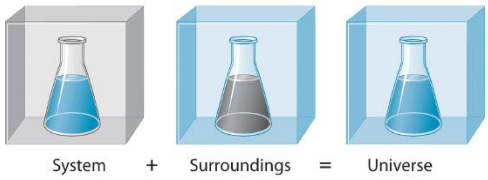


Figure 3.2.1: A System and Its Surroundings. The system is that part of the universe we are interested in studying, such as a chemical reaction inside a flask. The surroundings are the rest of the universe, including the container in which the reaction is carried out.

Three kinds of systems are important in chemistry. An **open system** can exchange both matter and energy with its surroundings. A pot of boiling water is an open system because a burner supplies energy in the form of heat, and matter in the form of water vapor is lost as the water boils. A **closed system** can exchange energy but not matter with its surroundings. The sealed pouch of a ready-made dinner that is dropped into a pot of boiling water is a closed system because thermal energy is transferred to the system from the boiling water but no matter is exchanged (unless the pouch leaks, in which case it is no longer a closed system). An **isolated system** exchanges neither energy nor matter with the surroundings. Energy is always exchanged between a system and its surroundings, although this process may take place very slowly. A truly isolated system does not actually exist. An insulated thermos containing hot coffee approximates an isolated system, but eventually the coffee cools as heat is transferred to the surroundings. In all cases, the amount of heat lost by a system is equal to the amount of heat gained by its surroundings and vice versa. That is, *the total energy of a system plus its surroundings is constant*, which must be true if *energy is conserved*.

The state of a system is a complete description of a system at a given time, including its temperature and pressure, the amount of matter it contains, its chemical composition, and the physical state of the matter. A state function is a property of a system whose magnitude depends on only the present state of the system, not its previous history. Temperature, pressure, volume, and potential energy are all state functions. The temperature of an oven, for example, is independent of however many steps it may have taken for it to reach that temperature. Similarly, the pressure in a tire is independent of how often air is pumped into the tire for it to reach that pressure, as is the final volume of air in the tire. Heat and work, on the other hand, are not state functions because they are *path dependent*. For example, a car sitting on the top level of a parking garage has the same potential energy whether it was lifted by a crane, set there by a helicopter, driven up, or pushed up by a group of students (Figure 3.2.2). The amount of work expended to get it there, however, can differ greatly depending on the path chosen. If the students decided to carry the car to the top of the ramp, they would perform a great deal more work than if they simply pushed the car up the ramp (unless, of course, they neglected to release the parking brake, in which case the work expended would increase substantially!). The potential energy of the car is the same, however, no matter which path they choose.



Figure 3.2.2: Elevation as an Example of a State Function. The change in elevation between state 1 (at the bottom of the parking garage) and state 2 (at the top level of the parking garage) is the same for both paths A and B; it does not depend on which path is taken from the bottom to the top. In contrast, the distance traveled and the work needed to reach the top do depend on which path is taken. Elevation is a state function, but distance and work are *not* state functions.

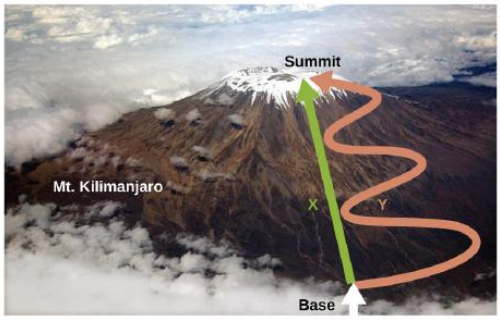


Figure 3.2.3: Paths X and Y represent two different routes to the summit of Mt. Kilimanjaro. Both have the same change in elevation (altitude or elevation on a mountain is a state function; it does not depend on path), but they have very different distances traveled (distance walked is not a state function; it depends on the path). credit: modification of work by Paul Shaffner

Direction of Heat Flow

The reaction of powdered aluminum with iron(III) oxide, known as the thermite reaction, generates an enormous amount of heat—enough, in fact, to melt steel (Figure 3.2.3). The balanced chemical equation for the reaction is as follows:

$$2\,\mathrm{Al(s)} + \mathrm{Fe_2O_3(s)} \longrightarrow 2\,\mathrm{Fe(s)} + \mathrm{Al_2O_3(s)} \tag{3.2.1}$$



Figure 3.2.4: The thermite reaction produces so much heat that the iron it produces comes out molten, a property that makes this reaction useful in welding. Image by Kingfisher [CC BY-SA 3.0 (Creative Commons [creativecommons.org])], from Wikimedia Commons.

We can also write this chemical equation as

$$2\,\mathrm{Al(s)} + \mathrm{Fe_2O_3(s)} \rightarrow 2\,\mathrm{Fe(s)} + \mathrm{Al_2O_3(s)} + \mathrm{heat} \tag{3.2.2}$$

to indicate that heat is one of the products. Chemical equations in which heat is shown as either a reactant or a product are called *thermochemical equations*. In this reaction, the system consists of aluminum, iron, and oxygen atoms; everything else, including the container, makes up the surroundings. During the reaction, so much heat is produced that the iron liquefies. Eventually, the

system cools; the iron solidifies as heat is transferred to the surroundings. A process in which heat (q) is transferred *from* a system *to* its surroundings is described as exothermic. By convention, $q < 0$ for an exothermic reaction.

When you hold an ice cube in your hand, heat from the surroundings (including your hand) is transferred to the system (the ice), causing the ice to melt and your hand to become cold. We can describe this process by the following thermochemical equation:

$$\text{heat} + \text{H}_2\text{O(s)} \rightarrow \text{H}_2\text{O(l)} \tag{3.2.3}$$

When heat is transferred *to* a system *from* its surroundings, the process is endothermic. By convention, $q > 0$ for an endothermic reaction.

Heat is technically not a component in Chemical Reactions

Technically, it is poor form to have a $heat$ term in the chemical reaction like in Equations 3.2.2 and 3.2.3 since is it not a true species in the reaction. However, this is a convenient approach to represent exothermic and endothermic behavior and is commonly used by chemists.

The First Law

The relationship between the energy change of a system and that of its surroundings is given by the **first law of thermodynamics**, which states that the energy of the universe is constant. We can express this law mathematically as follows:

$$\Delta U_{univ} = \Delta U_{sys} + \Delta U_{surr} = 0 \tag{3.2.4}$$

$$\Delta U_{sys} = -\Delta U_{surr} \tag{3.2.5}$$

where the subscripts univ, sys, and surr refer to the universe, the system, and the surroundings, respectively. Thus the change in energy of a system is identical in magnitude but opposite in sign to the change in energy of its surroundings.

The tendency of all systems, chemical or otherwise, is to move toward the state with the lowest possible energy.

An important factor that determines the outcome of a chemical reaction is the tendency of all systems, chemical or otherwise, to move toward the lowest possible overall energy state. As a brick dropped from a rooftop falls, its potential energy is converted to kinetic energy; when it reaches ground level, it has achieved a state of lower potential energy. Anyone nearby will notice that energy is transferred to the surroundings as the noise of the impact reverberates and the dust rises when the brick hits the ground. Similarly, if a spark ignites a mixture of isooctane and oxygen in an internal combustion engine, carbon dioxide and water form spontaneously, while potential energy (in the form of the relative positions of atoms in the molecules) is released to the surroundings as heat and work. The internal energy content of the CO_2/H_2O product mixture is less than that of the isooctane/ O_2 reactant mixture. The two cases differ, however, in the form in which the energy is released to the surroundings. In the case of the falling brick, the energy is transferred as work done on whatever happens to be in the path of the brick; in the case of burning isooctane, the energy can be released as solely heat (if the reaction is carried out in an open container) or as a mixture of heat and work (if the reaction is carried out in the cylinder of an internal combustion engine). Because heat and work are the only two ways in which energy can be transferred between a system and its surroundings, any change in the internal energy of the system is the sum of the heat transferred (q) and the work done (w):

$$\Delta U_{sys} = q + w \tag{3.2.6}$$

Although q and w are not state functions on their own, their sum (ΔU_{sys}) is independent of the path taken and is therefore a state function. A major task for the designers of any machine that converts energy to work is to maximize the amount of work obtained and minimize the amount of energy released to the environment as heat. An example is the combustion of coal to produce electricity. Although the maximum amount of energy available from the process is fixed by the energy content of the reactants and the products, the fraction of that energy that can be used to perform useful work is not fixed.

Because we focus almost exclusively on the changes in the energy of a system, we will not use “sys” as a subscript unless we need to distinguish explicitly between a system and its surroundings.

Although q and w are not state functions, their sum (ΔU_{sys}) is independent of the path taken and therefore is a state function.

Thus, because of the first law, we can determine ΔU for any process if we can measure both q and w. Heat, q, may be calculated by measuring a change in temperature of the surroundings. Work, w, may come in different forms, but it too can be measured. One important form of work for chemistry is *pressure-volume work* done by an expanding gas. At a constant external pressure (for example, atmospheric pressure)

$$w = -P\Delta V \tag{3.2.7}$$

The negative sign associated with PV work done indicates that the system loses energy when the volume increases. That is, an expanding gas does work on its surroundings, while a gas that is compressed has work done on it by the surroundings.

Example 3.2.1

A sample of an ideal gas in the cylinder of an engine is compressed from 400 mL to 50.0 mL during the compression stroke against a constant pressure of 8.00 atm. At the same time, 140 J of energy is transferred from the gas to the surroundings as heat. What is the total change in the internal energy (ΔU) of the gas in joules?

Given: initial volume, final volume, external pressure, and quantity of energy transferred as heat

Asked for: total change in internal energy

Strategy:

A. Determine the sign of q to use in Equation 3.2.6.

B. From Equation 3.2.7 calculate w from the values given. Substitute this value into Equation 3.2.6 to calculate ΔU.

Solution

A From Equation 3.2.6, we know that ΔU = q + w. We are given the magnitude of q (140 J) and need only determine its sign. Because energy is transferred from the system (the gas) to the surroundings, q is negative by convention.

B Because the gas is being compressed, we know that work is being done on the system, so w must be positive. From Equation 3.2.6,

$$w = -P_{\text{ext}}\Delta V = -8.00\ \text{atm}(0.0500\ \text{L} - 0.400\ \text{L})\left(\frac{101.3\ \text{J}}{\text{L}\cdot\text{atm}}\right) = 284\ \text{J}$$

Thus

$$\begin{aligned}\Delta U &= q + w \\ &= -140\ J + 284\ J \\ &= 144\ J\end{aligned}$$

In this case, although work is done on the gas, increasing its internal energy, heat flows from the system to the surroundings, decreasing its internal energy by 144 J. The work done and the heat transferred can have opposite signs.

Exercise 3.2.1

A sample of an ideal gas is allowed to expand from an initial volume of 0.200 L to a final volume of 3.50 L against a constant external pressure of 0.995 atm. At the same time, 117 J of heat is transferred from the surroundings to the gas. What is the total change in the internal energy (ΔU) of the gas in joules?

Answer

−216 J

By convention (to chemists), both heat flow and work have a negative sign when energy is transferred from a system to its surroundings and vice versa.

Summary

In chemistry, the small part of the universe that we are studying is the **system**, and the rest of the universe is the **surroundings**. **Open systems** can exchange both matter and energy with their surroundings, **closed systems** can exchange energy but not matter with their surroundings, and **isolated systems** can exchange neither matter nor energy with their surroundings. A **state function** is a property of a system that depends on only its present **state**, not its history. A reaction or process in which heat is transferred from a system to its surroundings is **exothermic**. A reaction or process in which heat is transferred to a system from its surroundings is **endothermic**. The first law of thermodynamics states that the energy of the universe is constant. The change in the internal energy of a system is the sum of the heat transferred and the work done. The heat flow is equal to the change in the internal energy of the system plus the PV work done. When the volume of a system is constant, changes in its internal energy can be calculated by substituting the ideal gas law into the equation for ΔU.

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3.3: Enthalpy

Learning Objectives

- To know the key features of a state function.
- To use Hess's law and thermochemical cycles to calculate enthalpy changes of chemical reactions.

Both heat and work represent energy transfer mechanisms. As discussed previously, the term "heat" refers to a *process* in which a body (the contents of a tea kettle, for example) acquires or loses energy as a direct consequence of its having a *different temperature* than its surroundings. Similarly, work refers to the transfer of energy that does not involve temperature differences. Hence, work, like energy, can take various forms, the most familiar being mechanical and electrical.

- *Mechanical work* arises when an object moves a distance Δx against an opposing force f:

$$w_{mechanical} = f\ \Delta x$$

- *Electrical work* is done when a body having a charge q moves through a potential difference ΔV.

$$w_{electrical} = q\Delta V$$

The unit of work is Joules. Work, like heat, exists only when energy is being transferred. When two bodies are placed in thermal contact and energy flows from the warmer body to the cooler one, this process is called "heat". A transfer of energy to or from a system by any means other than heat is called "work".

Enthalpy as a Composite Function

To further understand the relationship between heat flow (q) and the resulting change in internal energy (ΔU), we can look at two sets of limiting conditions: reactions that occur at constant volume and reactions that occur at constant pressure. We will assume that PV work is the only kind of work possible for the system, so we can substitute its definition $w = -P\Delta V$ into the first Law of Thermodynamics ($\Delta U = q + w$) to obtain the following:

$$\Delta U = q - P\Delta V \tag{3.3.1}$$

where the subscripts have been deleted.

If the reaction occurs in a closed vessel, the volume of the system is fixed, and ΔV is zero. Under these conditions, the heat flow (often given the symbol q_v to indicate constant volume) must equal ΔU:

$$\underset{\text{constant volume}}{q_v = \Delta U} \tag{3.3.2}$$

> *At constant volume, no PV work can be done, and the change in the internal energy of the system is equal to the amount of heat transferred from the system to the surroundings or vice versa.*

Many chemical reactions are not, however, carried out in sealed containers at constant volume but in open containers at a more or less constant pressure of about 1 atm. The heat flow under these conditions is given the symbol q_p to indicate constant pressure. Replacing q in Equation 3.3.2 by q_p and rearranging to solve for q_p,

$$\underset{\text{constant pressure}}{q_p = \Delta U + P\Delta V} \tag{3.3.3}$$

Thus, at constant pressure, the heat flow for any process is equal to the change in the internal energy of the system plus the PV work done.

Because conditions of constant pressure are so important in chemistry, a new state function called enthalpy (H) is defined as

$$H = U + PV$$

At constant pressure, the change in the enthalpy of a system is as follows:

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + P\Delta V \tag{3.3.4}$$

Comparing the previous two equations shows that at constant pressure, the change in the enthalpy of a system is equal to the heat flow: $\Delta H = q_p$. This expression is consistent with our definition of enthalpy, where we stated that enthalpy is the heat absorbed or produced during any process that occurs at constant pressure.

> *At constant pressure, the change in the enthalpy of a system is equal to the heat flow:* $\Delta H = q_p$.

Example 3.3.1

The molar enthalpy of fusion for ice at 0.0°C and a pressure of 1.00 atm is 6.01 kJ, and the molar volumes of ice and water at 0°C are 0.0197 L and 0.0180 L, respectively. Calculate ΔH and ΔU for the melting of ice at 0.0°C.

Given: enthalpy of fusion for ice, pressure, and molar volumes of ice and water

Asked for: ΔH and ΔU for ice melting at 0.0°C

Strategy:

A. Determine the sign of q and set this value equal to ΔH.
B. Calculate Δ(PV) from the information given.
C. Determine ΔU by substituting the calculated values into Equation 3.3.4.

Solution

A Because 6.01 kJ of heat is absorbed from the surroundings when 1 mol of ice melts, q = +6.01 kJ. When the process is carried out at constant pressure, $q = q_p = \Delta H = 6.01$ kJ.

B To find ΔU using Equation ???, we need to calculate Δ(PV). The process is carried out at a constant pressure of 1.00 atm, so

$$\Delta(PV) = P\Delta V = P(V_f - V) = (1.00\ \text{atm})(0.0180\ \text{L} - 0.0197\ \text{L}) \tag{3.3.5}$$

$$= (-1.7 \times 10^{-3}\ \text{L}\cdot\text{atm})(101.3\ \text{J/L}\cdot\text{atm}) = -0.0017\ \text{J} \tag{3.3.6}$$

C Substituting the calculated values of ΔH and PΔV into Equation 18.11,

$$\Delta U = \Delta H - P\Delta V = 6010\ \text{J} - (-0.0017\ \text{J}) = 6010\ \text{J} = 6.01\ \text{kJ}$$

Exercise 3.3.1

At 298 K and 1 atm, the conversion of graphite to diamond requires the input of 1.850 kJ of heat per mole of carbon. The molar volumes of graphite and diamond are 0.00534 L and 0.00342 L, respectively. Calculate ΔH and ΔU for the conversion of C (graphite) to C (diamond) under these conditions.

Answer a

ΔH = 1.85 kJ/mol

Answer b

ΔU = 1.85 kJ/mol

The Relationship between ΔH and ΔU

If ΔH for a reaction is known, we can use the change in the enthalpy of the system (Equation 3.3.4) to calculate its change in internal energy. When a reaction involves only solids, liquids, liquid solutions, or any combination of these, the volume does not change appreciably (ΔV = 0). Under these conditions, we can simplify Equation 3.3.4 to ΔH = ΔU. If gases are involved, however, ΔH and ΔU can differ significantly. We can calculate ΔU from the measured value of ΔH by using the right side of Equation 3.3.4 together with the ideal gas law, PV = nRT. Recognizing that Δ(PV) = Δ(nRT), we can rewrite Equation 3.3.4 as follows:

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + \Delta(nRT) \tag{3.3.7}$$

At constant temperature, Δ(nRT) = RTΔn, where Δn is the difference between the final and initial numbers of moles of gas. Thus

$$\Delta U = \Delta H - RT\Delta n \tag{3.3.8}$$

For reactions that result in a net production of gas, Δn > 0, so ΔU < ΔH. Conversely, endothermic reactions (ΔH > 0) that result in a net consumption of gas have Δn < 0 and ΔU > ΔH. The relationship between ΔH and ΔU for systems involving gases is illustrated in Example 3.3.2.

For reactions that result in a net production of gas, ΔU < ΔH. For endothermic reactions that result in a net consumption of gas, ΔU > ΔH.

Example 3.3.2: The Relationship Between ΔH and ΔU in Gas Evolving Reactions

The combustion of graphite to produce carbon dioxide is described by the equation

$$C_{(graphite,s)} + O_{2(g)} \rightarrow CO_{2(g)}$$

At 298 K and 1.0 atm, ΔH = −393.5 kJ/mol of graphite for this reaction, and the molar volume of graphite is 0.0053 L. What is ΔU for the reaction?

Given: balanced chemical equation, temperature, pressure, ΔH, and molar volume of reactant

Asked for: ΔU

Strategy:

A. Use the balanced chemical equation to calculate the change in the number of moles of gas during the reaction.
B. Substitute this value and the data given into Equation 3.3.8 to obtain ΔU.

Solution

A In this reaction, 1 mol of gas (CO_2) is produced, and 1 mol of gas (O_2) is consumed. Thus Δn = 1 − 1 = 0.

B Substituting this calculated value and the given values into Equation 3.3.8,

$$\begin{aligned}\Delta U &= \Delta H - RT\Delta n = (-393.5\text{ kJ/mol}) - [8.314\text{ J/(mol·K)}](298\text{ K})(0) \\ &= (-393.5\text{ kJ/mol}) - (0\text{ J/mol}) = -393.5\text{ kJ/mol}\end{aligned}$$

To understand why only the change in the volume of the gases needs to be considered, notice that the molar volume of graphite is only 0.0053 L. A change in the number of moles of gas corresponds to a volume change of 22.4 L/mol of gas at standard temperature and pressure (STP), so the volume of gas consumed or produced in this case is (1)(22.4 L) = 22.4 L, which is much, much greater than the volume of 1 mol of a solid such as graphite.

Exercise 3.3.2

Calculate ΔU for the conversion of oxygen gas to ozone at 298 K:

$$3O_2(g) \rightarrow 2O_3(g).$$

The value of ΔH for the reaction is 285.4 kJ.

Answer

288 kJ

As Example 3.3.2 illustrates, the magnitudes of ΔH and ΔU for reactions that involve gases are generally rather similar, even when there is a net production or consumption of gases.

Summary

Enthalpy is a state function, and the change in enthalpy of a system is equal to the sum of the change in the internal energy of the system and the PV work done. Enthalpy is a state function whose change indicates the amount of heat transferred from a system to its surroundings or vice versa, at constant pressure. The change in the internal energy of a system is the sum of the heat transferred and the work done. At constant pressure, heat flow (q) and internal energy (U) are related to the system's enthalpy (H). The heat flow is equal to the change in the internal energy of the system plus the PV work done. When the volume of a system is constant, changes in its internal energy can be calculated by substituting the ideal gas law into the equation for ΔU.

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3.4: Enthalpy of Reaction

Learning Objectives

- To understand how enthalpy pertains to chemical reactions

We have stated that the change in energy (ΔU) is equal to the sum of the heat produced and the work performed. Work done by an expanding gas is called *pressure-volume work*, (or just PV *work)*. Consider, for example, a reaction that produces a gas, such as dissolving a piece of copper in concentrated nitric acid. The chemical equation for this reaction is as follows:

$$\mathrm{Cu(s) + 4\,HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2\,H_2O(l) + 2\,NO_2(g)}$$

If the reaction is carried out in a closed system that is maintained at constant pressure by a movable piston, the piston will rise as nitrogen dioxide gas is formed (Figure 3.4.1). The system is performing work by lifting the piston against the downward force exerted by the atmosphere (i.e., *atmospheric pressure*). We find the amount of PV work done by multiplying the external pressure P by the change in volume caused by movement of the piston (ΔV). At a constant external pressure (here, atmospheric pressure),

$$w = -P\Delta V \tag{3.4.1}$$

The negative sign associated with PV work done indicates that the system loses energy when the volume increases. If the volume increases at constant pressure ($\Delta V > 0$), the work done by the system is negative, indicating that a system has lost energy by performing work on its surroundings. Conversely, if the volume decreases ($\Delta V < 0$), the work done by the system is positive, which means that the surroundings have performed work on the system, thereby increasing its energy.

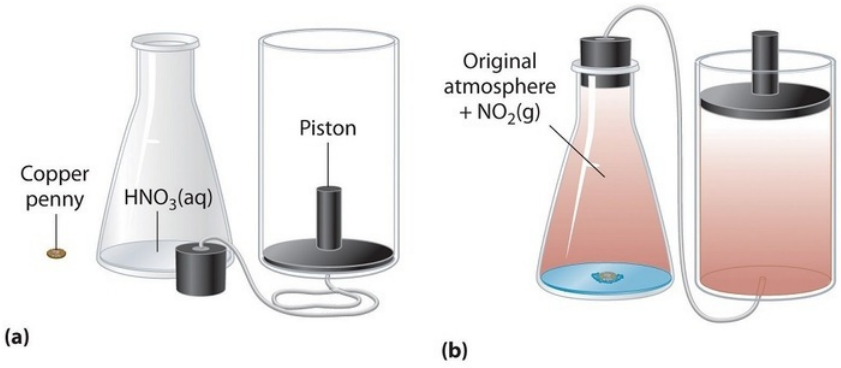


Figure 3.4.1: An Example of Work Performed by a Reaction Carried Out at Constant Pressure. (a) Initially, the system (a copper penny and concentrated nitric acid) is at atmospheric pressure. (b) When the penny is added to the nitric acid, the volume of NO_2 gas that is formed causes the piston to move upward to maintain the system at atmospheric pressure. In doing so, the system is performing work on its surroundings. (CC BY-NC-SA; anonymous)

The internal energy U of a system is the sum of the kinetic energy and potential energy of all its components. It is the change in internal energy that produces heat plus work. To measure the energy changes that occur in chemical reactions, chemists usually use a related thermodynamic quantity called **enthalpy** (H) (from the Greek *enthalpein*, meaning "to warm"). The enthalpy of a system is defined as the sum of its internal energy U plus the product of its pressure P and volume V:

\[H =U + PV \label{5.4.3} \]

Because internal energy, pressure, and volume are all state functions, enthalpy is also a state function. So we can define a change in enthalpy (ΔH) accordingly

$$\Delta H = H_{final} - H_{initial}$$

If a chemical change occurs at constant pressure (i.e., for a given P, $\Delta P = 0$), the change in enthalpy (ΔH) is

$$\Delta H = \Delta(U + PV) \tag{3.4.2}$$

$$= \Delta U + \Delta PV \tag{3.4.3}$$

$$= \Delta U + P\Delta V \tag{3.4.4}$$

Substituting $q + w$ for ΔU (First Law of Thermodynamics) and $-w$ for $P\Delta V$ (Equation 3.4.1) into Equation 3.4.4, we obtain

$$\Delta H = \Delta U + P\Delta V \tag{3.4.5}$$

$$= q_p + \cancel{w} - \cancel{w} \tag{3.4.6}$$

$$= q_p \tag{3.4.7}$$

The subscript p is used here to emphasize that this equation is true only for a process that occurs at constant pressure. From Equation 3.4.7 we see that at constant pressure the change in enthalpy, ΔH of the system, is equal to the heat gained or lost.

$$\Delta H = H_{final} - H_{initial} \tag{3.4.8}$$

$$= q_p \tag{3.4.9}$$

Just as with ΔU, because enthalpy is a state function, the magnitude of ΔH depends on only the initial and final states of the system, not on the path taken. Most important, the enthalpy change is the same even if the process does *not* occur at constant pressure.

> *To find ΔH for a reaction, measure q_p.*

When we study energy changes in chemical reactions, the most important quantity is usually the enthalpy of reaction (ΔH_{rxn}), the change in enthalpy that occurs during a reaction (such as the dissolution of a piece of copper in nitric acid). If heat flows from a system to its surroundings, the enthalpy of the system decreases, so ΔH_{rxn} is negative. Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, so ΔH_{rxn} is positive. Thus:

- $\Delta H_{rxn} < 0$ for an *exothermic reaction*, and
- $\Delta H_{rxn} > 0$ for an *endothermic reaction*.

In chemical reactions, bond breaking requires an input of energy and is therefore an endothermic process, whereas bond making releases energy, which is an exothermic process. The sign conventions for heat flow and enthalpy changes are summarized in the following table:

sign conventions for heat flow and enthalpy changes

Reaction Type	q	ΔH_{rxn}
exothermic	< 0	< 0 (heat flows from a system to its surroundings)
endothermic	> 0	> 0 (heat flows from the surroundings to a system)

If ΔH_{rxn} is negative, then the enthalpy of the products is less than the enthalpy of the reactants; that is, *an exothermic reaction is energetically downhill* (Figure 3.4.2*a*). Conversely, if ΔH_{rxn} is positive, then the enthalpy of the products is greater than the enthalpy of the reactants; thus, *an endothermic reaction is energetically uphill* (Figure 3.4.2*b*). Two important characteristics of enthalpy and changes in enthalpy are summarized in the following discussion.

> *Bond breaking **ALWAYS** requires an input of energy; bond making **ALWAYS** releases energy.y.*

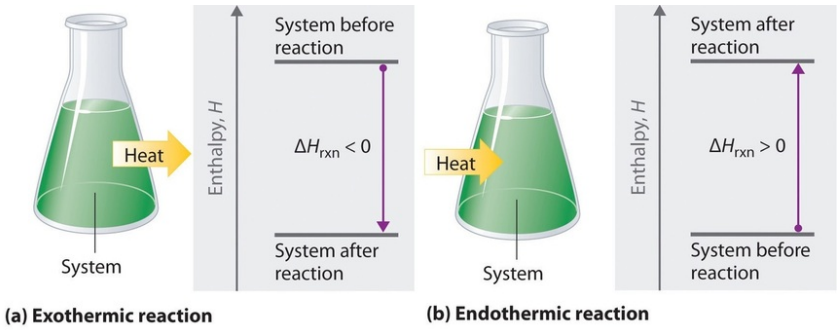


Figure 3.4.2: The Enthalpy of Reaction. Energy changes in chemical reactions are usually measured as changes in enthalpy. (a) If heat flows from a system to its surroundings, the enthalpy of the system decreases, ΔH_{rxn} is negative, and the reaction is exothermic; it is energetically downhill. (b) Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, ΔH_{rxn} is positive, and the reaction is endothermic; it is energetically uphill. (CC BY-NC-SA; anonymous)

- **Reversing a reaction or a process changes the sign of Δ*H*.** Ice *absorbs* heat when it melts (electrostatic interactions are broken), so liquid water must *release* heat when it freezes (electrostatic interactions are formed):

$$heat + H_2O(s) \rightarrow H_2O(l) \qquad \Delta H > 0$$
$$H_2O(l) \rightarrow H_2O(s) + heat \qquad \Delta H < 0$$

  In both cases, the *magnitude* of the enthalpy change is the same; only the *sign* is different.

- **Enthalpy is an extensive property (like mass).** The magnitude of ΔH for a reaction is proportional to the amounts of the substances that react. For example, a large fire produces more heat than a single match, even though the chemical reaction—the combustion of wood—is the same in both cases. For this reason, the enthalpy change for a reaction is usually given in kilojoules per mole of a particular reactant or product. Consider Equation 3.4.10, which describes the reaction of aluminum with iron(III) oxide (Fe_2O_3) at constant pressure. According to the reaction stoichiometry, 2 mol of Fe, 1 mol of Al_2O_3, and 851.5 kJ of heat are produced for every 2 mol of Al and 1 mol of Fe_2O_3 consumed:

$$2\,\mathrm{Al(s)} + \mathrm{Fe_2O_3(s)} \longrightarrow 2\,\mathrm{Fe(s)} + \mathrm{Al_2O_3(s)} + 815.5\ kJ \tag{3.4.10}$$

  Thus Δ*H* = −851.5 kJ/mol of Fe_2O_3. We can also describe Δ*H* for the reaction as −425.8 kJ/mol of Al: because 2 mol of Al are consumed in the balanced chemical equation, we divide −851.5 kJ by 2. When a value for Δ*H*, in kilojoules rather than kilojoules per mole, is written after the reaction, as in Equation 3.4.11, it is the value of Δ*H* corresponding to the reaction of the molar quantities of reactants as given in the balanced chemical equation:

$$2\,\mathrm{Al(s)} + \mathrm{Fe_2O_3(s)} \longrightarrow 2\,\mathrm{Fe(s)} + \mathrm{Al_2O_3(s)} \quad \Delta H_{rxn} = -851.5\ kJ \tag{3.4.11}$$

  If 4 mol of Al and 2 mol of Fe_2O_3 react, the change in enthalpy is 2 × (−851.5 kJ) = −1703 kJ. We can summarize the relationship between the amount of each substance and the enthalpy change for this reaction as follows:

$$-\frac{851.5\ kJ}{2\ mol\ Al} = -\frac{425.8\ kJ}{1\ mol\ Al} = -\frac{1703\ kJ}{4\ mol\ Al} \tag{3.4.12}$$

The relationship between the magnitude of the enthalpy change and the mass of reactants is illustrated in Example 3.4.1.

✔ Example 3.4.1: Melting Icebergs

Certain parts of the world, such as southern California and Saudi Arabia, are short of freshwater for drinking. One possible solution to the problem is to tow icebergs from Antarctica and then melt them as needed. If ΔH is 6.01 kJ/mol for the reaction at 0°C and constant pressure:

$$\mathrm{H_2O(s) \rightarrow H_2O(l)}$$

How much energy would be required to melt a moderately large iceberg with a mass of 1.00 million metric tons (1.00×10^6 metric tons)? (A metric ton is 1000 kg.)

Given: energy per mole of ice and mass of iceberg

Asked for: energy required to melt iceberg

Strategy:

A. Calculate the number of moles of ice contained in 1 million metric tons (1.00×10^6 metric tons) of ice.

B. Calculate the energy needed to melt the ice by multiplying the number of moles of ice in the iceberg by the amount of energy required to melt 1 mol of ice.

Solution:

A Because enthalpy is an extensive property, the amount of energy required to melt ice depends on the amount of ice present. We are given ΔH for the process—that is, the amount of energy needed to melt 1 mol (or 18.015 g) of ice—so we need to calculate the number of moles of ice in the iceberg and multiply that number by ΔH (+6.01 kJ/mol):

$$moles\ H_2O = 1.00 \times 10^6\ \cancel{\text{metric ton}}\ \mathrm{H_2O} \left(\frac{1000\ \cancel{kg}}{1\ \cancel{\text{metric ton}}}\right)\left(\frac{1000\ \cancel{g}}{1\ \cancel{kg}}\right)\left(\frac{1\ mol\ H_2O}{18.015\ \cancel{g\ H_2O}}\right)$$

$$= 5.55 \times 10^{10}\ mol\,\mathrm{H_2O}$$

B The energy needed to melt the iceberg is thus

$$\left(\frac{6.01\ kJ}{\cancel{mol\ H_2O}}\right)\left(5.55 \times 10^{10}\ \cancel{mol\ H_2O}\right) = 3.34 \times 10^{11}\ kJ$$

Because so much energy is needed to melt the iceberg, this plan would require a relatively inexpensive source of energy to be practical. To give you some idea of the scale of such an operation, the amounts of different energy sources equivalent to the amount of energy needed to melt the iceberg are shown below.

Possible sources of the approximately $3.34 \times 10^{11}\ kJ$ needed to melt a 1.00×10^6 metric ton iceberg

- Combustion of 3.8×10^3 ft^3 of natural gas
- Combustion of 68,000 barrels of oil
- Combustion of 15,000 tons of coal
- 1.1×10^8 kilowatt-hours of electricity

Alternatively, we can rely on ambient temperatures to slowly melt the iceberg. The main issue with this idea is the cost of dragging the iceberg to the desired place.

? Exercise 3.4.1: Thermite Reaction

If 17.3 g of powdered aluminum are allowed to react with excess $\mathrm{Fe_2O_3}$, how much heat is produced?

Answer

273 kJ

Enthalpies of Reaction

One way to report the heat absorbed or released would be to compile a massive set of reference tables that list the enthalpy changes for all possible chemical reactions, which would require an incredible amount of effort. Fortunately, since enthalpy is a state function, all we have to know is the initial and final states of the reaction. This allows us to calculate the enthalpy change for virtually any conceivable chemical reaction using a relatively small set of tabulated data, such as the following:

- Enthalpy of combustion (ΔH_{comb}) The change in enthalpy that occurs during a combustion reaction. Enthalpy changes have been measured for the combustion of virtually any substance that will burn in oxygen; these values are usually reported as the enthalpy of combustion per mole of substance.
- Enthalpy of fusion (ΔH_{fus}) The enthalpy change that acompanies the melting (fusion) of 1 mol of a substance. The enthalpy change that accompanies the melting, or fusion, of 1 mol of a substance; these values have been measured for almost all the elements and for most simple compounds.
- Enthalpy of vaporization (ΔH_{vap}) The enthalpy change that accompanies the vaporization of 1 mol of a substance. The enthalpy change that accompanies the vaporization of 1 mol of a substance; these values have also been measured for nearly all the

elements and for most volatile compounds.

- Enthalpy of solution (ΔH_{soln}) The change in enthalpy that occurs when a specified amount of solute dissolves in a given quantity of solvent. The enthalpy change when a specified amount of solute dissolves in a given quantity of solvent.

Table 3.4.1: Enthalpies of Vaporization and Fusion for Selected Substances at Their Boiling Points and Melting Points

Substance	ΔH_{vap} (kJ/mol)	ΔH_{fus} (kJ/mol)
argon (Ar)	6.3	1.3
methane (CH_4)	9.2	0.84
ethanol (CH_3CH_2OH)	39.3	7.6
benzene (C_6H_6)	31.0	10.9
water (H_2O)	40.7	6.0
mercury (Hg)	59.0	2.29
iron (Fe)	340	14

The sign convention is the same for all enthalpy changes: negative if heat is released by the system and positive if heat is absorbed by the system.



Enthalpy of Reaction: Enthalpy of Reaction, YouTube(opens in new window) [youtu.be]

Summary

For a chemical reaction, the **enthalpy of reaction** (ΔH_{rxn}) is the difference in enthalpy between products and reactants; the units of ΔH_{rxn} are kilojoules per mole. Reversing a chemical reaction reverses the sign of ΔH_{rxn}.

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3.5: Calorimetry

Learning Objectives

- To use calorimetric data to calculate enthalpy changes.

Thermal energy itself cannot be measured easily, but the temperature change caused by the flow of thermal energy between objects or substances can be measured. Calorimetry describes a set of techniques employed to measure enthalpy changes in chemical processes using devices called *calorimeters*. To have any meaning, the quantity that is actually measured in a calorimetric experiment, the change in the temperature of the device, must be related to the heat evolved or consumed in a chemical reaction. We begin this section by explaining how the flow of thermal energy affects the temperature of an object.

Heat Capacity

We have seen that the temperature of an object changes when it absorbs or loses thermal energy. The *magnitude* of the temperature change depends on both the *amount* of thermal energy transferred (*q*) and the *heat capacity* of the object. Its heat capacity (*C*) is the amount of energy needed to raise the temperature of the object exactly 1°C; the units of *C* are joules per degree Celsius (J/°C). Note that a degree Celsius is exactly the same as a Kelvin, so the heat capacities can be expresses equally well, and perhaps a bit more correctly in SI, as joules per Kelvin, J/K

The change in temperature (ΔT) is

$$\Delta T = \frac{q}{C} \tag{3.5.1}$$

where q is the amount of heat (in joules), C is the heat capacity (in joules per degree Celsius), and ΔT is $T_{final} - T_{initial}$ (in degrees Celsius). Note that ΔT is *always* written as the final temperature minus the initial temperature.

Which Temperature units to use

Since the scaling for Kelvin (K) and degrees Celsius (°C) are exactly the same, the DIFFERENCE

$$\Delta T = T_{final} - T_{initial}$$

is the same is either is used for temperature calculations, but make sure not to mix these two temperature units for BOTH T_{final} and $T_{initial}$.

The value of C is intrinsically a positive number, but ΔT and q can be either positive or negative, and they both must have the *same* sign. If ΔT and q are positive, then *heat flows from the surroundings into an object*. If ΔT and q are negative, then *heat flows from an object into its surroundings*.

The heat capacity of an object depends on both its *mass* and its *composition*. For example, doubling the mass of an object doubles its heat capacity. Consequently, the amount of substance must be indicated when the heat capacity of the substance is reported. The molar heat capacity (c_p) is the amount of energy needed to increase the temperature of 1 mol of a substance by 1°C; the units of c_p for molar heat capacity are thus J/(mol°C).The subscript *p* indicates that the value was measured at constant pressure. The specific heat capacity (c_p) is the amount of energy needed to increase the temperature of 1 g of a substance by 1°C; its units are thus J/(g°C).

We can relate the quantity of a substance, the amount of heat transferred, its specific heat, and the temperature change either via **moles**:

$$q = nc_p\Delta T \tag{3.5.2}$$

where n is the number of moles of substance and c_p is the molar heat capacity or via **mass**:

$$q = mc_p\Delta T \tag{3.5.3}$$

where m is the mass of substance in grams and c_p is the specific heat capacity.

The specific heat capacities of some common substances are given in Table 3.5.1. Note that the specific heat values of most solids are less than 1 J/(g°C), whereas those of most liquids are about 2 J/(g°C). Water in its solid and liquid states is an exception. The heat capacity of ice is twice as high as that of most solids; the heat capacity of liquid water, 4.18 J/(g°C), is one of the highest known. More values are given in the Reference Table T4.

Table 3.5.1: Specific Heats of Selected Substances at 25°C

Compound	Specific Heat [J/(g°C)]	Compound	Specific Heat [J/(g°C)]
H_2O (s) (-10°C)	2.05	Al(s)	0.897
H_2O (l)	4.18	Fe(s)	0.449
H_2O (g)	2.062	Cu(s)	0.385
CH_3OH (methanol)	2.531	Au(s)	0.129
CH_3CH_2OH (ethanol)	2.438	Hg(l)	0.140
n-C_6H_{14} (*n*-hexane)	2.270	NaCl(s)	0.864
C_6H_6 (benzene)	1.741	MgO(s)	0.918
C(s) (graphite)	0.709	SiO_2(s) (quartz)	0.742
C(s) (diamond)	0.509	$CaCO_3$(s) (calcite)	0.915

The high specific heat of liquid water has important implications for life on Earth. A given mass of water releases more than five times as much heat for a 1°C temperature change as does the same mass of limestone or granite. Consequently, coastal regions of our planet tend to have less variable climates than regions in the center of a continent. After absorbing large amounts of thermal energy from the sun in summer, the water slowly releases the energy during the winter, thus keeping coastal areas warmer than otherwise would be expected. Water's capacity to absorb large amounts of energy without undergoing a large increase in temperature also explains why swimming pools and waterbeds are usually heated. Heat must be applied to raise the temperature of the water to a comfortable level for swimming or sleeping and to maintain that level as heat is exchanged with the surroundings. Moreover, because the human body is about 70% water by mass, a great deal of energy is required to change its temperature by even 1 °C. Consequently, the mechanism for maintaining our body temperature at about 37 °C does not have to be as finely tuned as would be necessary if our bodies were primarily composed of a substance with a lower specific heat.

Example 3.5.1: Solar Heating

A home solar energy storage unit uses 400 L of water for storing thermal energy. On a sunny day, the initial temperature of the water is 22.0 °C. During the course of the day, the temperature of the water rises to 38.0 °C as it circulates through the water wall. How much energy has been stored in the water? (The density of water at 22.0 °C is 0.998 g/mL.)



Passive solar system. During the day (a), sunlight is absorbed by water circulating in the water wall. At night (b), heat stored in the water wall continues to warm the air inside the house.

Given: volume and density of water and initial and final temperatures

Asked for: amount of energy stored

Strategy:

A. Use the density of water at 22.0 °C to obtain the mass of water (m) that corresponds to 400 L of water. Then compute ΔT for the water.
B. Determine the amount of heat absorbed by substituting values for m, c_p, and ΔT into Equation 3.5.3.

Solution:

A The mass of water is

$$\text{mass of } H_2O = 400 \ \cancel{L}\left(\frac{1000 \ \cancel{mL}}{1 \ \cancel{L}}\right)\left(\frac{0.998 \ g}{1 \ \cancel{mL}}\right)$$
$$= 3.99 \times 10^5 g \ H_2O$$

The temperature change (ΔT) is

$$38.0^oC - 22.0^oC = +16.0^oC.$$

B From Table 3.5.1, the specific heat of water is 4.18 J/(g°C). From Equation 3.5.3, the heat absorbed by the water is thus

$$q = mc_p\Delta T$$
$$= \left(3.99 \times 10^5 \ \cancel{g}\right)\left(\frac{4.18 \ J}{\cancel{g} \cdot \ \cancel{^oC}}\right)\left(16.0 \ \cancel{^oC}\right)$$
$$= 2.67 \times 10^7 \ J = 2.67 \times 10^4 \ kJ$$

Both q and ΔT are positive, consistent with the fact that the water has absorbed energy.

? Exercise 3.5.1: Solar Heating

Some solar energy devices used in homes circulate air over a bed of rocks that absorb thermal energy from the sun. If a house uses a solar heating system that contains 2500 kg of sandstone rocks, what amount of energy is stored if the temperature of the rocks increases from 20.0 °C to 34.5 °C during the day? Assume that the specific heat of sandstone is the same as that of quartz (SiO_2) in Table 3.5.1.

Answer

$2.7 \times 10^4 \ kJ$

Even though the mass of sandstone is more than six times the mass of the water in Example 3.5.1, the amount of thermal energy stored is the same to two significant figures.

When two objects at different temperatures are placed in contact, heat flows from the warmer object to the cooler one until the temperature of both objects is the same. The law of conservation of energy says that the total energy cannot change during this process:

$$q_{cold} + q_{hot} = 0 \tag{3.5.4}$$

The equation implies that the amount of heat that flows *from* a warmer object is the same as the amount of heat that flows *into* a cooler object. Because the direction of heat flow is opposite for the two objects, the sign of the heat flow values must be opposite:

$$q_{cold} = -q_{hot} \tag{3.5.5}$$

Thus heat is conserved in any such process, consistent with the law of conservation of energy.

> *Equation 3.5.5 argues that the amount of heat lost by a warmer object equals the amount of heat gained by a cooler object.*

Substituting for q from Equation 3.5.3 into Equation 3.5.5 gives

$$[mc_p\Delta T]_{cold} + [mc_p\Delta T]_{hot} = 0 \tag{3.5.6}$$

which can be rearranged to give

$$[mc_p\Delta T]_{cold} = -[mc_p\Delta T]_{hot} \tag{3.5.7}$$

When two objects initially at different temperatures are placed in contact, we can use Equation 3.5.7 to calculate the final temperature if we know the chemical composition and mass of the objects.

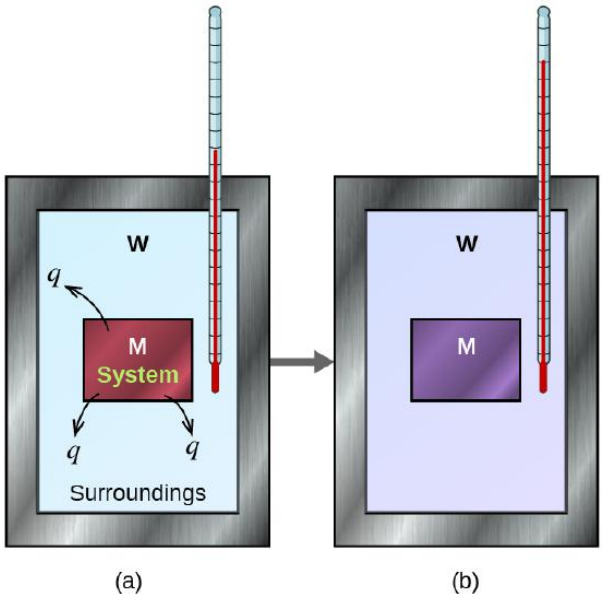


Figure 3.5.2: In a simple calorimetry process, (a) heat, q, is transferred from the hot metal, M, to the cool water, W, until (b) both are at the same temperature.

Example 3.5.2: Thermal Equilibration of Copper and Water

If a 30.0 g piece of copper pipe at 80.0 °C is placed in 100.0 g of water at 27.0 °C, what is the final temperature? Assume that no heat is transferred to the surroundings.

Given: mass and initial temperature of two objects

Asked for: final temperature

Strategy: Using Equation 3.5.7 and writing ΔT as $T_{final} - T_{initial}$ for both the copper and the water, substitute the appropriate values of m, c_p, and $T_{initial}$ into the equation and solve for T_{final}.

Solution

We can adapt Equation 3.5.7to solve this problem, remembering that ΔT is defined as $T_{final} - T_{initial}$:

$$[mc_p\,(T_{final} - T_{initial})]_{Cu} + [mc_p\,(T_{final} - T_{initial})]_{H_2O} = 0$$

Substituting the data provided in the problem and Table 3.5.1 gives

$$\begin{aligned}[(30\ g)\,(0.385\ J)\,(T_{final} - 80.0\,^\circ\text{C})]_{Cu} + [(100\,g)(4.18\,J/\,^\circ\text{C})\,(T_{final} - 27.0\,^\circ\text{C})]_{\text{H}_2\text{O}} &= 0\\ [T_{final}\,(11.6\ J/\,^\circ\text{C}) - 924\ J] + [T_{final}\,(418.4\ J/\,^\circ\text{C}) - 11,300\ J] &= 0\\ T_{final}\,(430\ J/\,(g\cdot\,^\circ\text{C})) &= 12,224\ J\\ T_{final} &= 28.4\ ^\circ\text{C}\end{aligned}$$

It is expected that the water will increase in temperature since the added copper pipe was hotter. However, the amount of the increase is not great and that is because there is more mass of water (three-fold), but mostly because the greater specific heat of water (order of magnitude) vs. copper.

Exercise 3.5.2A: Thermal Equilibration of Gold and Water

If a 14.0 g chunk of gold at 20.0°C is dropped into 25.0 g of water at 80.0 °C, what is the final temperature if no heat is transferred to the surroundings?

Answer

80.0°C

Exercise 3.5.2B: Thermal Equilibration of Aluminum and Water

A 28.0 g chunk of aluminum is dropped into 100.0 g of water with an initial temperature of 20.0 °C. If the final temperature of the water is 24.0 °C, what was the initial temperature of the aluminum? (Assume that no heat is transferred to the surroundings.)

Answer

90.6°C

In Example 3.5.1, radiant energy from the sun was used to raise the temperature of water. A calorimetric experiment uses essentially the same procedure, except that the thermal energy change accompanying a chemical reaction is responsible for the change in temperature that takes place in a calorimeter. If the reaction releases heat ($q_{rxn} < 0$), then heat is absorbed by the calorimeter ($q_{calorimeter} > 0$) and its temperature increases. Conversely, if the reaction absorbs heat ($q_{rxn} > 0$), then heat is transferred from the calorimeter to the system ($q_{calorimeter} < 0$) and the temperature of the calorimeter decreases. In both cases, *the amount of heat absorbed or released by the calorimeter is equal in magnitude and opposite in sign to the amount of heat produced or consumed by the reaction*. The heat capacity of the calorimeter or of the reaction mixture may be used to calculate the amount of heat released or absorbed by the chemical reaction. The amount of heat released or absorbed per gram or mole of reactant can then be calculated from the mass of the reactants.



Conservation of Energy: The Movement of Heat between Substances: Conservation of Energy: The Movement of Heat between Substances, YouTube(opens in new window) [youtu.be]

Constant-Pressure Calorimetry

Because ΔH is defined as the heat flow at constant pressure, measurements made using a constant-pressure calorimeter (a device used to measure enthalpy changes in chemical processes at constant pressure) give ΔH values directly. This device is particularly well suited to studying reactions carried out in solution at a constant atmospheric pressure. A “student” version, called a *coffee-cup calorimeter* (Figure 3.5.2), is often encountered in general chemistry laboratories. Commercial calorimeters operate on the same principle, but they can be used with smaller volumes of solution, have better thermal insulation, and can detect a change in temperature as small as several millionths of a degree (10^{-6} °C). Because the heat released or absorbed at constant pressure is equal to ΔH, the relationship between heat and ΔH_{rxn} is

$$\Delta H_{rxn} = q_{rxn} = -q_{calorimeter} = -mc_p\Delta T \tag{3.5.8}$$

The use of a constant-pressure calorimeter is illustrated in Example 3.5.3.

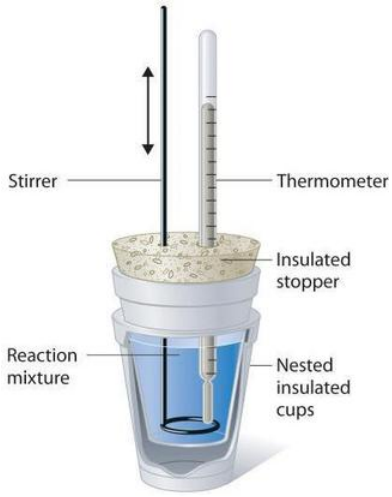


Figure 3.5.2: A Coffee-Cup Calorimeter. This simplified version of a constant-pressure calorimeter consists of two Styrofoam cups nested and sealed with an insulated stopper to thermally isolate the system (the solution being studied) from the surroundings (the air and the laboratory bench). Two holes in the stopper allow the use of a thermometer to measure the temperature and a stirrer to mix the reactants.

Example 3.5.3: Heat of solution for Potassium Hydroxide

When 5.03 g of solid potassium hydroxide are dissolved in 100.0 mL of distilled water in a coffee-cup calorimeter, the temperature of the liquid increases from 23.0 °C to 34.7 °C. The density of water in this temperature range averages 0.9969 g/cm^3. What is ΔH_{soln} (in kilojoules per mole)? Assume that the calorimeter absorbs a negligible amount of heat and, because of the large volume of water, the specific heat of the solution is the same as the specific heat of pure water.

Given: mass of substance, volume of solvent, and initial and final temperatures

Asked for: ΔH_{soln}

Strategy:

A. Calculate the mass of the solution from its volume and density and calculate the temperature change of the solution.
B. Find the heat flow that accompanies the dissolution reaction by substituting the appropriate values into Equation 3.5.8.
C. Use the molar mass of KOH to calculate ΔH_{soln}.

Solution:

A To calculate ΔH_{soln}, we must first determine the amount of heat released in the calorimetry experiment. The mass of the solution is

$$\left(100.0\ \cancel{mL}\ \text{H}_2\text{O}\right)\left(0.9969\ g/\ \cancel{mL}\right) + 5.03\ g\ \text{KOH} = 104.72\ g$$

The temperature change is therefore

$$(34.7\,^oC - 23.0\,^oC) = +11.7\,^oC.$$

B Because the solution is not very concentrated (approximately 0.9 M), we assume that the specific heat of the solution is the same as that of water. The heat flow that accompanies dissolution is thus

$$\begin{aligned} q_{calorimeter} &= mc_p\Delta T \\ &= \left(104.72\ \cancel{g}\right)\left(\frac{4.184\ J}{\cancel{g}\cdot\ \cancel{^oC}}\right)(11.7\ ^oC) \\ &= 5130\ J = 5.13\ kJ \end{aligned}$$

https://chem.libretexts.org/@go/page/393503

The temperature of the solution increased because heat was absorbed by the solution ($q > 0$). Where did this heat come from? It was released by KOH dissolving in water. From Equation 3.5.8, we see that

$$\Delta H_{rxn} = -q_{calorimeter} = -5.13\ kJ$$

This experiment tells us that dissolving 5.03 g of KOH in water is accompanied by the *release* of 5.13 kJ of energy. Because the temperature of the solution increased, the dissolution of KOH in water must be exothermic.

C The last step is to use the molar mass of KOH to calculate ΔH_{soln}, i.e., the heat released when dissolving 1 mol of KOH:

$$\Delta H_{soln} = \left(\frac{5.13\ kJ}{5.03\ \cancel{g}}\right)\left(\frac{56.11\ \cancel{g}}{1\ mol}\right)$$

$$= -57.2\ kJ/mol$$

Exercise 3.5.3A: Heat of solution for ammonium bromide

A coffee-cup calorimeter contains 50.0 mL of distilled water at 22.7 °C. Solid ammonium bromide (3.14 g) is added and the solution is stirred, giving a final temperature of 20.3°C. Using the same assumptions as in Example 3.5.3, find ΔH_{soln} for NH_4Br (in kilojoules per mole).

Answer

16.6 kJ/mol



Conservation of Energy: Coffee Cup Calorimetry: Conservation of Energy: Coffee Cup Calorimetry, YouTube(opens in new window) [youtu.be] (opens in new window)

Example 3.5.4

Heat Produced by an Exothermic Reaction

When 50.0 mL of 1.00 M HCl(*aq*) and 50.0 mL of 1.00 M NaOH(*aq*), both at 22.0 °C, are added to a coffee cup calorimeter, the temperature of the mixture reaches a maximum of 28.9 °C. What is the approximate amount of heat produced by this reaction?

$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$

Solution

To visualize what is going on, imagine that you could combine the two solutions so quickly that no reaction took place while they mixed; then after mixing, the reaction took place. At the instant of mixing, you have 100.0 mL of a mixture of HCl and NaOH at 22.0 °C. The HCl and NaOH then react until the solution temperature reaches 28.9 °C.

The heat given off by the reaction is equal to that taken in by the solution. Therefore:

$q_{reaction} = -q_{solution}$

(It is important to remember that this relationship only holds if the calorimeter does not absorb any heat from the reaction, and there is no heat exchange between the calorimeter and the outside environment.)

Next, we know that the heat absorbed by the solution depends on its specific heat, mass, and temperature change:

$q_{solution} = (c_p \times m \times \Delta T)_{solution}$

To proceed with this calculation, we need to make a few more reasonable assumptions or approximations. Since the solution is aqueous, we can proceed as if it were water in terms of its specific heat and mass values. The density of water is approximately 1.0 g/mL, so 100.0 mL has a mass of about 1.0×10^2 g (two significant figures). The specific heat of water is approximately 4.184 J/g °C, so we use that for the specific heat of the solution. Substituting these values gives:

$q_{solution} = (4.184 J/g^\circ C)(1.0 \times 102 g)(28.9^\circ C - 22.0^\circ C) = 2.9 \times 10^3 J$

Finally, since we are trying to find the heat of the reaction, we have:

$q_{reaction} = -q_{solution} = -2.9 \times 10^3 J$

The negative sign indicates that the reaction is exothermic. It produces 2.9 kJ of heat

Example 3.5.5

Thermochemistry of Hand Warmers

When working or playing outdoors on a cold day, you might use a hand warmer to warm your hands. A common reusable hand warmer contains a supersaturated solution of $NaC_2H_3O_2$ (sodium acetate) and a metal disc. Bending the disk creates nucleation sites around which the metastable $NaC_2H_3O_2$ quickly crystallizes (a later chapter on solutions will investigate saturation and supersaturation in more detail).

The process $NaC_2H^3O_2(aq) \longrightarrow NaC_2H_3O_2(s)$ is exothermic, and the heat produced by this process is absorbed by your hands, thereby warming them (at least for a while). If the hand warmer is reheated, the $NaC_2H_3O_2$ redissolves and can be reused.



Another common hand warmer produces heat when it is ripped open, exposing iron and water in the hand warmer to oxygen in the air. One simplified version of this exothermic reaction is $2Fe(s)+3_2O_2(g) \longrightarrow Fe_2O_3(s)$. Salt in the hand warmer catalyzes the reaction, so it produces heat more rapidly; cellulose, vermiculite, and activated carbon help distribute the heat evenly. Other types of hand warmers use lighter fluid (a platinum catalyst helps lighter fluid oxidize exothermically), charcoal (charcoal oxidizes in a special case), or electrical units that produce heat by passing an electrical current from a battery through resistive wires.

Exercise 3.5.1

Heat Flow in an Instant Ice Pack

When solid ammonium nitrate dissolves in water, the solution becomes cold. This is the basis for an “instant cold pack”. When 3.21 g of solid NH_4NO_3 dissolves in 50.0 g of water at 24.9 °C in a calorimeter, the temperature decreases to 20.3 °C. Calculate the value of *q* for this reaction and explain the meaning of its arithmetic sign. State any assumptions that you made.



Answer

We assume that the calorimeter prevents heat transfer between the solution and its external environment (including the calorimeter itself), therefore:

$q_{reaction} = -q_{solution}$

We also assume that the specific heat capacity of the solution is the same as water. so $c_{p,solution} = 4.184 J/g^oC$.

$q_{reaction} = -q_{solution} = (-c_{p,solution} \times m_{solution} \times \Delta T)_{solution}$

$q_{reaction} = -[(4.184 J/g^oC)(53.2 g)(20.3^oC - (-4.6^oC))]$

$q_{reaction} = 1.0 \times 10^3 J$

Constant-Volume Calorimetry

Constant-pressure calorimeters are not very well suited for studying reactions in which one or more of the reactants is a gas, such as a combustion reaction. The enthalpy changes that accompany combustion reactions are therefore measured using a constant-volume calorimeter, such as the bomb calorimeter(A device used to measure energy changes in chemical processes. shown schematically in Figure 3.5.3). The reactant is placed in a steel cup inside a steel vessel with a fixed volume (the “bomb”). The bomb is then sealed, filled with excess oxygen gas, and placed inside an insulated container that holds a known amount of water. Because combustion reactions are exothermic, the temperature of the bath and the calorimeter increases during combustion. If the heat capacity of the bomb and the mass of water are known, the heat released can be calculated.

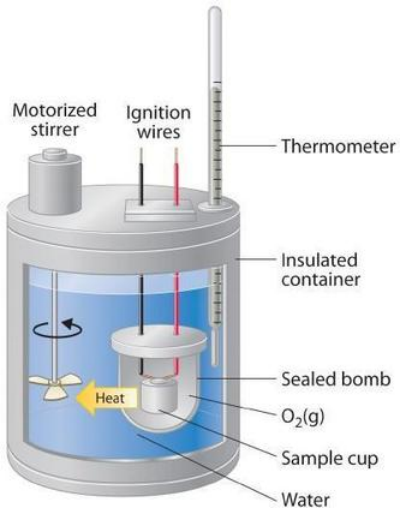


Figure 3.5.3: A Bomb Calorimeter. After the temperature of the water in the insulated container has reached a constant value, the combustion reaction is initiated by passing an electric current through a wire embedded in the sample. Because this calorimeter operates at constant volume, the heat released is not precisely the same as the enthalpy change for the reaction.

Because the volume of the system (the inside of the bomb) is fixed, the combustion reaction occurs under conditions in which the volume, but not the pressure, is constant. The heat released by a reaction carried out at constant volume is identical to the change in *internal energy* (ΔU) rather than the enthalpy change (ΔH); ΔU is related to ΔH by an expression that depends on the change in

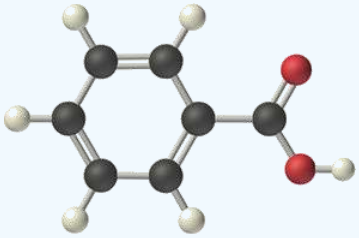
the number of moles of gas during the reaction. The difference between the heat flow measured at constant volume and the enthalpy change is usually quite small, however (on the order of a few percent). Assuming that $\Delta U < \Delta H$, the relationship between the measured temperature change and ΔH_{comb} is given in Equation 3.5.9, where c_{bomb} is the total heat capacity of the steel bomb and the water surrounding it:

$$\Delta H_{comb} < q_{comb} = q_{calorimeter} = c_{bomb}\Delta T \tag{3.5.9}$$

To measure the heat capacity of the calorimeter, we first burn a carefully weighed mass of a standard compound whose enthalpy of combustion is accurately known. Benzoic acid ($C_6H_5CO_2H$) is often used for this purpose because it is a crystalline solid that can be obtained in high purity. The combustion of benzoic acid in a bomb calorimeter releases 26.38 kJ of heat per gram (i.e., its $\Delta H_{comb} = -26.38\ kJ/g$). This value and the measured increase in temperature of the calorimeter can be used in Equation 3.5.9 to determine c_{bomb}. The use of a bomb calorimeter to measure the ΔH_{comb} of a substance is illustrated in Example 3.5.4.

Example 3.5.4: Combustion of Glucose

The combustion of 0.579 g of benzoic acid in a bomb calorimeter caused a 2.08 °C increase in the temperature of the calorimeter. The chamber was then emptied and recharged with 1.732 g of glucose and excess oxygen. Ignition of the glucose resulted in a temperature increase of 3.64°C. What is the ΔH_{comb} of glucose?



Benzoic acid

Given: mass and ΔT for combustion of standard and sample

Asked for: ΔH_{comb} of glucose

Strategy:

A. Calculate the value of q_{rxn} for benzoic acid by multiplying the mass of benzoic acid by its ΔH_{comb}. Then use Equation 3.5.9 to determine the heat capacity of the calorimeter (c_{bomb}) from q_{comb} and ΔT.

B. Calculate the amount of heat released during the combustion of glucose by multiplying the heat capacity of the bomb by the temperature change. Determine the ΔH_{comb} of glucose by multiplying the amount of heat released per gram by the molar mass of glucose.

Solution:

The first step is to use Equation 3.5.9 and the information obtained from the combustion of benzoic acid to calculate c_{bomb}. We are given ΔT, and we can calculate q_{comb} from the mass of benzoic acid:

$$\begin{aligned} q_{comb} &= \left(0.579\ \cancel{g}\right)\left(-26.38\ kJ/\cancel{g}\right) \\ &= -15.3\ kJ \end{aligned}$$

From Equation 3.5.9,

$$\begin{aligned} -c_{bomb} &= \frac{q_{comb}}{\Delta T} \\ &= \frac{-15.3\ kJ}{2.08\ ^oC} \\ &= -7.34\ kJ/^oC \end{aligned}$$

B According to the strategy, we can now use the heat capacity of the bomb to calculate the amount of heat released during the combustion of glucose:

$$\begin{aligned} q_{comb} &= -c_{bomb}\Delta T \\ &= (-7.34\ kJ/^oC)\,(3.64\ ^oC) \\ &= -26.7\ kJ \end{aligned}$$

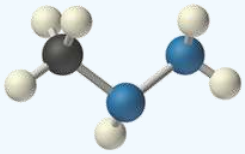
Because the combustion of 1.732 g of glucose released 26.7 kJ of energy, the ΔH_{comb} of glucose is

$$\begin{aligned} \Delta H_{comb} &= \left(\frac{-26.7\ kJ}{1.732\ \cancel{g}}\right)\left(\frac{180.16\ \cancel{g}}{mol}\right) \\ &= -2780\ kJ/mol \\ &= 2.78 \times 10^3\ J/mol \end{aligned}$$

This result is in good agreement (< 1% error) with the value of $\Delta H_{comb} = -2803\ kJ/mol$ that calculated using enthalpies of formation.

? Exercise 3.5.4: Combustion of Benzoic Acid

When 2.123 g of benzoic acid is ignited in a bomb calorimeter, a temperature increase of 4.75 °C is observed. When 1.932 g of methylhydrazine (CH_3NHNH_2) is ignited in the same calorimeter, the temperature increase is 4.64 °C. Calculate the ΔH_{comb} of methylhydrazine, the fuel used in the maneuvering jets of the US space shuttle.



Methylhydrazine

Answer

-1.30×10^3 kJ/mol



Conservation of Energy: Bomb Calorimetry: Conservation of Energy: Bomb Calorimetry, YouTube(opens in new window) [youtu.be]

Summary

Enthalpy is a state function used to measure the heat transferred from a system to its surroundings or vice versa at constant pressure. Only the **change in enthalpy (Δ*H*)** can be measured. A negative Δ*H* means that heat flows from a system to its surroundings; a positive Δ*H* means that heat flows into a system from its surroundings. Calorimetry measures enthalpy changes during chemical processes, where the magnitude of the temperature change depends on the amount of heat released or absorbed and

on the heat capacity of the system. **Calorimetry** is the set of techniques used to measure enthalpy changes during chemical processes. It uses devices called *calorimeters*, which measure the change in temperature when a chemical reaction is carried out. The magnitude of the temperature change depends on the amount of heat released or absorbed and on the heat capacity of the system. The **heat capacity (C)** of an object is the amount of energy needed to raise its temperature by 1°C; its units are joules per degree Celsius. The **specific heat (c_p)** of a substance is the amount of energy needed to raise the temperature of 1 g of the substance by 1°C, and the **molar heat capacity ($c_{p,\ molar}$)** is the amount of energy needed to raise the temperature of 1 mol of a substance by 1°C. Liquid water has one of the highest specific heats known. Heat flow measurements can be made with either a **constant-pressure calorimeter**, which gives ΔH values directly, or a **bomb calorimeter**, which operates at constant volume and is particularly useful for measuring enthalpies of combustion.

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3.6: Hess's Law

Learning Objectives

- To use Hess's law and thermochemical cycles to calculate enthalpy changes of chemical reactions.

Because enthalpy is a state function, the enthalpy change for a reaction depends on only two things: (1) the masses of the reacting substances and (2) the physical states of the reactants and products. It does not depend on the path by which reactants are converted to products. If you climbed a mountain, for example, the altitude change would not depend on whether you climbed the entire way without stopping or you stopped many times to take a break. If you stopped often, the overall change in altitude would be the sum of the changes in altitude for each short stretch climbed. Similarly, when we add two or more balanced chemical equations to obtain a net chemical equation, ΔH for the net reaction is the sum of the ΔH values for the individual reactions. This principle is called Hess's law, after the Swiss-born Russian chemist Germain Hess (1802–1850), a pioneer in the study of thermochemistry. Hess's law allows us to calculate ΔH values for reactions that are difficult to carry out directly by adding together the known ΔH values for individual steps that give the overall reaction, even though the overall reaction may not actually occur via those steps.

> *Hess's Law argues that ΔH for the net reaction is the sum of the ΔH values for the individual reactions. This is nothing more than arguing that ΔH is a state function.*

We can illustrate Hess's law using the thermite reaction. The overall reaction shown in Equation 3.6.1 can be viewed as occurring in three distinct steps with known ΔH values. As shown in Figure 3.6.1, the first reaction produces 1 mol of solid aluminum oxide (Al_2O_3) and 2 mol of liquid iron at its melting point of 1758°C (part (a) in Equation 3.6.1); the enthalpy change for this reaction is −732.5 kJ/mol of Fe_2O_3. The second reaction is the conversion of 2 mol of liquid iron at 1758°C to 2 mol of solid iron at 1758°C (part (b) in Equation 3.6.1); the enthalpy change for this reaction is −13.8 kJ/mol of Fe (−27.6 kJ per 2 mol Fe). In the third reaction, 2 mol of solid iron at 1758°C is converted to 2 mol of solid iron at 25°C (part (c) in Equation 3.6.1); the enthalpy change for this reaction is −45.5 kJ/mol of Fe (−91.0 kJ per 2 mol Fe). As you can see in Figure 3.6.1, the overall reaction is given by the longest arrow (shown on the left), which is the sum of the three shorter arrows (shown on the right). Adding parts (a), (b), and (c) in Equation 3.6.1 gives the overall reaction, shown in part (d):

$$\begin{array}{rcll} 2\,\mathrm{Al(s,25\,^\circ C)} + \mathrm{Fe_2O_3(s,25\,^\circ C)} & \longrightarrow & 2\,\mathrm{Fe(l,1758\,^\circ C)} + \mathrm{Al_2O_3(s,1758\,^\circ C)} & \Delta H = -732.5\,\mathrm{kJ} \quad \text{(a)} \\ 2\,\mathrm{Fe(l,1758\,^\circ C)} & \longrightarrow & 2\,\mathrm{Fe(s,1758\,^\circ C)} & \Delta H = -\ 27.6\,\mathrm{kJ} \quad \text{(b)} \\ 2\,\mathrm{Fe(s,1758\,^\circ C)} + \mathrm{Al_2O_3(s,1758\,^\circ C)} & \longrightarrow & 2\,\mathrm{Fe(s,25\,^\circ C)} + \mathrm{Al_2O_3(s,25\,^\circ C)} & \Delta H = -\ 91.0\,\mathrm{kJ} \quad \text{(c)} \\ \hline 2\,\mathrm{Al(s,25\,^\circ C)} + \mathrm{Fe_2O_3(s,25\,^\circ C)} & \longrightarrow & \mathrm{Al_2O_3(s,25\,^\circ C)} + 2\,\mathrm{Fe(s,25\,^\circ C)} & \Delta H = -851.1\,\mathrm{kJ} \quad \text{(d)} \end{array} \tag{3.6.1}$$

The net reaction in part (d) in Equation 3.6.1 is identical to the equation for the thermite reaction that we saw in a previous section. By Hess's law, the enthalpy change for part (d) is the sum of the enthalpy changes for parts (a), (b), and (c). In essence, Hess's law enables us to calculate the enthalpy change for the sum of a series of reactions without having to draw a diagram like that in Figure 3.6.1.

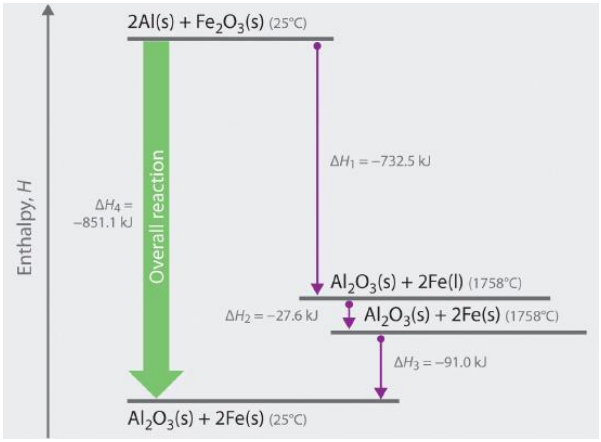


Figure 3.6.1: Energy Changes accompanying the thermite reaction. Because enthalpy is a state function, the overall enthalpy change for the reaction of 2 mol of Al(s) with 1 mol of Fe_2O_3(s) is −851.1 kJ, whether the reaction occurs in a single step (ΔH_4, shown on the left) or in three hypothetical steps (shown on the right) that involve the successive formation of solid Al_2O_3 and liquid iron (ΔH_1), solid iron at 1758°C (ΔH_2), and solid iron at 25°C (ΔH_3). Thus $\Delta H_4 = \Delta H_1 + \Delta H_2 + \Delta H_3$, as stated by Hess's law.

Comparing parts (a) and (d) in Equation 3.6.1 also illustrates an important point: The magnitude of ΔH for a reaction depends on the physical states of the reactants and the products (gas, liquid, solid, or solution). When the product is liquid iron at its melting point (part (a) in Equation 3.6.1), only 732.5 kJ of heat are released to the surroundings compared with 852 kJ when the product is solid iron at 25°C (part (d) in Equation 3.6.1). The difference, 120 kJ, is the amount of energy that is released when 2 mol of liquid iron solidifies and cools to 25°C. It is important to specify the physical state of all reactants and products when writing a thermochemical equation.

When using Hess's law to calculate the value of ΔH for a reaction, follow this procedure:

1. Identify the equation whose ΔH value is unknown and write individual reactions with known ΔH values that, when added together, will give the desired equation. We illustrate how to use this procedure in Example 3.6.1.
2. Arrange the chemical equations so that the reaction of interest is the sum of the individual reactions.
3. If a reaction must be reversed, change the sign of ΔH for that reaction. Additionally, if a reaction must be multiplied by a factor to obtain the correct number of moles of a substance, multiply its ΔH value by that same factor.
4. Add together the individual reactions and their corresponding ΔH values to obtain the reaction of interest and the unknown ΔH.

Example 3.6.1

We can think of the reaction of carbon with oxygen to form carbon dioxide as occurring either directly or by a two-step process. The energy changes are illustrated on the enthalpy diagram below.

Write the thermochemical reactions for each step along with the overall thermochemical reaction. Show that the enthalpy changes of the two steps equals the overall enthalpy change when added to give the overall reaction.

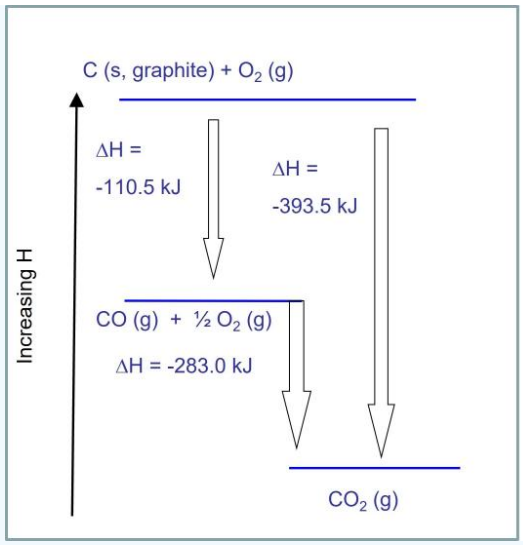


Figure 3.6.2: The formation of $CO_2(g)$ from its elements can be thought of as occurring in two steps, which sum to the overall reaction, as described by Hess's law. The horizontal blue lines represent enthalpies. For an exothermic process, the products are at lower enthalpy than are the reactants. The overall enthalpy change is the same if it is done in one step or two.

Solution

$$(overall)\ \mathrm{C(s,graphite)} + \mathrm{O_2(g)} \longrightarrow \mathrm{CO_2(g)} \quad \Delta H = -393.5\ \mathrm{kJ}$$

$$(1)\ \mathrm{C(s,graphite)} + \mathrm{O_2(g)} \longrightarrow \mathrm{CO(g)} + \tfrac{1}{2}\mathrm{O_2(g)} \quad \Delta H = -110.5\ \mathrm{kJ}$$

$$(2)\ \mathrm{CO(g)} + \tfrac{1}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{CO_2(g)} \quad \Delta H = -283.0\ \mathrm{kJ}$$

$\Delta H_1 + \Delta H_2$ = -110.5 kJ + (-283.0 kJ) = -393.5 kJ = $\Delta H_{overall}$

Example 3.6.2

When carbon is burned with limited amounts of oxygen gas (O_2), carbon monoxide (CO) is the main product:

$$(1)\ 2\,\mathrm{C(s)} + \mathrm{O_2(g)} \longrightarrow 2\,\mathrm{CO(g)} \quad \Delta H = -221.0\ \mathrm{kJ}$$

When carbon is burned in excess O_2, carbon dioxide (CO_2) is produced:

$$(2)\ \mathrm{C(s)} + \mathrm{O_2(g)} \longrightarrow \mathrm{CO_2(g)} \quad \Delta H = -393.5\ \mathrm{kJ}$$

Use this information to calculate the enthalpy change per mole of CO for the reaction of CO with O_2 to give CO_2.

Given: two balanced chemical equations and their ΔH values

Asked for: enthalpy change for a third reaction

Strategy:

A. After balancing the chemical equation for the overall reaction, write two equations whose ΔH values are known and that, when added together, give the equation for the overall reaction. (Reverse the direction of one or more of the equations as necessary, making sure to also reverse the sign of ΔH.)

B. Multiply the equations by appropriate factors to ensure that they give the desired overall chemical equation when added together. To obtain the enthalpy change per mole of CO, write the resulting equations as a sum, along with the enthalpy change for each.

Solution:

A We begin by writing the balanced chemical equation for the reaction of interest:

$$(3)\ \mathrm{CO(g)} + \tfrac{1}{2}\mathrm{O_2(g)} \longrightarrow \mathrm{CO_2(g)} \quad \Delta H_{rxn} = ?$$

There are at least two ways to solve this problem using Hess's law and the data provided. The simplest is to write two equations that can be added together to give the desired equation and for which the enthalpy changes are known. Observing that CO, a reactant in Equation 3, is a product in Equation 1, we can reverse Equation (1) to give

$$2\,CO(g) \longrightarrow 2\,C(s) + O_2(g) \quad \Delta H = +221.0\ kJ$$

Because we have reversed the direction of the reaction, the sign of ΔH is changed. We can use Equation 2 as written because its product, CO_2, is the product we want in Equation 3:

$$C(s) + O_2(g) \longrightarrow CO_2(s) \quad \Delta H = -393.5\ kJ$$

B Adding these two equations together does not give the desired reaction, however, because the numbers of C(s) on the left and right sides do not cancel. According to our strategy, we can multiply the second equation by 2 to obtain 2 mol of C(s) as the reactant:

$$2\,C(s) + 2\,O_2(g) \longrightarrow 2\,CO_2(s) \quad \Delta H = -787.0\ kJ$$

Writing the resulting equations as a sum, along with the enthalpy change for each, gives

$$\begin{array}{rll} 2\,CO(g) \longrightarrow \cancel{2\,C(s)} + \cancel{O_2(g)} & \Delta H = -\Delta H_1 = +221.0\ kJ \\ \cancel{2\,C(s)} + \cancel{2}\,O_2(g) \longrightarrow 2\,CO_2(g) & \Delta H = -2\Delta H_2 = -787.0\ kJ \\ \hline 2\,CO(g) + O_2(g) \longrightarrow 2\,CO_2(g) & \Delta H = -566.0\ kJ \end{array}$$

Note that the overall chemical equation and the enthalpy change for the reaction are both for the reaction of 2 mol of CO with O_2, and the problem asks for the amount per mole of CO. Consequently, we must divide both sides of the final equation and the magnitude of ΔH by 2:

$$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -283.0\ kJ$$

An alternative and equally valid way to solve this problem is to write the two given equations as occurring in steps. Note that we have multiplied the equations by the appropriate factors to allow us to cancel terms:

$$\begin{array}{lrll} (A) & 2\,C(s) + O_2(g) \longrightarrow \cancel{2\,CO(g)} & \Delta H_A = \Delta H_1 & = +221.0\ kJ \\ (B) & \cancel{2\,CO(g)} + O_2(g) \longrightarrow 2\,CO_2(g) & \Delta H_B & = ? \\ (C) & 2\,C(s) + 2\,O_2(g) \longrightarrow 2\,CO_2(g) & \Delta H = 2\Delta H_2 = 2 \times (-393.5\ kJ) & = -787.0\ kJ \end{array}$$

The sum of reactions A and B is reaction C, which corresponds to the combustion of 2 mol of carbon to give CO_2. From Hess's law, $\Delta H_A + \Delta H_B = \Delta H_C$, and we are given ΔH for reactions A and C. Substituting the appropriate values gives

$$-221.0\ kJ + \Delta H_B = -787.0\ kJ$$
$$\Delta H_B = -566.0$$

This is again the enthalpy change for the conversion of 2 mol of CO to CO_2. The enthalpy change for the conversion of 1 mol of CO to CO_2 is therefore −566.0 ÷ 2 = −283.0 kJ/mol of CO, which is the same result we obtained earlier. As you can see, there may be more than one correct way to solve a problem. The enthalpy diagram in Figure 3.6.2 also helps check this work.

? Exercise 3.6.1

The reaction of acetylene (C_2H_2) with hydrogen (H_2) can produce either ethylene (C_2H_4) or ethane (C_2H_6):

$$C_2H_2\,(g) + H_2\,(g) \rightarrow C_2H_4\,(g) \quad \Delta H = -175.7\ kJ/mol\ C_2H_2$$
$$C_2H_2\,(g) + 2H_2\,(g) \rightarrow C_2H_6\,(g) \quad \Delta H = -312.0\ kJ/mol\ C_2H_2$$

What is ΔH for the reaction of C_2H_4 with H_2 to form C_2H_6?

Answer

−136.3 kJ/mol of C_2H_4



Hess’s Law: Hess's Law, YouTube(opens in new window) [youtu.be]

Summary

Hess's law is arguing the overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions. For a chemical reaction, the **enthalpy of reaction (ΔH_{rxn})** is the difference in enthalpy between products and reactants; the units of ΔH_{rxn} are kilojoules per mole. Reversing a chemical reaction reverses the sign of ΔH_{rxn}. The magnitude of ΔH_{rxn} also depends on the physical state of the reactants and the products because processes such as melting solids or vaporizing liquids are also accompanied by enthalpy changes: the **enthalpy of fusion (ΔH_{fus})** and the **enthalpy of vaporization (ΔH_{vap})**, respectively. The overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions, which is **Hess’s law**. The **enthalpy of combustion (ΔH_{comb})** is the enthalpy change that occurs when a substance is burned in excess oxygen.

Contributors and Attributions

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3.7: Enthalpies of Formation

Learning Objectives

- To understand Enthalpies of Formation and be able to use them to calculate Enthalpies of Reaction

One way to report the heat absorbed or released by chemical reactions would be to compile a massive set of reference tables that list the enthalpy changes for all possible chemical reactions, which would require an incredible amount of effort. Fortunately, Hess's law allows us to calculate the enthalpy change for virtually any conceivable chemical reaction using a relatively small set of tabulated data, starting from the elemental forms of each atom at 25 °C and 1 atm pressure.

Enthalpy of formation (ΔH_f) is the enthalpy change for the formation of 1 mol of a compound from its component elements, such as the formation of carbon dioxide from carbon and oxygen. The formation of any chemical can be as a reaction from the corresponding elements:

$$\text{elements} \rightarrow \text{compound}$$

which in terms of the the Enthalpy of formation becomes

$$\Delta H_{rxn} = \Delta H_f \tag{3.7.1}$$

For example, consider the combustion of carbon:

$$\mathrm{C(s) + O_2(g) \longrightarrow CO_2(g)}$$

then

$$\Delta H_{rxn} = \Delta H_f \left[CO_2\left(g\right)\right]$$

The sign convention for ΔH_f is the same as for any enthalpy change: $\Delta H_f < 0$ if heat is released when elements combine to form a compound and $\Delta H_f > 0$ if heat is absorbed.

> The sign convention is the same for all enthalpy changes: negative if heat is released by the system and positive if heat is absorbed by the system.

Standard Enthalpies of Formation

The magnitude of ΔH for a reaction depends on the physical states of the reactants and the products (gas, liquid, solid, or solution), the pressure of any gases present, and the temperature at which the reaction is carried out. To avoid confusion caused by differences in reaction conditions and ensure uniformity of data, the scientific community has selected a specific set of conditions under which enthalpy changes are measured. These standard conditions serve as a reference point for measuring differences in enthalpy, much as sea level is the reference point for measuring the height of a mountain or for reporting the altitude of an airplane.

The standard conditions for which most thermochemical data are tabulated are a *pressure* of 1 atmosphere (atm) for all gases and a *concentration* of 1 M for all species in solution (1 mol/L). In addition, each pure substance must be in its standard state, which is usually its most stable form at a pressure of 1 atm at a specified temperature. We assume a temperature of 25°C (298 K) for all enthalpy changes given in this text, unless otherwise indicated. Enthalpies of formation measured under these conditions are called **standard enthalpies of formation** (ΔH_f^o) The enthalpy change for the formation of 1 mol of a compound from its component elements when the component elements are each in their standard states. The standard enthalpy of formation of any element in its most stable form is zero by definition.

> *The standard enthalpy of formation of any element in its standard state is zero by definition.*

For example, although oxygen can exist as ozone (O_3), atomic oxygen (O), and molecular oxygen (O_2), O_2 is the most stable form at 1 atm pressure and 25°C. Similarly, hydrogen is H_2(g), not atomic hydrogen (H). Graphite and diamond are both forms of elemental carbon, but because graphite is more stable at 1 atm pressure and 25°C, the standard state of carbon is graphite (Figure 3.7.1). Therefore, $\mathrm{O_2(g)}$, $\mathrm{H_2(g)}$, and graphite have ΔH_f^o values of zero.

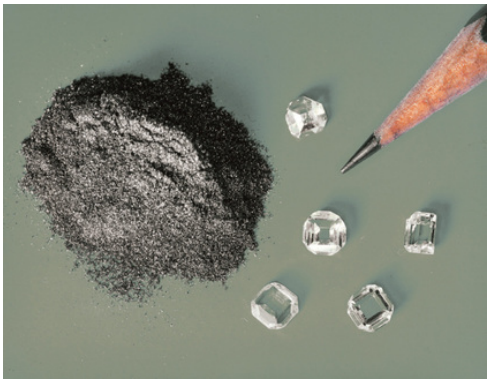


Figure 3.7.1: Elemental Carbon. Although graphite and diamond are both forms of elemental carbon, graphite is slightly more stable at 1 atm pressure and 25°C than diamond is. Given enough time, diamond will revert to graphite under these conditions. Hence graphite is the standard state of carbon.

The standard enthalpy of formation of glucose from the elements at 25°C is the enthalpy change for the following reaction:

$$6C\,(s, graphite) + 6H_2\,(g) + 3O_2\,(g) \rightarrow C_6H_{12}O_6\,(s) \quad \Delta H_f^o = -1273.3\ kJ \tag{3.7.2}$$

It is not possible to measure the value of $\Delta H^o o_f$ for glucose, −1273.3 kJ/mol, by simply mixing appropriate amounts of graphite, O_2, and H_2 and measuring the heat evolved as glucose is formed since the reaction shown in Equation 3.7.2 does not occur at a measurable rate under any known conditions. Glucose is not unique; most compounds cannot be prepared by the chemical equations that define their standard enthalpies of formation. Instead, values of $\Delta H^o o_f$ are obtained using **Hess's law** and standard enthalpy changes that have been measured for other reactions, such as combustion reactions. Values of ΔH_f^o for an extensive list of compounds are given in Table T1. Note that ΔH_f^o values are always reported in kilojoules per mole of the substance of interest. Also notice in Table T1 that the standard enthalpy of formation of O_2(g) is zero because it is the most stable form of oxygen in its standard state.

Example 3.7.1: Enthalpy of Formation

For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.

a. $HCl(g)$
b. $MgCO_3(s)$
c. $CH_3(CH_2)_{14}CO_2H(s)$ (*palmitic acid*)

Given:

compound formula and phase.

Asked for:

balanced chemical equation for its formation from elements in standard states

Strategy:

Use Table T1 to identify the standard state for each element. Write a chemical equation that describes the formation of the compound from the elements in their standard states and then balance it so that 1 mol of product is made.

Solution:

To calculate the standard enthalpy of formation of a compound, we must start with the elements in their standard states. The standard state of an element can be identified in Table T1: by a ΔH_f^o value of 0 kJ/mol.

Hydrogen chloride contains one atom of hydrogen and one atom of chlorine. Because the standard states of elemental hydrogen and elemental chlorine are $H_2(g)$ and $Cl_2(g)$, respectively, the unbalanced chemical equation is

$$H_2(g) + Cl_2(g) \rightarrow HCl(g)$$

Fractional coefficients are required in this case because ΔH^o_f values are reported for *1 mol* of the product, HCl. Multiplying both $H_2(g)$ and $Cl_2(g)$ by 1/2 balances the equation:

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) \rightarrow HCl(g)$$

The standard states of the elements in this compound are $\mathrm{Mg(s)}$, $\mathrm{C(s,\,graphite)}$, and $\mathrm{O_2(g)}$. The unbalanced chemical equation is thus

$$\mathrm{Mg(s) + C(s,\,graphite) + O_2(g) \rightarrow MgCO_3(s)}$$

This equation can be balanced by inspection to give

$$\mathrm{Mg(s) + C(s,\,graphite) + \tfrac{3}{2}O_2(g) \rightarrow MgCO_3(s)}$$

Palmitic acid, the major fat in meat and dairy products, contains hydrogen, carbon, and oxygen, so the unbalanced chemical equation for its formation from the elements in their standard states is as follows:

$$\mathrm{C(s,\,graphite) + H_2(g) + O_2(g) \rightarrow CH_3(CH_2)_{14}CO_2H(s)}$$

There are 16 carbon atoms and 32 hydrogen atoms in 1 mol of palmitic acid, so the balanced chemical equation is

$$\mathrm{16\,C(s,\,graphite) + 16\,H_2(g) + O_2(g) \longrightarrow CH_3(CH_2)_{14}CO_2H(s)}$$

? Exercise 3.7.1

For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.

a. $\mathrm{NaCl(s)}$
b. $\mathrm{H_2SO_4(l)}$
c. $\mathrm{CH_3CO_2H(l)}$ (*acetic acid*)

Answer a

$$\mathrm{Na(s) + \tfrac{1}{2}Cl_2(g) \rightarrow NaCl(s)}$$

Answer b

$$\mathrm{H_2(g) + \tfrac{1}{8}S_8(s) + 2\,O_2(g) \rightarrow H_2SO_4(l)}$$

Answer c

$$\mathrm{2\,C(s) + O_2(g) + 2\,H_2(g) \longrightarrow CH_3CO_2H(l)}$$



Definition of Heat of Formation Reactions: https://youtu.be/A20k0CK4doI

Standard Enthalpies of Reaction

Tabulated values of standard enthalpies of formation can be used to calculate enthalpy changes for *any* reaction involving substances whose ΔH_f^o values are known. The standard enthalpy of reaction ΔH_{rxn}^o is the enthalpy change that occurs when a reaction is carried out with all reactants and products in their standard states. Consider the general reaction

$$aA + bB \rightarrow cC + dD \tag{3.7.3}$$

where A, B, C, and D are chemical substances and a, b, c, and d are their stoichiometric coefficients. The magnitude of ΔH^o is the sum of the standard enthalpies of formation of the products, each multiplied by its appropriate coefficient, minus the sum of the standard enthalpies of formation of the reactants, also multiplied by their coefficients:

$$\Delta H^o_{rxn} = \underbrace{\left[c\Delta H^o_f(C) + d\Delta H^o_f(D)\right]}_{\text{products}} - \underbrace{\left[a\Delta H^o_f(A) + b\Delta H^o_f(B)\right]}_{\text{reactants}} \tag{3.7.4}$$

More generally, we can write

$$\Delta H^o_{rxn} = \sum m\Delta H^o_f(products) - \sum n\Delta H^o_f(reactants) \tag{3.7.5}$$

where the symbol $\sum$ means "sum of" and m and n are the stoichiometric coefficients of each of the products and the reactants, respectively. "Products minus reactants" summations such as Equation 3.7.5 arise from the fact that enthalpy is a state function. Because many other thermochemical quantities are also state functions, "products minus reactants" summations are very common in chemistry; we will encounter many others in subsequent chapters.

> "Products minus reactants" summations are typical of state functions.

To demonstrate the use of tabulated ΔH^o values, we will use them to calculate ΔH_{rxn} for the combustion of glucose, the reaction that provides energy for your brain:

$$C_6H_{12}O_6(s) + 6\,O_2(g) \rightarrow 6\,CO_2(g) + 6\,H_2O(l) \tag{3.7.6}$$

Using Equation 3.7.5, we write

$$\Delta H^o_f = \left\{6\Delta H^o_f[CO_2(g)] + 6\Delta H^o_f[H_2O(g)]\right\} - \left\{\Delta H^o_f[C_6H_{12}O_6(s)] + 6\Delta H^o_f[O_2(g)]\right\} \tag{3.7.7}$$

From Table T1, the relevant ΔH^o_f values are $\Delta H^o_f[CO_2(g)]$ = -393.5 kJ/mol, $\Delta H^o_f[H_2O(l)]$ = -285.8 kJ/mol, and $\Delta H^o_f[C_6H_{12}O_6(s)]$ = -1273.3 kJ/mol. Because $O_2(g)$ is a pure element in its standard state, $\Delta H^o_f[O_2(g)]$ = 0 kJ/mol. Inserting these values into Equation 3.7.7 and changing the subscript to indicate that this is a combustion reaction, we obtain

$$\Delta H^o_{comb} = [6(-393.5\ kJ/mol) + 6(-285.8\ kJ/mol)] - [-1273.3 + 6(0\ kJ\ mol)] \tag{3.7.8}$$

$$= -2802.5\ kJ/mol \tag{3.7.9}$$

As illustrated in Figure 3.7.2, we can use Equation 3.7.8 to calculate ΔH^o_f for glucose because enthalpy is a state function. The figure shows two pathways from reactants (middle left) to products (bottom). The more direct pathway is the downward green arrow labeled ΔH^o_{comb}. The alternative hypothetical pathway consists of **four separate reactions** that convert the reactants to the elements in their standard states (upward purple arrow at left) and then convert the elements into the desired products (downward purple arrows at right). The reactions that convert the reactants to the elements are the reverse of the equations that define the ΔH^o_f values of the reactants. Consequently, the enthalpy changes are

$$\begin{aligned}
\Delta H^o_1 &= \Delta H^o_f[glucose(s)] \\
&= -1\ \cancel{mol\ glucose}\left(\frac{1273.3\ kJ}{1\ \cancel{mol\ glucose}}\right) \\
&= +1273.3\ kJ \\
\Delta H^o_2 &= 6\Delta H^o_f[O_2(g)] \\
&= 6\ \cancel{mol\ O_2}\left(\frac{0\ kJ}{1\ \cancel{mol\ O_2}}\right) \\
&= 0\ kJ
\end{aligned} \tag{3.7.10}$$

> *Recall that when we reverse a reaction, we must also reverse the **sign** of the accompanying enthalpy change (Equation 3.7.4 since the products are now reactants and vice versa.*

The overall enthalpy change for conversion of the reactants (1 mol of glucose and 6 mol of O_2) to the elements is therefore +1273.3 kJ.

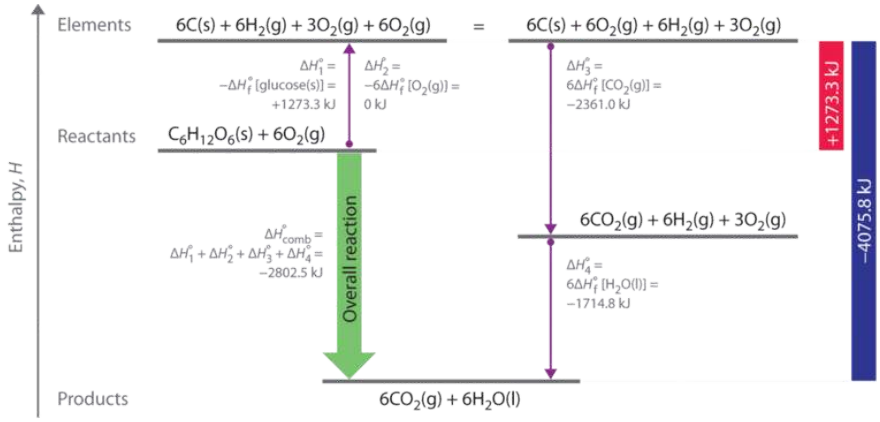


Figure 3.7.1: A Thermochemical Cycle for the Combustion of Glucose. Two hypothetical pathways are shown from the reactants to the products. The green arrow labeled ΔH^o_{comb} indicates the combustion reaction. Alternatively, we could first convert the reactants to the elements via the reverse of the equations that define their standard enthalpies of formation (the upward arrow, labeled ΔH^o_1 and ΔH^o_2). Then we could convert the elements to the products via the equations used to define their standard enthalpies of formation (the downward arrows, labeled ΔH^o_3 and ΔH^o_4). Because enthalpy is a state function, ΔH^o_{comb} is equal to the sum of the enthalpy changes $\Delta H^o_1 + \Delta H^o_2 + \Delta H^o_3 + \Delta H^o_4$.

The reactions that convert the elements to final products (downward purple arrows in Figure 3.7.2) are identical to those used to define the ΔH^o_f values of the products. Consequently, the enthalpy changes (from Table T1) are

$$\Delta H^o_3 = \Delta H^o_f\,[CO_2\,(g)] = 6\ \cancel{mol\ CO_2}\left(\frac{393.5\ kJ}{1\ \cancel{mol\ CO_2}}\right) = -2361.0\ kJ$$
$$\Delta H^o_4 = 6\Delta H^o_f\,[H_2O\,(l)] = 6\ \cancel{mol\ H_2O}\left(\frac{-285.8\ kJ}{1\ \cancel{mol\ H_2O}}\right) = -1714.8\ kJ \tag{3.7.11}$$

The overall enthalpy change for the conversion of the elements to products (6 mol of carbon dioxide and 6 mol of liquid water) is therefore −4075.8 kJ. Because enthalpy is a state function, the difference in enthalpy between an initial state and a final state can be computed using *any* pathway that connects the two. Thus the enthalpy change for the combustion of glucose to carbon dioxide and water is the sum of the enthalpy changes for the conversion of glucose and oxygen to the elements (+1273.3 kJ) and for the conversion of the elements to carbon dioxide and water (−4075.8 kJ):

$$\Delta H^o_{comb} = +1273.3\ kJ + (-4075.8\ kJ) = -2802.5\ kJ \tag{3.7.12}$$

This is the same result we obtained using the "products minus reactants" rule (Equation 3.7.5) and ΔH^o_f values. The two results must be the same because Equation 3.7.12 is just a more compact way of describing the thermochemical cycle shown in Figure 3.7.1.

✔ Example 3.7.2: Heat of Combustion

Long-chain fatty acids such as palmitic acid ($CH_3(CH_2)_{14}CO_2H$) are one of the two major sources of energy in our diet (ΔH^o_f =−891.5 kJ/mol). Use the data in Table T1 to calculate ΔH^o_{comb} for the combustion of palmitic acid. Based on the energy released in combustion *per gram*, which is the better fuel — glucose or palmitic acid?

Given: compound and ΔH^o_f values

Asked for: ΔH^o_{comb} per mole and per gram

Strategy:

A. After writing the balanced chemical equation for the reaction, use Equation 3.7.5 and the values from Table T1 to calculate ΔH^o_{comb} the energy released by the combustion of 1 mol of palmitic acid.

B. Divide this value by the molar mass of palmitic acid to find the energy released from the combustion of 1 g of palmitic acid. Compare this value with the value calculated in Equation 3.7.8 for the combustion of glucose to determine which is the better fuel.

Solution:

A To determine the energy released by the combustion of palmitic acid, we need to calculate its ΔH^o_f. As always, the first requirement is a balanced chemical equation:

$$C_{16}H_{32}O_{2(s)} + 23O_{2(g)} \rightarrow 16CO_{2(g)} + 16H_2O_{(l)}$$

Using Equation 3.7.5 ("products minus reactants") with ΔH^o_f values from Table T1 (and omitting the physical states of the reactants and products to save space) gives

$$\begin{aligned}\Delta H^o_{comb} &= \sum m\Delta H^o_f\,(products) - \sum n\Delta H^o_f\,(reactants)\\ &= [16\,(-393.5\ kJ/mol\ CO_2) + 16\,(-285.8\ kJ/mol\ H_2O\,)]\\ &\quad - [-891.5\ kJ/mol\ C_{16}H_{32}O_2 + 23\,(0\ kJ/mol\ O_2\,)]\\ &= -9977.3\ kJ/mol\end{aligned}$$

This is the energy released by the combustion of 1 mol of palmitic acid.

B The energy released by the combustion of 1 g of palmitic acid is

$$\Delta H^o_{comb}\ per\ gram = \left(\frac{9977.3\ kJ}{1\ \cancel{mol}}\right)\left(\frac{1\ \cancel{mol}}{256.42\ g}\right) = -38.910\ kJ/g$$

As calculated in Equation 3.7.8, \(ΔH^o_f\) of glucose is −2802.5 kJ/mol. The energy released by the combustion of 1 g of glucose is therefore

$$\Delta H^o_{comb}\ per\ gram = \left(\frac{-2802.5\ kJ}{1\ \cancel{mol}}\right)\left(\frac{1\ \cancel{mol}}{180.16\ g}\right) = -15.556\ kJ/g$$

The combustion of fats such as palmitic acid releases more than twice as much energy per gram as the combustion of sugars such as glucose. This is one reason many people try to minimize the fat content in their diets to lose weight.

? Exercise 3.7.2: Water–gas shift reaction

Use Table T1 to calculate ΔH^o_{rxn} for the *water–gas shift reaction*, which is used industrially on an enormous scale to obtain $H_2(g)$:

$$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$$

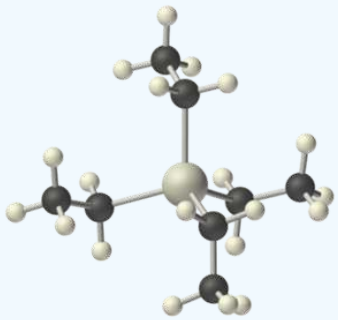
Answer

−41.2 kJ/mol

We can also measure the enthalpy change for another reaction, such as a combustion reaction, and then use it to calculate a compound's ΔH^o_f which we cannot obtain otherwise. This procedure is illustrated in Example 3.7.3.

✓ Example 3.7.3: Tetraethyllead

Beginning in 1923, tetraethyllead $[(C_2H_5)_4Pb]$ was used as an antiknock additive in gasoline in the United States. Its use was completely phased out in 1986 because of the health risks associated with chronic lead exposure. Tetraethyllead is a highly poisonous, colorless liquid that burns in air to give an orange flame with a green halo. The combustion products are $CO_2(g)$, $H_2O(l)$, and red $PbO(s)$. What is the standard enthalpy of formation of tetraethyllead, given that ΔH^o_f is −19.29 kJ/g for the combustion of tetraethyllead and ΔH^o_f of red PbO(s) is −219.0 kJ/mol?



Tetraethyllead

Given: reactant, products, and ΔH^o_{comb} values

Asked for: ΔH_f^o of the reactants

Strategy:

A. Write the balanced chemical equation for the combustion of tetraethyl lead. Then insert the appropriate quantities into Equation 3.7.5 to get the equation for ΔH^o_f of tetraethyl lead.

B. Convert ΔH_{comb}^o per gram given in the problem to ΔH_{comb}^o per mole by multiplying ΔH_{comb}^o per gram by the molar mass of tetraethyllead.

C. Use Table T1 to obtain values of ΔH_f^o for the other reactants and products. Insert these values into the equation for ΔH_f^o of tetraethyl lead and solve the equation.

Solution:

A The balanced chemical equation for the combustion reaction is as follows:

$$2\,(\mathrm{C_2H_5})_4\mathrm{Pb(l)} + 27\,\mathrm{O_2(g)} \rightarrow 2\,\mathrm{PbO(s)} + 16\,\mathrm{CO_2(g)} + 20\,\mathrm{H_2O(l)}$$

Using Equation 3.7.5 gives

$$\Delta H_{comb}^o = \left[2\Delta H_f^o\,(PbO) + 16\Delta H_f^o\,(CO_2) + 20\Delta H_f^o\,(H_2O)\right] - \left[2\Delta H_f^o\,((C_2H_5)_4Pb) + 27\Delta H_f^o\,(O_2)\right]$$

Solving for $\Delta H_f^o[(\mathrm{C_2H_5})_4\mathrm{Pb}]$ gives

$$\Delta H_f^o\,((C_2H_5)_4Pb) = \Delta H_f^o\,(PbO) + 8\Delta H_f^o\,(CO_2) + 10\Delta H_f^o\,(H_2O) - \frac{27}{2}\Delta H_f^o\,(O_2) - \frac{\Delta H_{comb}^o}{2}$$

The values of all terms other than $\Delta H_f^o[(\mathrm{C_2H_5})_4\mathrm{Pb}]$ are given in Table T1.

B The magnitude of ΔH_{comb}^o is given in the problem in kilojoules per *gram* of tetraethyl lead. We must therefore multiply this value by the molar mass of tetraethyl lead (323.44 g/mol) to get ΔH_{comb}^o for 1 mol of tetraethyl lead:

$$\Delta H_{comb}^o = \left(\frac{-19.29\ kJ}{\cancel{g}}\right)\left(\frac{323.44\ \cancel{g}}{mol}\right)$$
$$= -6329\ kJ/mol$$

Because the balanced chemical equation contains 2 mol of tetraethyllead, ΔH_{rxn}^o is

$$\Delta H_{rxn}^o = 2\ \ mol\ \cancel{(C_2H5)_4Pb}\left(\frac{-6329\ kJ}{1\ \ mol\ \cancel{(C_2H5)_4Pb}}\right)$$
$$= -12,480\ kJ$$

C Inserting the appropriate values into the equation for $\Delta H_f^o[(\mathrm{C_2H_5})_4\mathrm{Pb}]$ gives

$$\Delta H_f^o\,[(C_2H_4)_4Pb] = [1\ mol\ PbO\ \times 219.0\ kJ/mol] + [8\ mol\ CO_2 \times (-393.5\ kJ/mol)] + [10\ mol\ H_2O \times (-285.8\ kJ/mol)]$$
$$+ [-27/2\ mol\ O_2) \times 0\ kJ/mol\ O_2]\,[12,480.2\ kJ/mol\ (C_2H_5)_4Pb]$$
$$= -219.0\ kJ - 3148\ kJ - 2858kJ - 0kJ + 6240\ kJ = 15kJ/mol$$

? Exercise 3.7.3

Ammonium sulfate, $(\mathrm{NH_4})_2\mathrm{SO_4}$, is used as a fire retardant and wood preservative; it is prepared industrially by the highly exothermic reaction of gaseous ammonia with sulfuric acid:

$$2\,\mathrm{NH_3(g)} + \mathrm{H_2SO_4(aq)} \rightarrow (\mathrm{NH_4})_2\mathrm{SO_4(s)}$$

The value of ΔH_{rxn}^o is -179.4 kJ/mole $\mathrm{H_2SO_4}$. Use the data in Table T1 to calculate the standard enthalpy of formation of ammonium sulfate (in kilojoules per mole).

Answer

−1181 kJ/mol



Calculating DH° using DHf°: https://youtu.be/Y3aJJno9W2c

Summary

- The standard state for measuring and reporting enthalpies of formation or reaction is 25 °C and 1 atm.
- The elemental form of each atom is that with the lowest enthalpy in the standard state.
- The standard state heat of formation for the elemental form of each atom is zero.

The **enthalpy of formation** (ΔH_f) is the enthalpy change that accompanies the formation of a compound from its elements. **Standard enthalpies of formation** (ΔH_f^o) are determined under **standard conditions**: a pressure of 1 atm for gases and a concentration of 1 M for species in solution, with all pure substances present in their **standard states** (their most stable forms at 1 atm pressure and the temperature of the measurement). The standard heat of formation of any element in its most stable form is defined to be zero. The **standard enthalpy of reaction** (ΔH_{rxn}^o) can be calculated from the sum of the **standard enthalpies of formation** of the products (each multiplied by its stoichiometric coefficient) minus the sum of the standard enthalpies of formation of the reactants (each multiplied by its stoichiometric coefficient)—the "products minus reactants" rule. The **enthalpy of solution** (ΔH_{soln}) is the heat released or absorbed when a specified amount of a solute dissolves in a certain quantity of solvent at constant pressure.

Contributors and Attributions

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3.8: Types of Solutions and Solubility

Learning Objectives

- To understand how enthalpy changes in solution formation.
- To use the magnitude of the changes in enthalpy to predict whether a given solute–solvent combination will spontaneously form a solution.

In all solutions, whether gaseous, liquid, or solid, the substance present in the greatest amount is the solvent, and the substance or substances present in lesser amounts are the solute(s). The solute does not have to be in the same physical state as the solvent, but the physical state of the solvent usually determines the state of the solution. As long as the solute and solvent combine to give a homogeneous solution, the solute is said to be soluble in the solvent. Table 3.8.1 lists some common examples of gaseous, liquid, and solid solutions and identifies the physical states of the solute and solvent in each.

Table 3.8.1: Types of Solutions

Solution	Solute	Solvent	Examples
gas	gas	gas	air, natural gas
liquid	gas	liquid	seltzer water (CO_2 gas in water)
liquid	liquid	liquid	alcoholic beverage (ethanol in water), gasoline
liquid	solid	liquid	tea, salt water
solid	gas	solid	H_2 in Pd (used for H_2 storage)
solid	solid	liquid	mercury in silver or gold (amalgam often used in dentistry)
solid	solid	solid	alloys and other "solid solutions"

Forming a Solution

The formation of a solution from a solute and a solvent is a physical process, not a chemical one. That is, both solute and solvent can be recovered in chemically unchanged forms using appropriate separation methods. For example, solid zinc nitrate dissolves in water to form an aqueous solution of zinc nitrate:

$$\mathrm{Zn(NO_3)_2(s) + H_2O(l) \rightarrow Zn^{2+}(aq) + 2\,NO_3^-(aq)} \tag{3.8.1}$$

Because $Zn(NO_3)_2$ can be recovered easily by evaporating the water, this is a physical process. In contrast, metallic zinc appears to dissolve in aqueous hydrochloric acid. In fact, the two substances undergo a chemical reaction to form an aqueous solution of zinc chloride with evolution of hydrogen gas:

$$\mathrm{Zn(s) + 2\,H^+(aq) + 2\,Cl^-(aq) \rightarrow Zn^{2+}(aq) + 2\,Cl^-(aq) + H_2(g)} \tag{3.8.2}$$

When the solution evaporates, we do not recover metallic zinc, so we cannot say that metallic zinc is soluble in aqueous hydrochloric acid because it is chemically transformed when it dissolves. The dissolution of a solute in a solvent to form a solution does not involve a chemical transformation (that it is a physical change).

> *Dissolution of a solute in a solvent to form a solution does not involve a chemical transformation.*

Substances that form a single homogeneous phase in all proportions are said to be completely *miscible* in one another. Ethanol and water are miscible, just as mixtures of gases are miscible. If two substances are essentially insoluble in each other, such as oil and water, they are *immiscible*. Examples of gaseous solutions that we have already discussed include Earth's atmosphere.

The Role of Enthalpy in Solution Formation

Energy is required to overcome the intermolecular interactions in a solute, which can be supplied only by the new interactions that occur in the solution, when each solute particle is surrounded by particles of the solvent in a process called solvation (or hydration when the solvent is water). Thus all of the solute–solute interactions and many of the solvent–solvent interactions must be disrupted for a solution to form. In this section, we describe the role of enthalpy in this process.

Because enthalpy is a state function, we can use a thermochemical cycle to analyze the energetics of solution formation. The process occurs in three discrete steps, indicated by ΔH_1, ΔH_2, and ΔH_3 in Figure 3.8.2. The overall enthalpy change in the formation of the solution (ΔH_{soln}) is the sum of the enthalpy changes in the three steps:

$$\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3 \tag{3.8.3}$$

When a solvent is added to a solution, steps 1 and 2 are both endothermic because energy is required to overcome the intermolecular interactions in the solvent (ΔH_1) and the solute (ΔH_2). Because ΔH is positive for both steps 1 and 2, the solute–solvent interactions (ΔH_3) must be stronger than the solute–solute and solvent–solvent interactions they replace in order for the dissolution process to be exothermic ($\Delta H_{soln} < 0$). When the solute is an ionic solid, ΔH_2 corresponds to the lattice energy that must be overcome to form a solution. The higher the charge of the ions in an ionic solid, the higher the lattice energy. Consequently, solids that have very high lattice energies, such as MgO (−3791 kJ/mol), are generally insoluble in all solvents.

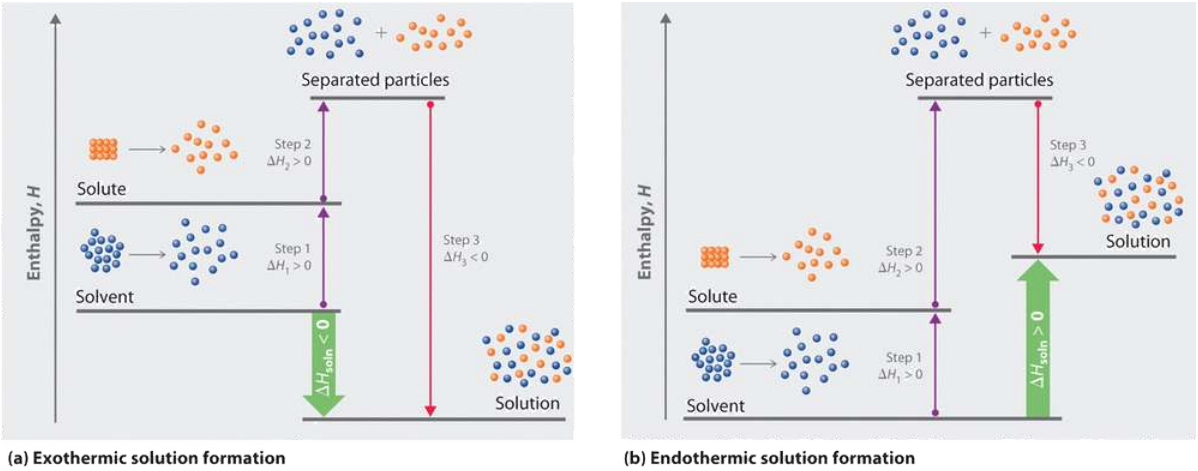


Figure 3.8.2: Enthalpy Changes That Accompany the Formation of a Solution. Solvation can be an exothermic or endothermic process depending on the nature of the solute and solvent. In both cases, step 1, separation of the solvent particles, is energetically uphill ($\Delta H_1 > 0$), as is step 2, separation of the solute particles ($\Delta H_2 > 0$). In contrast, energy is released in step 3 ($\Delta H_3 < 0$) because of interactions between the solute and solvent. (a) When ΔH_3 is larger in magnitude than the sum of ΔH_1 and ΔH_2, the overall process is exothermic ($\Delta H_{soln} < 0$), as shown in the thermochemical cycle. (b) When ΔH_3 is smaller in magnitude than the sum of ΔH_1 and ΔH_2, the overall process is endothermic ($\Delta H_{soln} > 0$).

A positive value for ΔH_{soln} does not mean that a solution will not form. Whether a given process, including formation of a solution, occurs spontaneously depends on whether the total energy of the system is lowered as a result. Enthalpy is only one of the contributing factors. A high ΔH_{soln} is usually an indication that the substance is not very soluble. Instant cold packs used to treat athletic injuries, for example, take advantage of the large positive ΔH_{soln} of ammonium nitrate during dissolution (+25.7 kJ/mol), which produces temperatures less than 0°C (Figure 3.8.3).



Figure 3.8.3: Commercial Cold Packs for Treating Injuries. These packs contain solid NH_4NO_3 and water in separate compartments. When the seal between the compartments is broken, the NH_4NO_3 dissolves in the water. Because ΔH_{soln} for NH_4NO_3 is much greater than zero, heat is absorbed by the cold pack during the dissolution process, producing local temperatures less than 0°C.

Table 3.8.2 summarizes how enthalpic factors affect solution formation for four general cases. The column on the far right uses the relative magnitudes of the enthalpic contributions to predict whether a solution will form from each of the four. In two of the cases the enthalpy of solution is expected to be relatively small and can be either positive or negative and we would expect a solution to form. In the other two cases the enthalpy of solution is expected to be large and positive. Hence we expect that a solution will not form readily.

Table 3.8.2: Relative Changes in Enthalpies for Different Solute–Solvent Combinations*

ΔH_1 (separation of solvent molecules)	ΔH_2 (separation of solute particles)	ΔH_3 (solute–solvent interactions)	ΔH_{soln} (ΔH_1 + ΔH_2 +ΔH_3)	Result of Mixing Solute and Solvent
large; positive	large; positive	large; negative	small; positive or negative	solution will usually form
small; positive	large; positive	small; negative	large; positive	solution will not form
large; positive	small; positive	small; negative	large; positive	solution will not form
small; positive	small; positive	small; negative	small; positive or negative	solution will usually form

*ΔH_1, ΔH_2, and ΔH_3 refer to the processes indicated in the thermochemical cycle shown in Figure 3.8.2

In contrast to liquid solutions, the intermolecular interactions in gases are weak (they are considered to be nonexistent in ideal gases). Hence mixing gases is usually a thermally neutral process ($\Delta H_{soln} \approx 0$), and the entropic factor due to the increase in disorder is dominant (Figure 3.8.4). Consequently, all gases dissolve readily in one another in all proportions to form solutions.

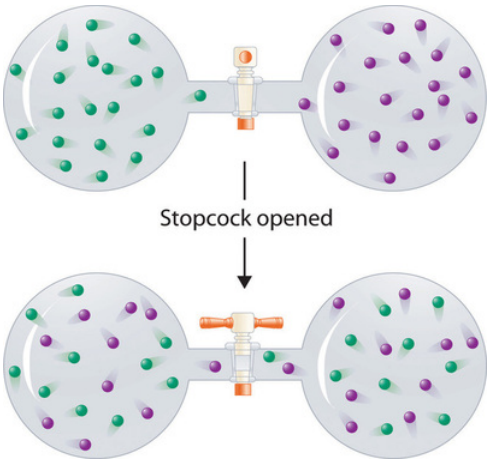
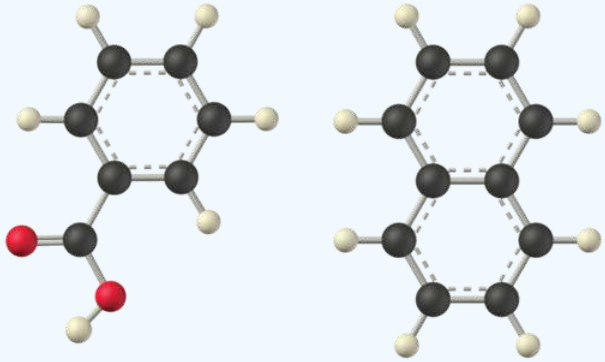


Figure 3.8.4: Formation of a Solution of Two Gases. (top) Pure samples of two different gases are in separate bulbs. (bottom) When the connecting stopcock is opened, diffusion causes the two gases to mix together and form a solution. Even though ΔH_{soln} is zero for the process, the increased entropy of the solution (the increased disorder) versus that of the separate gases favors solution formation.

Example 3.8.1

Considering LiCl, benzoic acid ($\mathrm{C_6H_5CO_2H}$), and naphthalene, which will be most soluble and which will be least soluble in water?



Given: three compounds

Asked for: relative solubilities in water

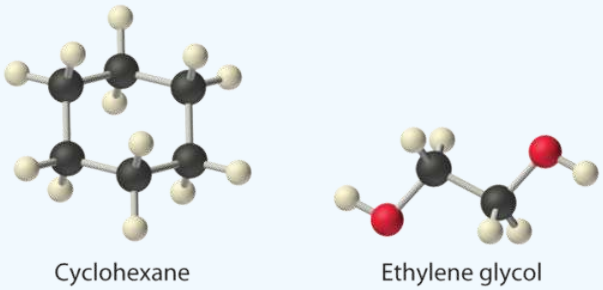
Strategy: Assess the relative magnitude of the enthalpy change for each step in the process shown in Figure 3.8.2. Then use Table 3.8.2 to predict the solubility of each compound in water and arrange them in order of decreasing solubility.

Solution:

The first substance, LiCl, is an ionic compound, so a great deal of energy is required to separate its anions and cations and overcome the lattice energy (ΔH_2 is far greater than zero in Equation 3.8.1). Because water is a polar substance, the interactions between both Li^+ and Cl^- ions and water should be favorable and strong. Thus we expect ΔH_3 to be far less than zero, making LiCl soluble in water. In contrast, naphthalene is a nonpolar compound, with only London dispersion forces holding the molecules together in the solid state. We therefore expect ΔH_2 to be small and positive. We also expect the interaction between polar water molecules and nonpolar naphthalene molecules to be weak $\Delta H_3 \approx 0$. Hence we do not expect naphthalene to be very soluble in water, if at all. Benzoic acid has a polar carboxylic acid group and a nonpolar aromatic ring. We therefore expect that the energy required to separate solute molecules (ΔH_2) will be greater than for naphthalene and less than for LiCl. The strength of the interaction of benzoic acid with water should also be intermediate between those of LiCl and naphthalene. Hence benzoic acid is expected to be more soluble in water than naphthalene but less soluble than LiCl. We thus predict LiCl to be the most soluble in water and naphthalene to be the least soluble.

Exercise 3.8.1

Considering ammonium chloride, cyclohexane, and ethylene glycol ($HOCH_2CH_2OH$), which will be most soluble and which will be least soluble in benzene?



Answer

The most soluble is cyclohexane; the least soluble is ammonium chloride.

Summary

Solutions are homogeneous mixtures of two or more substances whose components are uniformly distributed on a microscopic scale. The component present in the greatest amount is the solvent, and the components present in lesser amounts are the solute(s). The formation of a solution from a solute and a solvent is a physical process, not a chemical one. Substances that are miscible, such as gases, form a single phase in all proportions when mixed. Substances that form separate phases are immiscible. Solvation is the process in which solute particles are surrounded by solvent molecules. When the solvent is water, the process is called hydration. The overall enthalpy change that accompanies the formation of a solution, ΔH_{soln}, is the sum of the enthalpy change for breaking the intermolecular interactions in both the solvent and the solute and the enthalpy change for the formation of new solute–solvent interactions. Exothermic ($\Delta H_{soln} < 0$) processes favor solution formation.

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3.9: Foods and Fuels

Learning Objectives

- To understand the relationship between thermochemistry and nutrition.

The thermochemical quantities that you probably encounter most often are the caloric values of food. Food supplies the raw materials that your body needs to replace cells and the energy that keeps those cells functioning. About 80% of this energy is released as heat to maintain your body temperature at a sustainable level to keep you alive. The nutritional Calorie (with a capital C) that you see on food labels is equal to 1 kcal (kilocalorie). The caloric content of food is determined from its enthalpy of combustion (ΔH_{comb}) per gram, as measured in a bomb calorimeter, using the general reaction

$$\text{food} + \text{excess } \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + \text{N}_2(\text{g}) \tag{3.9.1}$$

There are two important differences, however, between the caloric values reported for foods and the ΔH_{comb} of the same foods burned in a calorimeter. First, the ΔH_{comb} described in joules (or kilojoules) are negative for all substances that can be burned. In contrast, the caloric content of a food is always expressed as a *positive* number because it is *stored energy*. Therefore,

$$\text{caloric content} = -\Delta H_{\text{comb}} \tag{3.9.2}$$

Second, when foods are burned in a calorimeter, any nitrogen they contain (largely from proteins, which are rich in nitrogen) is transformed to N_2. In the body, however, nitrogen from foods is converted to urea [$(H_2N)_2C{=}O$], rather than N_2 before it is excreted. The ΔH_{comb} of urea measured by bomb calorimetry is −632.0 kJ/mol. Consequently, the enthalpy change measured by calorimetry for any nitrogen-containing food is greater than the amount of energy the body would obtain from it. The difference in the values is equal to the ΔH_{comb} of urea multiplied by the number of moles of urea formed when the food is broken down. This point is illustrated schematically in the following equations:

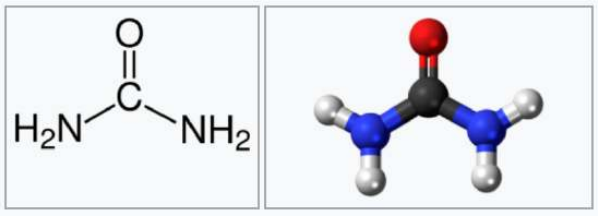
$$\text{food} + \text{excess } \text{O}_2(\text{g}) \xrightarrow{\Delta H_1 < 0} \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + \cancel{(\text{H}_2\text{N})_2\text{C}{=}\text{O}(\text{s})}$$

$$\cancel{(\text{H}_2\text{N})_2\text{C}{=}\text{O}(\text{s})} + \tfrac{3}{2}\text{O}_2(\text{g}) \xrightarrow{\Delta H_2 = 632.0\,\text{kJ/mol}} \text{CO}_2(\text{g}) + 2\,\text{H}_2\text{O}(\text{l}) + \text{N}_2(\text{g})$$

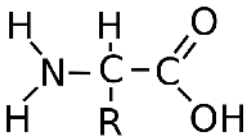
which adds up to

$$\text{food} + \text{excess } \text{O}_2(\text{g}) \xrightarrow{\Delta H_3 = \Delta H_1 + \Delta H_2 < 0} 2\,\text{CO}_2(\text{g}) + 3\,\text{H}_2\text{O}(\text{l}) + \text{N}_2(\text{g})$$

All three ΔH values are negative, and, by Hess's law, $\Delta H_3 = \Delta H_1 + \Delta H_2$. The magnitude of ΔH_1 must be less than ΔH_3, the calorimetrically measured ΔH_{comb} for a food. By producing urea rather than N_2, therefore, humans are excreting some of the energy that was stored in their food.



Because of their different chemical compositions, foods vary widely in caloric content. As we saw previously, for instance, a fatty acid such as palmitic acid produces about 39 kJ/g during combustion, while a sugar such as glucose produces 15.6 kJ/g. Fatty acids and sugars are the building blocks of fats and carbohydrates, respectively, two of the major sources of energy in the diet. Nutritionists typically assign average values of 38 kJ/g (about 9 Cal/g) and 17 kJ/g (about 4 Cal/g) for fats and carbohydrates, respectively, although the actual values for specific foods vary because of differences in composition. Proteins, the third major source of calories in the diet, vary as well. Proteins are composed of amino acids, which have the following general structure:



General structure of an amino acid. An amino acid contains an amine group ($-NH_2$) and a carboxylic acid group ($-CO_2H$).

In addition to their amine and carboxylic acid components, amino acids may contain a wide range of other functional groups: R can be hydrogen (–H); an alkyl group (e.g., $–CH_3$); an aryl group (e.g., $–CH_2C_6H_5$); or a substituted alkyl group that contains an amine, an alcohol, or a carboxylic acid (Figure 3.9.1). Of the 20 naturally occurring amino acids, 10 are required in the human diet; these 10 are called *essential amino acids* because our bodies are unable to synthesize them from other compounds. Because R can be any of several different groups, each amino acid has a different value of ΔH_{comb}. Proteins are usually estimated to have an average ΔH_{comb} of 17 kJ/g (about 4 Cal/g).

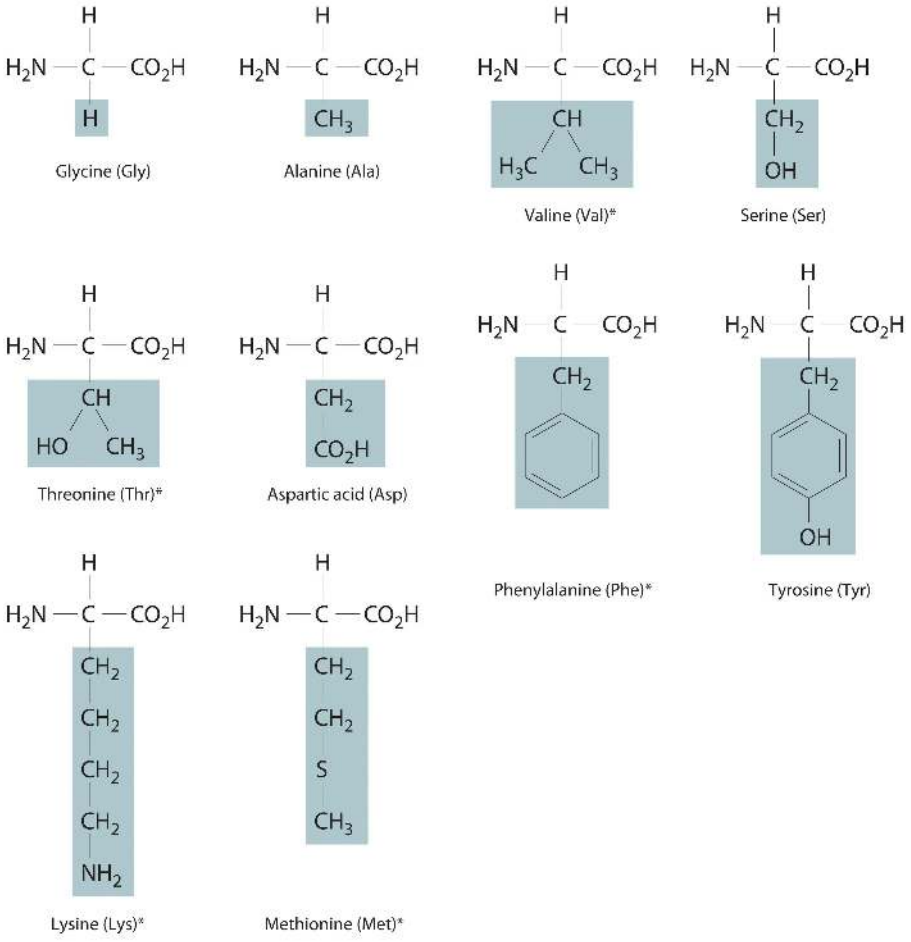
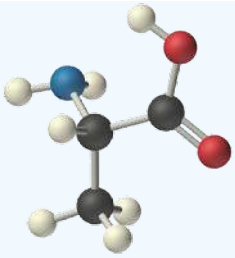


Figure 3.9.1: The Structures of 10 Amino Acids. Essential amino acids in this group are indicated with an asterisk. Structures of glycine, alanine, valine, serine, threonine, aspartic acid, phenylalanine, tyrosine, lysine, methionine.

Example 3.9.1

Calculate the amount of available energy obtained from the biological oxidation of 1.000 g of alanine (an amino acid). Remember that the nitrogen-containing product is urea, not N_2, so biological oxidation of alanine will yield *less* energy than will combustion. The value of ΔH_{comb} for alanine is −1577 kJ/mol.

https://chem.libretexts.org/@go/page/393508



Alanine

Given: amino acid and ΔH_{comb} per mole

Asked for: caloric content per gram

Strategy:

A. Write balanced chemical equations for the oxidation of alanine to CO_2, H_2O, and urea; the combustion of urea; and the combustion of alanine. Multiply both sides of the equations by appropriate factors and then rearrange them to cancel urea from both sides when the equations are added.

B. Use Hess's law to obtain an expression for ΔH for the oxidation of alanine to urea in terms of the ΔH_{comb} of alanine and urea. Substitute the appropriate values of ΔH_{comb} into the equation and solve for ΔH for the oxidation of alanine to CO_2, H_2O, and urea.

C. Calculate the amount of energy released per gram by dividing the value of ΔH by the molar mass of alanine.

Solution:

The actual energy available biologically from alanine is less than its ΔH_{comb} because of the production of urea rather than N_2. We know the ΔH_{comb} values for alanine and urea, so we can use Hess's law to calculate ΔH for the oxidation of alanine to CO_2, H_2O, and urea.

A We begin by writing balanced chemical equations for (1) the oxidation of alanine to CO_2, H_2O, and urea; (2) the combustion of urea; and (3) the combustion of alanine. Because alanine contains only a single nitrogen atom, whereas urea and N_2 each contain two nitrogen atoms, it is easier to balance Equations 1 and 3 if we write them for the oxidation of 2 mol of alanine:

$$(1)\quad 2C_3H_7NO_2\,(s)+6O_2\,(g)\rightarrow 5CO_2\,(g)+5H_2O\,(l)+(H_2N)_2C=O\,(s)$$

$$(2)\quad (H_2N)_2C=O\,(s)+\frac{3}{2}O_2\,(g)\rightarrow CO_2\,(g)+2H_2O\,(l)+N_2\,(g)$$

$$(3)\quad (1)\quad 2C_3H_7NO_2\,(s)+\frac{15}{2}O_2\,(g)\rightarrow 6CO_2\,(g)+7H_2O\,(l)+N_2\,(g)$$

Adding Equations 1 and 2 and canceling urea from both sides give the overall chemical equation directly:

$$(1)\quad 2C_3H_7NO_2\,(s)+6O_2\,(g)\rightarrow 5CO_2\,(g)+5H_2O\,(l)+\cancel{(H_2N)_2C=O\,(s)}$$

$$(2)\quad \cancel{(H_2N)_2C=O\,(s)}+\frac{3}{2}O_2\,(g)\rightarrow CO_2\,(g)+2H_2O\,(l)+N_2\,(g)$$

$$(3)\quad (1)\quad 2C_3H_7NO_2\,(s)+\frac{15}{2}O_2\,(g)\rightarrow 6CO_2\,(g)+7H_2O\,(l)+N_2\,(g)$$

B By Hess's law, $\Delta H_3 = \Delta H_1 + \Delta H_2$. We know that $\Delta H_3 = 2\Delta H_{comb}$ (alanine), $\Delta H_2 = \Delta H_{comb}$ (urea), and $\Delta H_1 = 2\Delta H$ (alanine → urea). Rearranging and substituting the appropriate values gives

$$\Delta H_1=\Delta H_3-\Delta H_2$$

$$=2\,(-1577\ kJ/mol)-(-632.0\ kJ/mol)$$

= -2522 \; kJ/\left (2 \;mol\; analine \right) \nonumber \]

Thus ΔH (alanine → urea) = −2522 kJ/(2 mol of alanine) = −1261 kJ/mol of alanine. Oxidation of alanine to urea rather than to nitrogen therefore results in about a 20% decrease in the amount of energy released (−1261 kJ/mol versus −1577 kJ/mol).

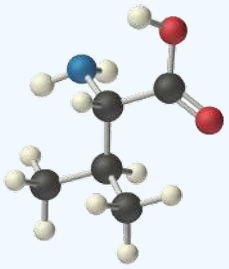
C The energy released per gram by the biological oxidation of alanine is

$$\left(\frac{-1261\ kJ}{1\ \cancel{mol}}\right)\left(\frac{1\ \cancel{mol}}{89.094\ g}\right) = -14.15\ kJ/g$$

This is equal to −3.382 Cal/g.

? Exercise 3.9.1

Calculate the energy released per gram from the oxidation of valine (an amino acid) to CO_2, H_2O, and urea. Report your answer to three significant figures. The value of ΔH_{comb} for valine is −2922 kJ/mol.



Valine

Answer

−22.2 kJ/g (−5.31 Cal/g)

The reported caloric content of foods does not include ΔH_{comb} for those components that are not digested, such as fiber. Moreover, meats and fruits are 50%−70% water, which cannot be oxidized by O_2 to obtain energy. So water contains no calories. Some foods contain large amounts of fiber, which is primarily composed of sugars. Although fiber can be burned in a calorimeter just like glucose to give carbon dioxide, water, and heat, humans lack the enzymes needed to break fiber down into smaller molecules that can be oxidized. Hence fiber also does not contribute to the caloric content of food.

Table 3.9.1: Approximate Composition and Fuel Value of an 8 oz Slice of Roast Beef

Composition	Calories
97.5 g of water	× 0 Cal/g = 0
58.7 g of protein	× 4 Cal/g = 235
69.3 g of fat	× 9 Cal/g = 624
0 g of carbohydrates	× 4 Cal/g = 0
1.5 g of minerals	× 0 Cal/g = 0
Total mass: 227.0 g	**Total calories: about 900 Cal**

We can determine the caloric content of foods in two ways. The most precise method is to dry a carefully weighed sample and carry out a combustion reaction in a bomb calorimeter. The more typical approach, however, is to analyze the food for protein, carbohydrate, fat, water, and "minerals" (everything that doesn't burn) and then calculate the caloric content using the average values for each component that produces energy (9 Cal/g for fats, 4 Cal/g for carbohydrates and proteins, and 0 Cal/g for water and minerals). An example of this approach is shown in Table 3.9.1 for a slice of roast beef. The compositions and caloric contents of some common foods are given in Table 3.9.2.

Table 3.9.2: Approximate Compositions and Fuel Values of Some Common Foods

Food (quantity)	Approximate Composition (%)	Food Value (Cal/g)	Calories

Food (quantity)	Approximate Composition (%)				Food Value (Cal/g)	Calories
	Water	**Carbohydrate**	**Protein**	**Fat**		
beer (12 oz)	92	3.6	0.3	0	0.4	150
coffee (6 oz)	100	~0	~0	~0	~0	~0
milk (1 cup)	88	4.5	3.3	3.3	0.6	150
egg (1 large)	75	2	12	12	1.6	80
butter (1 tbsp)	16	~0	~0	79	7.1	100
apple (8 oz)	84	15	~0	0.5	0.6	125
bread, white (2 slices)	37	48	8	4	2.6	130
brownie (40 g)	10	55	5	30	4.8	190
hamburger (4 oz)	54	0	24	21	2.9	326
fried chicken (1 drumstick)	53	8.3	22	15	2.7	195
carrots (1 cup)	87	10	1.3	~0	0.4	70

Because the Calorie represents such a large amount of energy, a few of them go a long way. An average 73 kg (160 lb) person needs about 67 Cal/h (1600 Cal/day) to fuel the basic biochemical processes that keep that person alive. This energy is required to maintain body temperature, keep the heart beating, power the muscles used for breathing, carry out chemical reactions in cells, and send the nerve impulses that control those automatic functions. Physical activity increases the amount of energy required but not by as much as many of us hope (Table 3.9.2). A moderately active individual requires about 2500−3000 Cal/day; athletes or others engaged in strenuous activity can burn 4000 Cal/day. Any excess caloric intake is stored by the body for future use, usually in the form of fat, which is the most compact way to store energy. When more energy is needed than the diet supplies, stored fuels are mobilized and oxidized. We usually exhaust the supply of stored carbohydrates before turning to fats, which accounts in part for the popularity of low-carbohydrate diets.

Table 3.9.3: Approximate Energy Expenditure by a 160 lb Person Engaged in Various Activities

Activity	Cal/h
sleeping	80
driving a car	120
standing	140
eating	150
walking 2.5 mph	210
mowing lawn	250
swimming 0.25 mph	300
roller skating	350
tennis	420
bicycling 13 mph	660
running 10 mph	900

Example 3.9.2

What is the minimum number of Calories expended by a 72.6 kg person who climbs a 30-story building? (Assume each flight of stairs is 14 ft high.) How many grams of glucose are required to supply this amount of energy? (The energy released during the combustion of glucose was calculated in Example 5.5.4).

Given: mass, height, and energy released by combustion of glucose

Asked for: calories expended and mass of glucose needed

Strategy:

A. Convert mass and height to SI units and then substitute these values into Equation 5.6 to calculate the change in potential energy (in kilojoules). Divide the calculated energy by 4.184 Cal/kJ to convert the potential energy change to Calories.

B. Use the value obtained in Example 5.5.4 for the combustion of glucose to calculate the mass of glucose needed to supply this amount of energy.

Solution:

The energy needed to climb the stairs equals the difference between the person's potential energy (*PE*) at the top of the building and at ground level.

A Recall that *PE* = *mgh*. Because *m* and *h* are given in non-SI units, we must convert them to kilograms and meters, respectively

$$PE = (72.6\ kg)\left(9.81\ m/s^2\right)(128m) = 8.55 \times 10^4\left(kg \cdot m^2/s^2\right) = 91.2kJ$$

To convert to Calories, we divide by 4.184 kJ/kcal:

$$PE = \left(91.2\ \cancel{kJ}\right)\left(\frac{1\ kcal}{4.184\ \cancel{kJ}}\right) = 21.8\ kcal = 21.8\ Cal$$

B Because the combustion of glucose produces 15.6 kJ/g (Example 5), the mass of glucose needed to supply 85.5 kJ of energy is

$$PE = \left(91.2\ \cancel{kJ}\right)\left(\frac{1\ g\ glucose}{15.6\ \cancel{kJ}}\right) = 5.85\ g\ glucose$$

This mass corresponds to only about a teaspoonful of sugar! Because the body is only about 30% efficient in using the energy in glucose, the actual amount of glucose required would be higher: (100%/30%) × 5.85 g = 19.5 g. Nonetheless, this calculation illustrates the difficulty many people have in trying to lose weight by exercise alone.

Exercise 3.9.2

Calculate how many times a 160 lb person would have to climb the tallest building in the United States, the 110-story Willis Tower in Chicago, to burn off 1.0 lb of stored fat. Assume that each story of the building is 14 ft high and use a calorie content of 9.0 kcal/g of fat.

Answer

About 55 times

The calculations in Example 5.8.2 ignore various factors, such as how fast the person is climbing. Although the rate is irrelevant in calculating the change in potential energy, it is very relevant to the amount of energy actually required to ascend the stairs. The calculations also ignore the fact that the body's conversion of chemical energy to mechanical work is significantly less than 100% efficient. According to the average energy expended for various activities listed in Table 5.8.3, a person must run more than 4.5 h at 10 mph or bicycle for 6 h at 13 mph to burn off 1 lb of fat (1.0 lb × 454 g/lb × 9.0 Cal/g = 4100 Cal). But if a person rides a bicycle at 13 mph for only 1 h per day 6 days a week, that person will burn off 50 lb of fat in the course of a year (assuming, of course, the cyclist doesn't increase his or her intake of calories to compensate for the exercise).

Summary

Thermochemical concepts can be applied to determine the actual energy available in food. The nutritional **Calorie** is equivalent to 1 kcal (4.184 kJ). The caloric content of a food is its ΔH_{comb} per gram. The combustion of nitrogen-containing substances produces $N_2(g)$, but the biological oxidation of such substances produces urea. Hence the actual energy available from nitrogen-containing substances, such as proteins, is less than the ΔH_{comb} of urea multiplied by the number of moles of urea produced. The typical caloric contents for food are 9 Cal/g for fats, 4 Cal/g for carbohydrates and proteins, and 0 Cal/g for water and minerals.

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3.E: Thermochemistry (Exercises)

3.1: The Nature of Energy

Exercise 3.E.1

If a person exerts a force on an immovable object, does that person do work? Explain your answer.

Answer

Technically, the person is not doing any work, since the object does not move.

Exercise 3.E.2

Why does hammering a piece of sheet metal cause the metal to heat up?

Answer

The kinetic energy of the hammer is transferred to the metal.

Exercise 3.E.3

Describe the mathematical relationship between (a) the thermal energy stored in an object and that object's mass and (b) the thermal energy stored in an object and that object's temperature.

Answer

a. The thermal energy content of an object is directly proportional to its mass.

b. The thermal energy content of an object is directly proportional to its temperature.

Exercise 3.E.4

Calculate how much energy (in kilojoules) is released or stored when each of the following occurs:

a. A 130 lb ice skater is lifted 7.50 ft off the ice.

b. 48 lb child jumps from a height of 4.0 ft.

c. An 18.5 lb light fixture falls from a 10.0 ft ceiling.

Answer

a. 1.3 kJ stored

b. 0.26 kJ released

c. 0.251 kJ released

3.2: The First Law of Thermodynamics

Exercise 3.E.5

What is the relationship between enthalpy and internal energy for a reaction that occurs at constant pressure?

Answer

At constant pressure, $\Delta H = \Delta U + P\Delta V$

Exercise 3.E.6

An intrepid scientist placed an unknown salt in a small amount of water. All the salt dissolved in the water, and the temperature of the solution dropped several degrees.

a. What is the sign of q for this reaction?
b. What is the sign of the enthalpy change for this reaction?
c. Is the dissolution exothermic or endothermic?

Answer

a. The temperature of the solution dropped, so the solution lost heat. That means the reaction gained heat so q for the reaction is positive.

b. Since the q of the reaction is positive, the sign of the enthalpy change is also positive.

c. Since heat is transferred from the surroundings to the system, it is endothermic.

3.3 & 3.4: Enthalpy

Exercise 3.E.7

Heat implies the flow of energy from one object to another. Describe the energy flow in an

a. exothermic reaction.

b. endothermic reaction.

Answer

a. In an exothermic reaction heat energy flows from the sytem to the surroundings

b. In an endothermic reaction heat energy flows from the surroundings to the system.

Exercise 3.E.8

In each scenario, the system is defined as the mixture of chemical substances that undergoes a reaction. State whether each process is endothermic or exothermic.

a. Water is added to sodium hydroxide pellets, and the flask becomes hot.

b. Ammonium nitrate crystals are dissolved in water, causing the solution to become cool.

Answer

a. exothermic

b. endothermic

Exercise 3.E.9

Given the following thermochemical equation, what is ΔH for the reverse reaction?

$$N_2\,(g) + 3H_2\,(g) \rightarrow 2NH_3\,(g)\ \Delta H = -91.8\ kJ/mol$$

Answer

ΔH = 91.8 kJ/mol

Exercise 3.E.10

Given the following thermochemical equation,

$$C_6H_6\ (l) \rightarrow 3C_2H2\ (g)\ \Delta H = 630.0\ kJ/mol$$

a. Write the complete thermochemical equation for the reverse reaction. Sketch an enthalpy diagram showing the relative positions of all species and include arrows indicating both of the above reactions with appropriate values for ΔH reaction.

b. what is ΔH for this reaction?

$$6C_2H2\ (g) \rightarrow 2C_6H_6\ (l)\ \Delta H = ?$$

Answer

b. -1260.0 kJ/mol

Exercise 3.E.11

Given the following thermochemical equation,

$$C_6H_6\ (l) \rightarrow 3C_2H2\ (g)\ \Delta H = 630.0\ kJ/mol$$

what is ΔH when 0.50 mole of C_6H_6 (l) reacts to form C_2H2 (g)?

Answer

315.0 kJ/mol

3.5: Calorimetry

Exercise 3.E.11

How much heat is required to heat a 28.4-g ice cube from −23.0 °C to −1.0 °C? Use ice c_p = 2.05 J/gK

Answer

1.3 kJ

Exercise 3.E.12

Using the data below, how much heat (q) is needed to raise the temperature of a 2.50 g piece of copper wire from 20.0 °C to 80.0 °C? How much heat is needed to increase the temperature of an equivalent mass of aluminum by the same amount?

Cu c_p = 0.386 J/gK

Al c_p = 0.900 J/gK

Answer

For Cu: q = 57.9 J

For Al: q = 135 J

Solution

$\Delta T = T_f - T_i$ = 80.0 °C - 20.0 °C = 60.0 °C = 60.0 K

$q = c_p$ mass ΔT

For Cu: q = 0.386 J/gK(2.50 g)(60.0 K) = 57.9 J

For Al: q = 0.900 J/gK(2.50 g)(60.0 K) = 135 J

Since mass and change in temperature are the same, it is the value of the specific heat capacity that affects q for the two metals. Since Al has a larger specific heat capacity, we would expect that it would take more heat to cause the same change intemperate of Al than Cu.

Exercise 3.*E*. 13

In an exothermic reaction, how much heat would need to be evolved to raise the temperature of 150.0 mL of water 7.5°C?

Answer

4.7×10^3 J = 4.7 kJ

Solution

Use the density of water as 1.00 g/mL, therefore we have 150.0 g of water.

The specific heat capaity of water is 4.186 J/gK.

ΔT = 7.5 oC = 7.5 K

$q = c_p$ mass ΔT

q = 4.186 J/gK(150.0 g)(7.5 K) = 4.7×10^3 J = 4.7 kJ

Exercise 3.*E*. 14

Ethylene glycol, used as a coolant in automotive engines, has a specific heat capacity of 2.42 J g^{-1} K^{-1}. Calculate q for the system when 3.65×10^3 g of ethylene glycol is cooled from 115.0°C to 85.0°C.

Answer

q = -265 kJ

Exercise 3.*E*. 15

When 5.03 g of solid potassium hydroxide are dissolved in 100.0 mL of distilled water in a coffee-cup calorimeter, the temperature of the liquid increases from 23.0°C to 34.7°C. The density of water in this temperature range averages 0.9969 g/cm^3. What is ΔH_{soln} (in kilojoules per mole)?

Assume that the calorimeter absorbs a negligible amount of heat and, because of the large volume of water, the specific heat of the solution is the same as the specific heat of pure water.

Answer

ΔH_{soln} = -57.2 kJ/mol

Exercise 3.*E*. 16

When 0.50 moles of solid ammonium nitrate is dissolved in 60.0 g of water in a coffee cup calorimeter, the q of the surroundings is determined to be -12.5 kJ. What is the enthalpy change for the reaction in kJ/mol of NH_4NO_3?

Answer

25 kJ/mol

Exercise 3.E.17

Dissolving 3.0 g of $CaCl_2(s)$ in 150.0 g of water in a coffe cup calorimeter at 22.4 °C causes the temperature of the solution to rise to 25.8 °C. What is the approximate amount of heat involved in the dissolution, assuming the heat capacity of the resulting solution is 4.18 J/g °C? Is the reaction exothermic or endothermic?

Answer

2.2 kJ; The heat produced shows that the reaction is exothermic.

Exercise 3.E.18

The addition of 3.15 g of $Ba(OH)_2 \cdot 8H_2O$ to a solution of 1.52 g of NH_4SCN in 100 g of water in a calorimeter caused the temperature to fall by 3.1 °C. Assuming the specific heat of the solution and products is 4.20 J/g °C, calculate the approximate amount of heat absorbed by the reaction, which can be represented by the following equation:

$$Ba(OH)2 \cdot 8H_2O(s) + 2NH_4SCN(aq) \rightarrow Ba(SCN)_2(aq) + 2NH_3(aq) + 10H\ O(l)$$

Answer

1.4 kJ

Exercise 3.E.19

When a 0.740-g sample of trinitrotoluene (TNT), $C_7H_5N_2O_6$, is burned in a bomb calorimeter, the temperature increases from 23.4 °C to 26.9 °C. The heat capacity of the calorimeter is 534 J/°C, and it contains 675 mL of water. How much heat was produced by the combustion of the TNT sample?

Answer

11.7 kJ

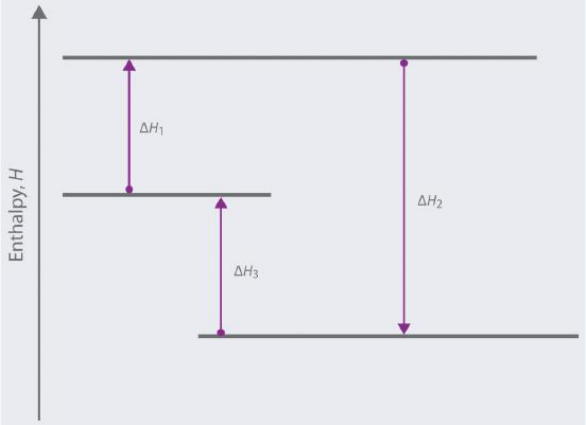
3.6: Hess's Law

Exercise 3.E.20

Based on the following energy diagram,

a. write an equation showing how the value of ΔH_2 could be determined if the values of ΔH_1 and ΔH_3 are known.

b. identify each step as being exothermic or endothermic.



Answer

a. $\Delta H_2 = -\Delta H_1 + (-\Delta H_3)$

b. $-\Delta H_1$ is exothermic since it is the reverse of ΔH_1 which is endothermic (we know this since the final H is greater than the initial H following the direction of the arrow). $-\Delta H_3$ is exothermic for the same reason.

Exercise 3.E.21

The following sequence of reactions occurs produces aqueous nitric acid:

$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)\ \Delta H = -907\ kJ$

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)\ \Delta H = -113\ kJ$

$3NO_2 + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)\ \Delta H = -139\ kJ$

The overall reaction is:

$$4NH_3(g) + 6O_2(g) + NO_3(g) \rightarrow 2HNO_3(aq) + 3NO(g) + 5H_3O(l) \quad (3.E.1)$$

Determine the total enthalpy change for the production of one mole of aqueous nitric acid by this overall reaction.

Answer

-580. kJ/mol

Exercise 3.E.22

Calculate ΔH for the process

$Hg_2Cl2(s) \rightarrow 2Hg(l) + Cl_2(g)$

from the following information:

$Hg(l) + Cl_2(g) \rightarrow HgCl_2(s)\ \Delta H = -224kJ$

$Hg(l) + HgCl_2(s) \rightarrow Hg_2Cl_2(s)\ \Delta H = -41.2kJ$

Answer

265 kJ

Exercise 3.E.23

Calculate ΔH for the process $Zn(s) + S(s) + 2O_2(g) \rightarrow ZnSO_4(s)$

from the following information:

$Zn(s) + S(s) \rightarrow ZnS(s)\ \Delta H = -206.0kJ$

$ZnS(s) + 2O_2(g) \rightarrow ZnSO4(s)\ \Delta H = -776.8kJ$

Answer

-982.8 kJ

Exercise 3.E.24

a. Use the enthalpies of combustion given in the following table to determine which organic compound releases the greatest amount of energy per gram during combustion.

Fuel	$\Delta H^{o}_{combustion}$(kJ/mol)
methanol	−726.1
1-ethyl-2-methylbenzene	−5210.2
n-octane	−5470.5

b. Calculate the standard enthalpy of formation of 1-ethyl-2-methylbenzene.

Answer

a.

methanol: ΔH/g = −22.6 kJ

C_9H_{12}: ΔH/g = −43.3 kJ

octane: ΔH/g = −47.9 kJ

Octane provides the largest amount of heat per gram upon combustion.

b. $\Delta H_f(C_9H_{17})$ = −46.1 kJ/mol

3.7: Enthalpies of Formation

Exercise 3.E.25

Using data from table T1: Standard Thermodynamic Quantities, determine ΔH^{o}_{rxn} for each chemical reaction.

a. $2Na(s) + Pb(NO_3)_2(s) \rightarrow 2NaNO_3(s) + Pb(s)$

b. $Na_2CO_3(s) + H_2SO_4(l) \rightarrow Na_2SO_4(s) + CO_2(g) + H_2O(l)$

c. $2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$

Answer

a. −1203 kJ/mol O_2

b. 179.2 kJ

c. −59.3 kJ

Exercise 3.E.26

Use the data in table T1: Standard Thermodynamic Quantities to calculate ΔH^{o}_{rxn} for the reaction

$Sn(s, white) + 4HNO_3(l) \rightarrow SnO_2(s) + 4NO_2(g) + 2H_2O(l)$.

Answer

−174.1 kJ/mol

Exercise 3.E.27

How much heat is released or required in the reaction of 0.50 mol of HBr(g) with 1.0 mol of chlorine gas to produce bromine gas? Use the data in table T1: Standard Thermodynamic Quantities.

Answer

−20.3 kJ

Exercise 3.E.28

In the mid-1700s, a method was devised for preparing chlorine gas from the following reaction:

$$NaCl(s) + H_2SO_4(l) + MnO_2(s) \rightarrow Na_2SO_4(s) + MnCl_2(s) + H_2O(l) + Cl_2(g)$$

Use the data in table T1: Standard Thermodynamic Quantities and the given data below to calculate ΔH for this reaction. Is the reaction exothermic or endothermic?

Given: $\Delta H_f^o H_2SO_4$ (l) = -814.0 kj/mol

Answer

−34.3 kJ/mol; exothermic

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3.S: Thermochemistry (Study Guide)

- **thermodynamics** – study of energy and its transformations
- **thermochemistry** – relationships between chemical reactions and energy changes

3.1: The Nature of Energy

- **Force**: symbolized by *F*, any kind of push or pull exerted on an object
- **Work**: symbolized by *w*, movement of an object against some force

$$w = F \times d$$

- where *w* is work, *F* is force, and *d* is distance that the object is being moved
- **Heat**: energy that is transferred from one object to another because of difference in temperature
- **Energy**: the capacity to do work or to transfer heat

Kinetic and Potential Energy

Kinetic energy: energy of motion

$E_k = ½ mv^2$ where E_k is the kinetic energy, *m* is the mass, and *v* is the velocity.

Potential energy: energy that an object possesses as a result of its composition or its position with respect to another object

Energy Units

- **Joule**: SI unit for energy, 1J = kgm^2/s^2
- **Calorie**: abbreviated *cal*, originally defined as the amount of energy required to raise the temperature of 1 g of water by 1°C. 1 cal = 4.184 J

Systems and Surroundings

- **System**: portion singled out for study
- **Surroundings**: everything beyond the system

Systems exchanges energy with surroundings in the form of heat and work, but not matter

Lowering the Energy of the System

Systems tend to attain as low an energy as possible. Systems with a high potential energy are less stable and more likely to undergo change than systems with a low potential energy.

3.2: The First Law of Thermodynamics

First law of thermodynamics: aka **The Law of Conservation of Energy**; a statement of our experience that energy is conserved in any process. We can express the first law in many ways. One of the more useful expressions is that the change in internal energy, ΔE, of a system in any process is equal to the heat, *q*, added to the system, plus the work, *w*, done *on* the system by its surroundings: $\Delta E = q + w$.

Internal Energy

The total energy of a system is the sum of all the kinetic and potential energies of its components parts.

Internal energy: total energy of the system (see above)

Because there are so many types of motion and interactions, we cannot determine the exact energy of any system. However, we can measure the changes *in internal energy that accompany chemical and physical processes.*

$\Delta E = E_{final} - E_{initial}$

$E_{final} > E_{initial}$ = system has gained energy

$E_{final} < E_{initial}$ = system has lost energy

Initial state refers to reactants, final state to products.

Relating ΔE to Heat and Work

The internal energy of a system changes in magnitude as heat is added to or removed from the system, or as work is done on it or by it.

?E = q + w where ΔE is internal energy, q is heat, and w is work

Heat added to the system is assigned a positive sign. Likewise, work on the system is positive. On the other hand, both the heat lost by the system and the work done by the system on its surroundings are negative; they reduce the internal energy.

Ex. A system absorbs 50 J of heat and does 10 J of work on its surroundings, q = 50 J and w = 10 J. Thus, ΔE = 50 J + (10 J) = 40 J.

State Functions

The total energy of a system is proportional to the total quantity of matter in the system; energy is an extensive property.

State function: a property of a system that is determined by the state or condition of the system and not by how it got to that state; its value is fixed when temperature, pressure, composition, and physical form are specified. The internal energy of a system is a state function.

The value of a state function does not depend on the particular history of the sample, only on its present condition. Because E is a state function, ΔE depends only on the initial and final states of the system and not on how the change occurs.

However, the work done by a system in a given process is not a state function!!!

3.3: Enthalpy

Heat flows between system and surroundings until *both are at the same temperature*.

Endothermic process: a process in which a system absorbs heat from its surroundings

Exothermic process: a process in which a system releases heat to its surroundings

Enthalpy

Enthalpy: represented by *H*; deals with the amount of heat absorbed or released during a chemical reaction under constant pressure

The change in enthalpy, ΔH, equals the heat, q_p, added to or lost by the system when the process occurs under constant pressure:

$\Delta H = q_p$

(The subscript P on q is a reminder that we are considering a special case where pressures is constant)

$\Delta H = H_{final} - H_{initial}$

$H_{final} > H_{initial}$ = positive Δ*H*; system has gained heat from surroundings (endothermic)

$H_{final} < H_{initial}$ = negative Δ*H*; system has lost heat to the surroundings (exothermic)

3.4: Enthalpy of Reaction

$$\Delta H = H(\text{products}) - H(\text{reactants})$$

Thermochemical equations: balanced chemical equations that show the associated enthalpy change

1. Enthalpy is an *extensive* property (depends on amount of matter present). *This fact means that the magnitude of ΔH is directly proportional to the amount of reactant consumed in the process*
2. The enthalpy change for a reaction is equal in magnitude but opposite in sign to ΔH for the reverse reaction. *When we reverse a reaction, the reactants become the products, and vice versa. Reversing the products and reactants leads to the same magnitude but a change in sign for ΔH.*
3. The enthalpy change for a reaction depends on the state of the reactants and products.

3.5: Calorimetry

Calorimetry: measurement of heat flow

Calorimeter: apparatus that measures heat flow

Heat Capacity and Specific Heat

Heat capacity: amount of energy required to raise the temperature of a given object by 1°C. The greater the capacity of a body, the more heat it requires to raise its temperature.

Molar heat capacity: when referring to pure substances; heat capacity of 1 mol of substance

Specific heat capacity: heat capacity of 1 g of a substance (as opposed to a mole)

Specific heat capacity= quantity of heat transferred / (grams of substance) X (temperature change)

= q / m X ΔT

q = (specific heat capacity) X (grams of substance) X Δ*T*

Constant Pressure Calorimetry

Calorimeters are simple instruments to control pressure. Because the calorimeter prevents the gain or loss of heat from its surroundings, the heat released by the reaction, q_{rxn}, equals that gained by the surroundings (solution and calorimeter), q_{soln}+ $q_{cal.}$ Thus,

$q_{system} = -q_{surroundings}$

$q_{rxn} = -(q_{soln} + q_{cal})$ = ((specific heat capacity solution) X (grams of solution) X Δ*T) + ((heat capacity calorimeter) x* Δ*T)*

Bomb Calorimetry

Bomb calorimeter: device for measuring the heat evolved in the combustion of a substance under constant volume conditions. Most used for combustion reactions.

$q_{evolved} = C_{calorimeter}$ X Δ*T* , where $C_{calorimeter}$ is the heat capacity of the calorimeter

3.6: Hess's Law

Because enthalpy is a state function, the enthalpy change, Δ*H*, associated with any chemical process depends only on the *amount of matter that undergoes change*, and on the nature of the *initial state of the reactants* and the *final state of the products*.

$CH_{4\,(g)} + 2O_{2\,(g)} \rightarrow CO_{2\,(g)} + 2H_2O_{\,(g)}$ Δ*H* = 802 kJ

(Add) $2H_2O_{\,(g)} \rightarrow 2H_2O_{\,(l)}$?*H* = 88 kJ

$CH_{4\,(g)} + 2O_{2\,(g)} + 2H_2O_{\,(g)} \rightarrow CO_{2\,(g)} + 2H_2O_{\,(l)} + 2H_2O_{\,(g)}$

Net equation:

$CH_{4\,(g)} + 2O_{2\,(g)} \rightarrow CO_{2\,(g)} + 2H_2O_{\,(l)}$

To obtain the net equation, the sum of the reactants of the two equations is placed on one side of the arrow, and the sum of the products on the other side. Because $2H_2O_{\,(g)}$ occurs on both sides of the equation, it can be cancelled.

Hess's law: states that *if a reaction is carried out in a series of steps,* Δ*H for the reaction will be equal to the sum of the enthalpy changes for individual steps.* The overall enthalpy change for the process is independent of the number of steps or the particular nature of the path by which the reaction is carried out.

The first law of thermodynamics, in the form of Hess's law, teaches us that we can never expect to obtain more (or less) energy from a chemical reaction by changing the method of carrying out the reaction.

3.7: Enthalpies of Formation

- *Enthalpies of vaporization* (Δ*H* for converting liquids to gas)
- *Enthalpies of fusion* (Δ*H* for melting solids)
- *Enthalpies of combustion* (Δ*H* for combusting a substance in oxygen)

Enthalpy of formation: aka **Heat of formation**; enthalpy change that accompanies the formation of a substance from the most stable forms of its component elements. Labeled ΔH_f, where the subscript *f* indicates that the substance has been formed from its elements.

The magnitude of any enthalpy change depends on the conditions of temperature, pressure, and state (gas, liquid, solid) of the reactants and product.

Standard state: for a substance is the form most stable at the particular temperature of interest and at standard atmospheric pressure.

Standard enthalpy of formation: $\Delta H°_f$. change in enthalpy that accompanies the formation of 1 mol of that substance from its elements, with all substances in their standard states.

Using Enthalpies of Formation to Calculate Enthalpies of Reaction

$$\Delta H°_{rxn} = \sum n\Delta H°_f \text{ (products)} - \sum m\Delta H°_f \text{ (reactants)}$$

$\sum$ = the sum of

m and n = stoichiometric coefficients of the chemical reaction

$C_3H_{8\,(g)} + 5O_{2\,(g)} \rightarrow 3CO_{2\,(g)} + 4H_2O_{\,(l)}$

$\Delta H°_{rxn} = [3\Delta H°_f\,(CO_2) + 4\Delta H°_f\,(H_2O)] - [\Delta H°_f\,(C_3H_8) + 5\Delta H°_f\,(O_2)]$

$\Delta H°_{rxn} = [(3 \text{ mol } CO_2)\,(393.5 \text{ kJ/mol}) + (4 \text{ mol } H_2O)\,(285.5 \text{ kJ/mol})]$

= (2324 kJ) – (103.85 kJ)

=2220 kJ

3.8: Foods and Fuels

Fuel value: energy released when 1g of a material is combusted

Foods

- Main sources of energy for the body are from carbohydrates and fat
- Breakdown of carbohydrates is rapid, so energy is quickly supplied to the body
- Fats are well suited for the body because (1) they are insoluble in water, which permits their storage in the human body. (2) they produce more energy per gram thatneither proteins or carbohydrates.

Fuels

- **Fossil fuels**: coal, petroleum, and natural gas
- **Natural gas**: consists of gaseous hydrocarbons, compounds of hydrogen and carbon
- **Petroleum**: liquid composed of hundreds of compounds
- **Coal**: solid; contains hydrocarbons of high molecular weight as well as compounds containing sulfur, oxygen, and nitrogen. Most abundant fossil fuel
- **Syngas**: synthetic gas abbreviation

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CHAPTER OVERVIEW

4: Kinetics

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General Chemistry

Chemical kinetics is the study of rates of chemical processes and includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction.

4.1: Prelude to Kinetics
4.2: Chemical Reaction Rates
4.3: Factors Affecting Reaction Rates
4.4: Rate Laws
4.5: Integrated Rate Laws
4.6: Collision Theory
4.7: Reaction Mechanisms
4.8: Catalysis
4.E: Kinetics (Exercises)
4.S: Kinetics (Study Guide)

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4.1: Prelude to Kinetics

The lizard in the photograph is not simply enjoying the sunshine or working on its tan. The heat from the sun's rays is critical to the lizard's survival. A warm lizard can move faster than a cold one because the chemical reactions that allow its muscles to move occur more rapidly at higher temperatures. In the absence of warmth, the lizard is an easy meal for predators.



Figure 4.1.1: *An agama lizard basks in the sun. As its body warms, the chemical reactions of its metabolism speed up.*

From baking a cake to determining the useful lifespan of a bridge, rates of chemical reactions play important roles in our understanding of processes that involve chemical changes. When planning to run a chemical reaction, we should ask at least two questions. The first is: "Will the reaction produce the desired products in useful quantities?" The second question is: "How rapidly will the reaction occur?" A reaction that takes 50 years to produce a product is about as useful as one that never gives a product at all. A third question is often asked when investigating reactions in greater detail: "What specific molecular-level processes take place as the reaction occurs?" Knowing the answer to this question is of practical importance when the yield or rate of a reaction needs to be controlled.

The study of chemical kinetics concerns the second and third questions—that is, the rate at which a reaction yields products and the molecular-scale means by which a reaction occurs. In this chapter, we will examine the factors that influence the rates of chemical reactions, the mechanisms by which reactions proceed, and the quantitative techniques used to determine and describe the rate at which reactions occur.

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

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4.2: Chemical Reaction Rates

Learning Objectives

- Define chemical reaction rate
- Derive rate expressions from the balanced equation for a given chemical reaction
- Calculate reaction rates from experimental data

A *rate* is a measure of how some property varies with time. Speed is a familiar rate that expresses the distance traveled by an object in a given amount of time. Wage is a rate that represents the amount of money earned by a person working for a given amount of time. Likewise, the rate of a chemical reaction is a measure of how much reactant is consumed, or how much product is produced, by the reaction in a given amount of time.

The rate of reaction is the change in the amount of a reactant or product per unit time. Reaction rates are therefore determined by measuring the time dependence of some property that can be related to reactant or product amounts. Rates of reactions that consume or produce gaseous substances, for example, are conveniently determined by measuring changes in volume or pressure. For reactions involving one or more colored substances, rates may be monitored via measurements of light absorption. For reactions involving aqueous electrolytes, rates may be measured via changes in a solution's conductivity.

The progress of a simple reaction (A → B) is shown in (Figure 4.2.1); the beakers are snapshots of the composition of the solution at 10 s intervals. The number of molecules of reactant (A) and product (B) are plotted as a function of time in the graph. Each point in the graph corresponds to one beaker in (Figure 4.2.1). The reaction rate is the change in the concentration of either the reactant or the product over a period of time. The concentration of A decreases with time, while the concentration of B increases with time.

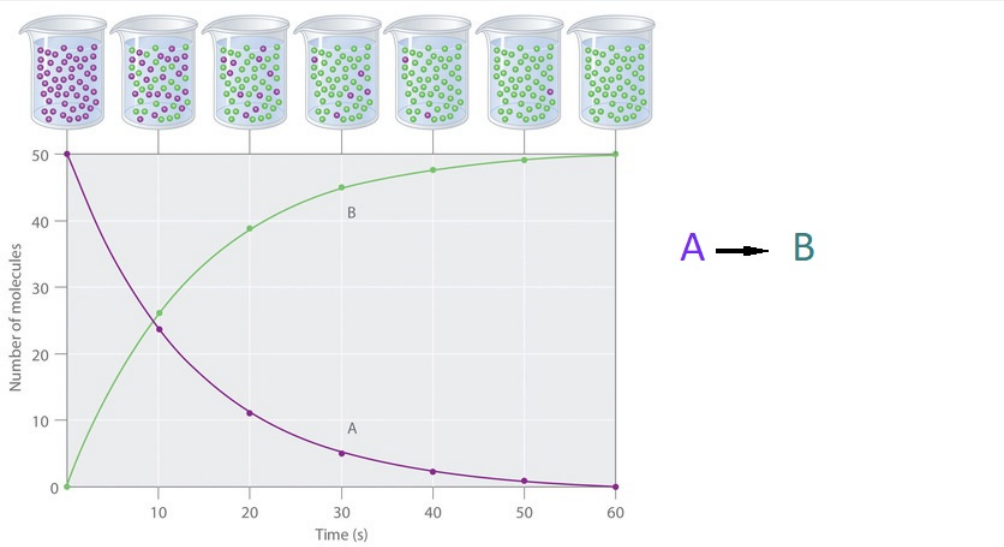


Figure 4.2.1: The Progress of a Simple Reaction (A → B). The mixture initially contains only A molecules (purple). Over time, the number of A molecules decreases and more B molecules (green) are formed (top). The graph shows the change in the number of A and B molecules in the reaction as a function of time over a 1 min period (bottom).

$$\text{rate} = \frac{\Delta[\text{B}]}{\Delta t} = -\frac{\Delta[\text{A}]}{\Delta t} \tag{4.2.1}$$

Square brackets indicate molar concentrations, and the capital Greek delta (Δ) means "change in." Because chemists follow the convention of expressing all reaction rates as positive numbers, however, a negative sign is inserted in front of Δ[A]/Δt to convert that expression to a positive number. The formula shows that the rate of the reaction is equal to the negative of the rate of disappearance of A, and is equal to the rate of appearance of B.

For reactants and products in solution, their relative amounts (concentrations) are conveniently used for purposes of expressing reaction rates. If we measure the concentration of hydrogen peroxide, H_2O_2, in an aqueous solution, we find that it changes slowly over time as the H_2O_2 decomposes, according to the equation:

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

The rate at which the hydrogen peroxide decomposes can be expressed in terms of the rate of change of its concentration, as shown here:

$$\begin{aligned}\text{rate of decomposition of } H_2O_2 &= -\frac{\text{change in concentration of reactant}}{\text{time interval}} \\ &= -\frac{[H_2O_2]_{t_2} - [H_2O_2]_{t_1}}{t_2 - t_1} \\ &= -\frac{\Delta[H_2O_2]}{\Delta t}\end{aligned}$$

This mathematical representation of the change in species concentration over time is the rate expression for the reaction. The brackets indicate molar concentrations, and the symbol delta (Δ) indicates "change in." Thus, $[H_2O_2]_{t_1}$ represents the molar concentration of hydrogen peroxide at some time t_1; likewise, $[H_2O_2]_{t_2}$ represents the molar concentration of hydrogen peroxide at a later time t_2; and $\Delta[H_2O_2]$ represents the change in molar concentration of hydrogen peroxide during the time interval Δt (that is, $t_2 - t_1$). Since the reactant concentration decreases as the reaction proceeds, $\Delta[H_2O_2]$ is a negative quantity; we place a negative sign in front of the expression because reaction rates are, by convention, positive quantities. Figure 4.2.1 provides an example of data collected during the decomposition of H_2O_2.

Time (h)	$[H_2O_2]$ (mol L^{-1})	$\Delta[H_2O_2]$ (mol L^{-1})	Δt (h)	Rate of Decomposition, (mol/L/h)
0.00	1.000			
		−0.500	6.00	−0.0833
6.00	0.500			
		−0.250	6.00	−0.0417
12.00	0.250			
		−0.125	6.00	−0.0208
18.00	0.125			
		−0.062	6.00	−0.0103
24.00	0.0625			

Figure 4.2.2: The rate of decomposition of H_2O_2 in an aqueous solution decreases as the concentration of H_2O_2 decreases.

To obtain the tabulated results for this decomposition, the concentration of hydrogen peroxide was measured every 6 hours over the course of a day at a constant temperature of 40 °C. Reaction rates were computed for each time interval by dividing the change in concentration by the corresponding time increment, as shown here for the first 6-hour period:

$$\frac{-\Delta[H_2O_2]}{\Delta t} = \frac{-(0.500\text{ mol/L} - 1.000\text{ mol/L})}{(6.00\text{ h} - 0.00\text{ h})} = 0.0833\text{ mol L}^{-1}\text{ h}^{-1}$$

Notice that the reaction rates vary with time, decreasing as the reaction proceeds. Results for the last 6-hour period yield a reaction rate of:

$$\frac{-\Delta[H_2O_2]}{\Delta t} = \frac{-(0.0625\text{ mol/L} - 0.125\text{ mol/L})}{(24.00\text{ h} - 18.00\text{ h})} = 0.0104\text{ mol L}^{-1}\text{ h}^{-1}$$

This behavior indicates the reaction continually slows with time. Using the concentrations at the beginning and end of a time period over which the reaction rate is changing results in the calculation of an average rate for the reaction over this time interval. At any specific time, the rate at which a reaction is proceeding is known as its instantaneous rate. The instantaneous rate of a reaction at "time zero," when the reaction commences, is its initial rate. Consider the analogy of a car slowing down as it approaches a stop sign. The vehicle's initial rate—analogous to the beginning of a chemical reaction—would be the speedometer reading at the moment the driver begins pressing the brakes (t_0). A few moments later, the instantaneous rate at a specific moment—call it t_1—would be somewhat slower, as indicated by the speedometer reading at that point in time. As time passes, the instantaneous rate will continue to fall until it reaches zero, when the car (or reaction) stops. Unlike instantaneous speed, the car's average speed is not indicated by the speedometer; but it can be calculated as the ratio of the distance traveled to the time required to bring the vehicle to a complete stop (Δt). Like the decelerating car, the average rate of a chemical reaction will fall somewhere between its initial and final rates.

The instantaneous rate of a reaction may be determined one of two ways. If experimental conditions permit the measurement of concentration changes over very short time intervals, then average rates computed as described earlier provide reasonably good approximations of instantaneous rates. Alternatively, a graphical procedure may be used that, in effect, yields the results that would be obtained if short time interval measurements were possible. If we plot the concentration of hydrogen peroxide against time, the instantaneous rate of decomposition of H_2O_2 at any time *t* is given by the slope of a straight line that is tangent to the curve at that time (Figure 4.2.2). We can use calculus to evaluating the slopes of such tangent lines, but the procedure for doing so is beyond the scope of this chapter.

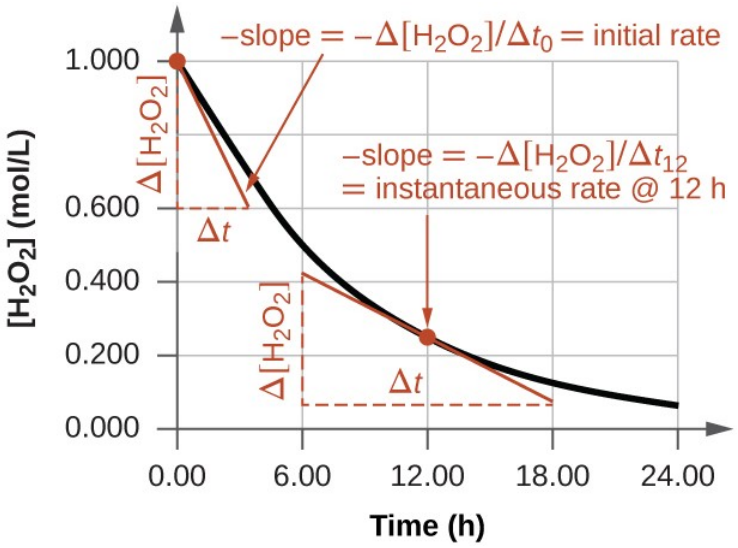


Figure 4.2.3: This graph shows a plot of concentration versus time for a 1.000 M solution of H_2O_2. The rate at any instant is equal to the opposite of the slope of a line tangential to this curve at that time. Tangents are shown at t = 0 h ("initial rate") and at t = 12 h ("instantaneous rate" at that particular time).

Reaction Rates in Analysis: Test Strips for Urinalysis

Physicians often use disposable test strips to measure the amounts of various substances in a patient's urine (Figure 4.2.4). These test strips contain various chemical reagents, embedded in small pads at various locations along the strip, which undergo changes in color upon exposure to sufficient concentrations of specific substances. The usage instructions for test strips often stress that proper read time is critical for optimal results. This emphasis on read time suggests that kinetic aspects of the chemical reactions occurring on the test strip are important considerations.

The test for urinary glucose relies on a two-step process represented by the chemical equations shown here:

$$C_6H_{12}O_6 + O_2 \xrightarrow[\text{catalyst}]{} C_6H_{10}O_6 + H_2O_2 \tag{4.2.2}$$

$$2\,H_2O_2 + 2\,I^- \xrightarrow[\text{catalyst}]{} I_2 + 2\,H_2O + O_2 \tag{4.2.3}$$

Equation 4.2.2 depicts the oxidation of glucose in the urine to yield glucolactone and hydrogen peroxide. The hydrogen peroxide produced subsequently oxidizes colorless iodide ion to yield brown iodine (Equation 4.2.3), which may be visually detected. Some strips include an additional substance that reacts with iodine to produce a more distinct color change.

The two test reactions shown above are inherently very slow, but their rates are increased by special enzymes embedded in the test strip pad. This is an example of *catalysis*, a topic discussed later in this chapter. A typical glucose test strip for use with urine requires approximately 30 seconds for completion of the color-forming reactions. Reading the result too soon might lead one to conclude that the glucose concentration of the urine sample is lower than it actually is (a *false-negative* result). Waiting too long to assess the color change can lead to a *false positive* due to the slower (not catalyzed) oxidation of iodide ion by other substances found in urine.



Figure 4.2.4: Test strips are commonly used to detect the presence of specific substances in a person's urine. Many test strips have several pads containing various reagents to permit the detection of multiple substances on a single strip. (credit: Iqbal Osman).

4.2.1: Relative Rates of Reaction

The rate of a reaction may be expressed in terms of the change in the amount of any reactant or product, and may be simply derived from the stoichiometry of the reaction.

For a balanced reaction equation:

$$\mathrm{aA} + bB \longrightarrow \mathrm{cC} + \mathrm{dD}$$

The rate can be expressed in terms of the decrease in reactant concentration over time or increase in product concentration over time using the stoichiometric coefficients:

$$\text{rate } = -\left(\frac{1}{\mathrm{a}}\right)\left(\frac{\Delta[\mathrm{A}]}{\Delta t}\right) = -\left(\frac{1}{\mathrm{b}}\right)\left(\frac{\Delta[\mathrm{B}]}{\Delta t}\right) = \left(\frac{1}{\mathrm{c}}\right)\left(\frac{\Delta[\mathrm{C}]}{\Delta t}\right) = \left(\frac{1}{\mathrm{d}}\right)\left(\frac{\Delta[\mathrm{D}]}{\Delta t}\right) \tag{4.2.4}$$

Reaction rate is positive, so rate of reaction is equal to the negative of the rate of disappearance of reactants.

Consider the reaction represented by the following equation:

$$2\,\mathrm{NH_3}(g) \longrightarrow \mathrm{N_2}(g) + 3\,\mathrm{H_2}(g)$$

The stoichiometric factors derived from this equation may be used to relate reaction rates in the same manner that they are used to related reactant and product amounts. The relation between the reaction rates expressed in terms of nitrogen production and ammonia consumption, for example, is:

$$-\frac{\Delta\text{mol NH}_3}{\Delta t} \times \frac{1\text{ mol N}_2}{2\text{ mol NH}_3} = \frac{\Delta\text{mol N}_2}{\Delta t}$$

We can express this more simply without showing the stoichiometric factor's units:

$$-\frac{1}{2}\frac{\Delta\text{mol NH}_3}{\Delta t} = \frac{\Delta\text{mol N}_2}{\Delta t}$$

Note that a negative sign has been added to account for the opposite signs of the two amount changes (the reactant amount is decreasing while the product amount is increasing). If the reactants and products are present in the same solution, the molar amounts may be replaced by concentrations:

$$-\frac{1}{2}\frac{\Delta[\mathrm{NH_3}]}{\Delta t} = \frac{\Delta[\mathrm{N_2}]}{\Delta t}$$

Similarly, the rate of formation of $\mathrm{H_2}$ is three times the rate of formation of $\mathrm{N_2}$ because three moles of $\mathrm{H_2}$ form during the time required for the formation of one mole of $\mathrm{N_2}$:

$$\frac{1}{3}\frac{\Delta[\mathrm{H_2}]}{\Delta t} = \frac{\Delta[\mathrm{N_2}]}{\Delta t}$$

Figure 4.2.3 illustrates the change in concentrations over time for the decomposition of ammonia into nitrogen and hydrogen at 1100 °C. We can see from the slopes of the tangents drawn at t = 500 seconds that the instantaneous rates of change in the concentrations of the reactants and products are related by their stoichiometric factors. The rate of hydrogen production, for example, is observed to be three times greater than that for nitrogen production:

$$\frac{2.91 \times 10^{-6}\ M/\text{s}}{9.71 \times 10^{-6}\ M/\text{s}} \approx 3$$

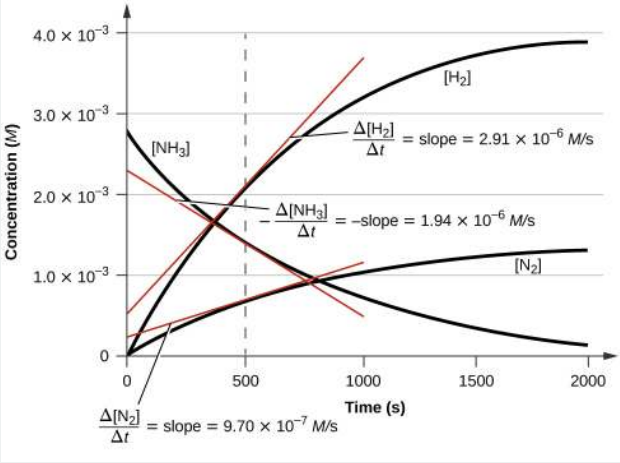


Figure 4.2.3: This graph shows the changes in concentrations of the reactants and products during the reaction $2\,\text{NH}_3 \longrightarrow \text{N}_2 + 3\,\text{H}_2$. *The rates of change of the three concentrations are related by their stoichiometric factors, as shown by the different slopes of the tangents at t = 500 s.*

Example 4.2.1

Consider the conversion of dinitrogen tetroxide, N_2O_4 (g) to nitrogen dioxide, NO_2 (g):

$$\text{N}_2\text{O}_4(\text{ g}) \longrightarrow 2\text{NO}_2(\text{ g})$$

Write the rate expression for the reaction in terms of disappearance of the reactants and appearance of the products.

Solution

For every one mole of reactant that disappears, two moles of product are formed. The rate of disappearance of N_2O_4 must be must be half of the rate of appearance of NO_2. The rate of reaction therefore may be expressed as:

$$\text{rate} = -\frac{\Delta[\text{ N}_2\text{O}_4]}{\Delta t} = \frac{1}{2}\frac{\Delta[\text{ NO}_2]}{\Delta t}$$

Example 4.2.2: Expressions for Relative Reaction Rates

The first step in the production of nitric acid is the combustion of ammonia:

$$4\,\text{NH}_3(g) + 5\,\text{O}_2(g) \longrightarrow 4\,\text{NO}(g) + 6\,\text{H}_2\text{O}(g)$$

Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

Solution

Considering the stoichiometry of this homogeneous reaction, the rates for the consumption of reactants and formation of products are:

$$-\frac{1}{4}\frac{\Delta[\text{NH}_3]}{\Delta t} = -\frac{1}{5}\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{4}\frac{\Delta[\text{NO}]}{\Delta t} = \frac{1}{6}\frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

Exercise 4.2.1

The rate of formation of Br_2 is 6.0×10^{-6} mol/L/s in a reaction described by the following net ionic equation:

$$5\,Br^- + BrO_3^- + 6\,H^+ \longrightarrow 3\,Br_2 + 3\,H_2O$$

Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

Answer

$$-\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = -\frac{1}{6}\frac{\Delta[H^+]}{\Delta t} = \frac{1}{3}\frac{\Delta[Br_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[H_2O]}{\Delta t}$$

Example 4.2.3: Reaction Rate Expressions for Decomposition of H_2O_2

The graph in Figure 4.2.3 shows the rate of the decomposition of H_2O_2 over time:

$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$$

Based on these data, the instantaneous rate of decomposition of H_2O_2 at t = 11.1 h is determined to be 3.20×10^{-2} mol/L/h, that is:

$$-\frac{\Delta[H_2O_2]}{\Delta t} = 3.20 \times 10^{-2}\ \text{mol}\ L^{-1}\ h^{-1}$$

What is the instantaneous rate of production of H_2O and O_2?

Solution

Using the stoichiometry of the reaction, we may determine that:

$$-\frac{1}{2}\frac{\Delta[H_2O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

Therefore:

$$\frac{1}{2} \times 3.20 \times 10^{-2}\ \text{mol}\ L^{-1}\ h^{-1} = \frac{\Delta[O_2]}{\Delta t}$$

and

$$\frac{\Delta[O_2]}{\Delta t} = 1.60 \times 10^{-2}\ \text{mol}\ L^{-1}\ h^{-1}$$

Exercise 4.2.2

If the rate of decomposition of ammonia, NH_3, at 1150 K is 2.10×10^{-6} mol/L/s, what is the rate of production of nitrogen and hydrogen?

Answer

1.05×10^{-6} mol/L/s, N_2 and 3.15×10^{-6} mol/L/s, H_2.

Summary

The rate of a reaction can be expressed either in terms of the decrease in the amount of a reactant or the increase in the amount of a product per unit time. Relations between different rate expressions for a given reaction are derived directly from the stoichiometric coefficients of the equation representing the reaction.

Glossary

average rate

rate of a chemical reaction computed as the ratio of a measured change in amount or concentration of substance to the time interval over which the change occurred

initial rate

instantaneous rate of a chemical reaction at $t = 0$ s (immediately after the reaction has begun)

instantaneous rate

rate of a chemical reaction at any instant in time, determined by the slope of the line tangential to a graph of concentration as a function of time

rate of reaction

measure of the speed at which a chemical reaction takes place

rate expression

mathematical representation relating reaction rate to changes in amount, concentration, or pressure of reactant or product species per unit time

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4.3: Factors Affecting Reaction Rates

Learning Objectives

- Describe the effects of chemical nature, physical state, temperature, concentration, and catalysis on reaction rates

The rates at which reactants are consumed and products are formed during chemical reactions vary greatly. We can identify five factors that affect the rates of chemical reactions: the chemical nature of the reacting substances, the state of subdivision (one large lump versus many small particles) of the reactants, the temperature of the reactants, the concentration of the reactants, and the presence of a catalyst.

4.3.1: The Chemical Nature of the Reacting Substances

The rate of a reaction depends on the nature of the participating substances. Reactions that appear similar may have different rates under the same conditions, depending on the identity of the reactants. For example, when small pieces of the metals iron and sodium are exposed to air, the sodium reacts completely with air overnight, whereas the iron is barely affected. The active metals calcium and sodium both react with water to form hydrogen gas and a base. Yet calcium reacts at a moderate rate, whereas sodium reacts so rapidly that the reaction is almost explosive.

4.3.2: The State of Subdivision of the Reactants

Except for substances in the gaseous state or in solution, reactions occur at the boundary, or interface, between two phases. Hence, the rate of a reaction between two phases depends to a great extent on the surface contact between them. A finely divided solid has more surface area available for reaction than does one large piece of the same substance. Thus a liquid will react more rapidly with a finely divided solid than with a large piece of the same solid. For example, large pieces of iron react slowly with acids; finely divided iron reacts much more rapidly (Figure 4.3.1). Large pieces of wood smolder, smaller pieces burn rapidly, and saw dust burns explosively.



Figure 4.3.1: (a) Iron powder reacts rapidly with dilute hydrochloric acid and produces bubbles of hydrogen gas because the powder has a large total area: 2Fe(s) + 6HCl(aq) ⟶ 2FeCl3(aq) + 3H2(g). (surfaceb) An iron nail reacts more slowly.

This figure shows two photos labeled (a) and (b). Photo (a) shows the bottom of a test tube. The test tube is filled with a dark gas, and there is a dark substance and bubbles in the bottom. Photo (b) shows a rod and bubbles in a test tube similar to photo (a), but the gas in the test tube is not as dark.



***Video* 4.3.1**: *The reaction of cesium with water in slow motion and a discussion of how the state of reactants and particle size affect reaction rates.*

4.3.3: Temperature of the Reactants

Chemical reactions typically occur faster at higher temperatures. Food can spoil quickly when left on the kitchen counter. However, the lower temperature inside of a refrigerator slows that process so that the same food remains fresh for days. We use a burner or a hot plate in the laboratory to increase the speed of reactions that proceed slowly at ordinary temperatures. In many cases, an increase in temperature of only 10 °C will approximately double the rate of a reaction in a homogeneous system.

4.3.4: Concentrations of the Reactants

The rates of many reactions depend on the concentrations of the reactants. Rates usually increase when the concentration of one or more of the reactants increases. For example, calcium carbonate ($CaCO_3$) deteriorates as a result of its reaction with the pollutant sulfur dioxide. The rate of this reaction depends on the amount of sulfur dioxide in the air (Figure 4.3.2). As an acidic oxide, sulfur dioxide combines with water vapor in the air to produce sulfurous acid in the following reaction:

$$SO_{2(g)} + H_2O_{(g)} \longrightarrow H_2SO_{3(aq)} \tag{4.3.1}$$

Calcium carbonate reacts with sulfurous acid as follows:

$$CaCO_{3(s)} + H_2SO_{3(aq)} \longrightarrow CaSO_{3(aq)} + CO_{2(g)} + H_2O_{(l)} \tag{4.3.2}$$

In a polluted atmosphere where the concentration of sulfur dioxide is high, calcium carbonate deteriorates more rapidly than in less polluted air. Similarly, phosphorus burns much more rapidly in an atmosphere of pure oxygen than in air, which is only about 20% oxygen.

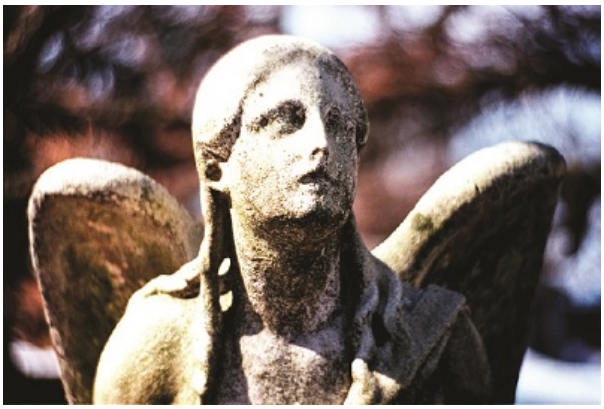


Figure 4.3.2: Statues made from carbonate compounds such as limestone and marble typically weather slowly over time due to the actions of water, and thermal expansion and contraction. However, pollutants like sulfur dioxide can accelerate weathering. As the concentration of air pollutants increases, deterioration of limestone occurs more rapidly. (credit: James P Fisher III).

A photograph is shown of an angel statue. While some details of the statue, including facial features, are present, effects of weathering appear to be diminishing these features.



***Video* 4.3.2**: *Phosphorous burns rapidly in air, but it will burn even more rapidly if the concentration of oxygen in is higher.*

4.3.5: The Presence of a Catalyst

Hydrogen peroxide solutions foam when poured onto an open wound because substances in the exposed tissues act as catalysts, increasing the rate of hydrogen peroxide's decomposition. However, in the absence of these catalysts (for example, in the bottle in the medicine cabinet) complete decomposition can take months. A catalyst is a substance that increases the rate of a chemical reaction by lowering the activation energy without itself being consumed by the reaction. Activation energy is the minimum amount of energy required for a chemical reaction to proceed in the forward direction. A catalyst increases the reaction rate by providing an alternative pathway or mechanism for the reaction to follow (Figure 4.3.3). Catalysis will be discussed in greater detail later in this chapter as it relates to mechanisms of reactions.

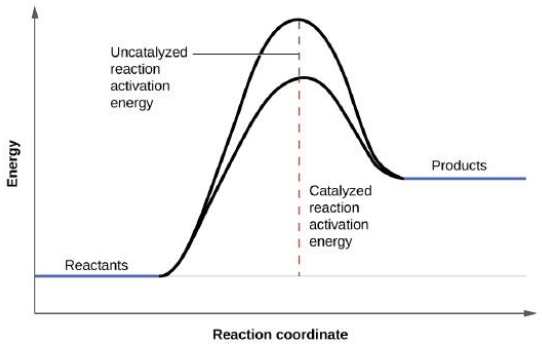


Figure 4.3.3: The presence of a catalyst increases the rate of a reaction by lowering its activation energy.

A graph is shown with the label, "Reaction coordinate," on the x-axis. The x-axis is depicted as an arrow. The y-axis is also an arrow and is labeled, "Energy." There is a horizontal line that runs the width of the graph and appears just above the x-axis. A segment of this line is blue and is labeled, "Reactants." From the right end of this line segment, a solid black, concave down curve is shown which reaches the level just below the end of the y-axis. The curve ends at another short, blue line labeled, "Products." The "Products" line appears at a higher level than the "Reactants" line. An arrow extends from the horizontal line to the apex of the curve. The arrow is labeled, "Uncatalyzed reaction activation energy." A second, black concave down curve is shown. This curve also meets the reactants and products blue line segments, but only extends to about two-thirds the height of the initial curve. From the horizontal line is another arrow pointing to the apex of the second curve. This arrow is labeled, "Catalyzed reaction activation energy."

> *Chemical reactions occur when molecules collide with each other and undergo a chemical transformation. Before physically performing a reaction in a laboratory, scientists can use molecular modeling simulations to predict how the parameters discussed earlier will influence the rate of a reaction. Use the PhET Reactions & Rates interactive to explore how temperature, concentration, and the nature of the reactants affect reaction rates.*

Summary

The rate of a chemical reaction is affected by several parameters. Reactions involving two phases proceed more rapidly when there is greater surface area contact. If temperature or reactant concentration is increased, the rate of a given reaction generally increases as well. A catalyst can increase the rate of a reaction by providing an alternative pathway that causes the activation energy of the reaction to decrease.

Glossary

catalyst

substance that increases the rate of a reaction without itself being consumed by the reaction

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4.4: Rate Laws

Learning Objectives

- Explain the form and function of a rate law
- Use rate laws to calculate reaction rates
- Use rate and concentration data to identify reaction orders and derive rate laws

As described in the previous module, the rate of a reaction is affected by the concentrations of reactants. Rate laws or rate equations are mathematical expressions that describe the relationship between the rate of a chemical reaction and the concentration of its reactants. In general, a rate law (or differential rate law, as it is sometimes called) takes this form:

$$\text{rate} = k[A]^m[B]^n[C]^p \ldots$$

in which [*A*], [*B*], and [*C*] represent the molar concentrations of reactants, and *k* is the rate constant, which is specific for a particular reaction at a particular temperature. The exponents *m*, *n*, and *p* are usually positive integers (although it is possible for them to be fractions or negative numbers). The rate constant *k* and the exponents *m*, *n*, and *p* must be determined experimentally by observing how the rate of a reaction changes as the concentrations of the reactants are changed. The rate constant *k* is independent of the concentration of *A*, *B*, or *C*, but it does vary with temperature and surface area.

The exponents in a rate law describe the effects of the reactant concentrations on the reaction rate and define the reaction order. Consider a reaction for which the rate law is:

$$\text{rate} = k[A]^m[B]^n$$

If the exponent *m* is 1, the reaction is first order with respect to *A*. If *m* is 2, the reaction is second order with respect to *A*. If *n* is 1, the reaction is first order in *B*. If *n* is 2, the reaction is second order in *B*. If *m* or *n* is zero, the reaction is zero order in *A* or *B*, respectively, and the rate of the reaction is not affected by the concentration of that reactant. The overall reaction order is the sum of the orders with respect to each reactant. If *m* = 1 and *n* = 1, the overall order of the reaction is second order (*m* + *n* = 1 + 1 = 2).

The rate law:

$$\text{rate} = k[\text{H}_2\text{O}_2]$$

describes a reaction that is first order in hydrogen peroxide and first order overall. The rate law:

$$\text{rate} = k[\text{C}_4\text{H}_6]^2$$

describes a reaction that is second order in C_4H_6 and second order overall. The rate law:

$$\text{rate} = k[\text{H}^+][\text{OH}^-]$$

describes a reaction that is first order in H^+, first order in OH^-, and second order overall.

Example 4.4.1: Writing Rate Laws from Reaction Orders

An experiment shows that the reaction of nitrogen dioxide with carbon monoxide:

$$\text{NO}_2(g) + \text{CO}(g) \longrightarrow \text{NO}(g) + \text{CO}_2(g)$$

is second order in NO_2 and zero order in CO at 100 °C. What is the rate law for the reaction?

Solution

The reaction will have the form:

$$\text{rate} = k[\text{NO}_2]^m[\text{CO}]^n$$

The reaction is second order in NO_2; thus *m* = 2. The reaction is zero order in CO; thus *n* = 0. The rate law is:

$$\text{rate} = k[\text{NO}_2]^2[\text{CO}]^0 = k[\text{NO}_2]^2$$

Remember that a number raised to the zero power is equal to 1, thus $[CO]^0 = 1$, which is why we can simply drop the concentration of CO from the rate equation: the rate of reaction is solely dependent on the concentration of NO_2. When we consider rate mechanisms later in this chapter, we will explain how a reactant's concentration can have no effect on a reaction despite being involved in the reaction.

Exercise 4.4.1A

The rate law for the reaction:

$$H_2(g) + 2\,NO(g) \longrightarrow N_2O(g) + H_2O(g)$$

has been experimentally determined to be rate = $k[NO]^2[H_2]$. What are the orders with respect to each reactant, and what is the overall order of the reaction?

Answer

- order in NO = 2;
- order in H_2 = 1;
- overall order = 3

Exercise 4.4.1B

In a transesterification reaction, a triglyceride reacts with an alcohol to form an ester and glycerol. Many students learn about the reaction between methanol (CH_3OH) and ethyl acetate ($CH_3CH_2OCOCH_3$) as a sample reaction before studying the chemical reactions that produce biodiesel:

$$CH_3OH + CH_3CH_2OCOCH_3 \longrightarrow CH_3OCOCH_3 + CH_3CH_2OH$$

The rate law for the reaction between methanol and ethyl acetate is, under certain conditions, experimentally determined to be:

$$\text{rate} = k[CH_3OH]$$

What is the order of reaction with respect to methanol and ethyl acetate, and what is the overall order of reaction?

Answer

- order in CH_3OH = 1;
- order in $CH_3CH_2OCOCH_3$ = 0;
- overall order = 1

It is sometimes helpful to use a more explicit algebraic method, often referred to as the method of initial rates, to determine the orders in rate laws. To use this method, we select two sets of rate data that differ in the concentration of only one reactant and set up a ratio of the two rates and the two rate laws. After canceling terms that are equal, we are left with an equation that contains only one unknown, the coefficient of the concentration that varies. We then solve this equation for the coefficient.

Example 4.4.2: Determining a Rate Law from Initial Rates

Ozone in the upper atmosphere is depleted when it reacts with nitrogen oxides. The rates of the reactions of nitrogen oxides with ozone are important factors in deciding how significant these reactions are in the formation of the ozone hole over Antarctica (Figure 4.4.1). One such reaction is the combination of nitric oxide, NO, with ozone, O_3:

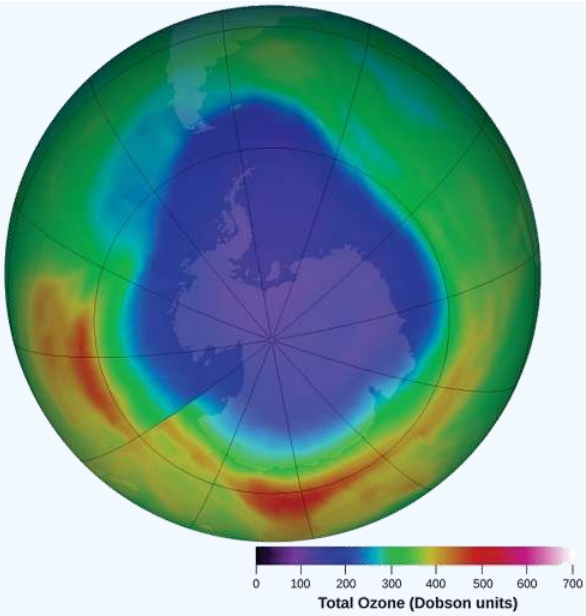


Figure 4.4.1: Over the past several years, the atmospheric ozone concentration over Antarctica has decreased during the winter. This map shows the decreased concentration as a purple area. (credit: modification of work by NASA)

A view of Earth's southern hemisphere is shown. A nearly circular region of approximately half the diameter of the image is shown in shades of purple, with Antarctica appearing in a slightly lighter color than the surrounding ocean areas. Immediately outside this region is a narrow bright blue zone followed by a bright green zone. In the top half of the figure, the purple region extends slightly outward from the circle and the blue zone extends more outward to the right of the center as compared to the lower half of the image. In the upper half of the image, the majority of the space outside the purple region is shaded green, with a few small strips of interspersed blue regions. The lower half however shows the majority of the space outside the central purple zone in yellow, orange, and red. The red zones appear in the lower central and left regions outside the purple zone. To the lower right of this image is a color scale that is labeled "Total Ozone (Dobsone units)." This scale begins at 0 and increases by 100's up to 700. At the left end of the scale, the value 0 shows a very deep purple color, 100 is indigo, 200 is blue, 300 is green, 400 is a yellow-orange, 500 is red, 600 is pink, and 700 is white.

$$\mathrm{NO}(g) + \mathrm{O_3}(g) \longrightarrow \mathrm{NO_2}(g) + \mathrm{O_2}(g)$$

This reaction has been studied in the laboratory, and the following rate data were determined at 25 °C.

Trial	$[\mathrm{NO}]$ (mol/L)	$[\mathrm{O_3}]$ (mol/L)	$\frac{\Delta[\mathrm{NO_2}]}{\Delta t}$ $(\mathrm{mol\ L^{-1}\ s^{-1}})$
1	1.00×10^{-6}	3.00×10^{-6}	6.60×10^{-5}
2	1.00×10^{-6}	6.00×10^{-6}	1.32×10^{-4}
3	1.00×10^{-6}	9.00×10^{-6}	1.98×10^{-4}
4	2.00×10^{-6}	9.00×10^{-6}	3.96×10^{-4}
5	3.00×10^{-6}	9.00×10^{-6}	5.94×10^{-4}

Determine the rate law and the rate constant for the reaction at 25 °C.

Solution

The rate law will have the form:

$$\text{rate} = k[\mathrm{NO}]^m[\mathrm{O_3}]^n$$

We can determine the values of *m*, *n*, and *k* from the experimental data using the following three-part process:

1. *Determine the value of* m *from the data in which [NO] varies and [O_3] is constant.* In the last three experiments, [NO] varies while [O_3] remains constant. When [NO] doubles from trial 3 to 4, the rate doubles, and when [NO] triples from trial 3 to 5, the rate also triples. Thus, the rate is also directly proportional to [NO], and *m* in the rate law is equal to 1.
2. *Determine the value of* n *from data in which [O_3] varies and [NO] is constant.* In the first three experiments, [NO] is constant and [O_3] varies. The reaction rate changes in direct proportion to the change in [O_3]. When [O_3] doubles from trial 1 to 2, the rate doubles; when [O_3] triples from trial 1 to 3, the rate increases also triples. Thus, the rate is directly proportional to [O_3], and *n* is equal to 1.The rate law is thus:

$$\text{rate} = k[\text{NO}]^1[\text{O}_3]^1 = k[\text{NO}][\text{O}_3]$$

3. *Determine the value of* k *from one set of concentrations and the corresponding rate*.

$$\begin{aligned} k &= \frac{\text{rate}}{[\text{NO}][\text{O}_3]} \\ &= \frac{6.60 \times 10^{-5}\ \text{mol L}^{-1}\ \text{s}^{-1}}{(1.00 \times 10^{-6}\ \text{mol L}^{-1})(3.00 \times 10^{-6}\ \text{mol L}^{-1})} \\ &= 2.20 \times 10^{7}\ \text{L mol}^{-1}\ \text{s}^{-1} \end{aligned}$$

The large value of *k* tells us that this is a fast reaction that could play an important role in ozone depletion if [NO] is large enough.

Exercise 4.4.2

Acetaldehyde decomposes when heated to yield methane and carbon monoxide according to the equation:

$$\text{CH}_3\text{CHO}(g) \longrightarrow \text{CH}_4(g) + \text{CO}(g)$$

Determine the rate law and the rate constant for the reaction from the following experimental data:

Trial	**[CH_3CHO] (mol/L)**	$-\frac{\Delta[\text{CH}_3\text{CHO}]}{\Delta t}$ **(mol L^{-1} s^{-1})**
1	1.75×10^{-3}	2.06×10^{-11}
2	3.50×10^{-3}	8.24×10^{-11}
3	7.00×10^{-3}	3.30×10^{-10}

Answer

rate $= k[\text{CH}_3\text{CHO}]^2$ with $k = 6.73 \times 10^{-6}$ L/mol/s

Example 4.4.3: Determining Rate Laws from Initial Rates

Using the initial rates method and the experimental data, determine the rate law and the value of the rate constant for this reaction:

$$2\,\text{NO}(g) + \text{Cl}_2(g) \longrightarrow 2\,\text{NOCl}(g)$$

Trial	[NO] (mol/L)	[Cl_2] (mol/L)	$-\frac{\Delta[\text{NO}]}{2\Delta t}$ (mol L^{-1} s^{-1})
1	0.10	0.10	0.00300
2	0.10	0.15	0.00450
3	0.15	0.10	0.00675

Solution

The rate law for this reaction will have the form:

$$\text{rate} = k[\text{NO}]^m[\text{Cl}_2]^n$$

As in Example 4.4.2, we can approach this problem in a stepwise fashion, determining the values of *m* and *n* from the experimental data and then using these values to determine the value of *k*. In this example, however, we will use a different approach to determine the values of *m* and *n*:

Determine the value of m *from the data in which [NO] varies and [Cl$_2$] is constant.* We can write the ratios with the subscripts *x* and *y* to indicate data from two different trials:

$$\frac{\text{rate}_x}{\text{rate}_y} = \frac{k[\text{NO}]_x^m[\text{Cl}_2]_x^n}{k[\text{NO}]_y^m[\text{Cl}_2]_y^n}$$

Using the third trial and the first trial, in which [Cl$_2$] does not vary, gives:

$$\frac{\text{rate 3}}{\text{rate 1}} = \frac{0.00675}{0.00300} = \frac{k(0.15)^m(0.10)^n}{k(0.10)^m(0.10)^n}$$

After canceling equivalent terms in the numerator and denominator, we are left with:

$$\frac{0.00675}{0.00300} = \frac{(0.15)^m}{(0.10)^m}$$

which simplifies to:

$$2.25 = (1.5)^m$$

We can use natural logs to determine the value of the exponent *m*:

$$\ln(2.25) = m\ln(1.5)\frac{\ln(2.25)}{\ln(1.5)} \qquad = m2 = m$$

We can confirm the result easily, since:

$$1.5^2 = 2.25$$

- *Determine the value of* n *from data in which [Cl$_2$] varies and [NO] is constant.*

  $$\frac{\text{rate 2}}{\text{rate 1}} = \frac{0.00450}{0.00300} = \frac{k(0.10)^m(0.15)^n}{k(0.10)^m(0.10)^n}$$

  Cancelation gives:

  $$\frac{0.0045}{0.0030} = \frac{(0.15)^n}{(0.10)^n}$$

  which simplifies to:

  $$1.5 = (1.5)^n$$

  Thus *n* must be 1, and the form of the rate law is:

  $$\text{Rate} = k[\text{NO}]^m[\text{Cl}_2]^n = k[\text{NO}]^2[\text{Cl}_2]$$

- *Determine the numerical value of the rate constant* k *with appropriate units.* The units for the rate of a reaction are mol/L/s. The units for *k* are whatever is needed so that substituting into the rate law expression affords the appropriate units for the rate. In this example, the concentration units are mol^3/L^3. The units for *k* should be mol^{-2} L^2/s so that the rate is in terms of mol/L/s.

  To determine the value of *k* once the rate law expression has been solved, simply plug in values from the first experimental trial and solve for *k*:

  $$0.00300 \text{ mol L}^{-1} \text{ s}^{-1} = k(0.10 \text{ mol L}^{-1})^2(0.10 \text{ mol L}^{-1})^1$$
  $$k = 3.0 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$$

Exercise 4.4.3

Use the provided initial rate data to derive the rate law for the reaction whose equation is:

$$\mathrm{OCl^-}(aq) + \mathrm{I^-}(aq) \longrightarrow \mathrm{OI^-}(aq) + \mathrm{Cl^-}(aq)$$

Trial	[OCl^-] (mol/L)	[I^-] (mol/L)	Initial Rate (mol/L/s)
1	0.0040	0.0020	0.00184
2	0.0020	0.0040	0.00092
3	0.0020	0.0020	0.00046

Determine the rate law expression and the value of the rate constant *k* with appropriate units for this reaction.

Answer

$$\frac{\text{rate 2}}{\text{rate 3}} = \frac{0.00092}{0.00046} = \frac{k(0.0020)^x(0.0040)^y}{k(0.0020)^x(0.0020)^y}$$

$$2.00 = 2.00^y$$

$$y = 1$$

$$\frac{\text{rate 1}}{\text{rate 2}} = \frac{0.00184}{0.00092} = \frac{k(0.0040)^x(0.0020)^y}{k(0.0020)^x(0.0040)^y}$$

$$2.00 = \frac{2^x}{2^y}$$

$$2.00 = \frac{2^x}{2^1}$$

$$4.00 = 2^x$$

$$x = 2$$

Substituting the concentration data from trial 1 and solving for *k* yields:

$$\text{rate} = k[\mathrm{OCl^-}]^2[\mathrm{I^-}]^1$$

$$0.00184 = k(0.0040)^2(0.0020)^1$$

$$k = 5.75 \times 10^4 \text{ mol}^{-2}\text{ L}^2\text{ s}^{-1}$$

4.4.1: Reaction Order and Rate Constant Units

In some of our examples, the reaction orders in the rate law happen to be the same as the coefficients in the chemical equation for the reaction. This is merely a coincidence and very often not the case. Rate laws may exhibit fractional orders for some reactants, and negative reaction orders are sometimes observed when an increase in the concentration of one reactant causes a decrease in reaction rate. A few examples illustrating these points are provided:

$$\mathrm{NO_2} + \mathrm{CO} \longrightarrow \mathrm{NO} + \mathrm{CO_2} \quad \text{rate} = k[\mathrm{NO_2}]^2$$

$$\mathrm{CH_3CHO} \longrightarrow \mathrm{CH_4} + \mathrm{CO} \quad \text{rate} = k[\mathrm{CH_3CHO}]^2$$

$$2\,\mathrm{N_2O_5} \longrightarrow 2\,\mathrm{NO_2} + \mathrm{O_2} \quad \text{rate} = k[\mathrm{N_2O_5}]$$

$$2\,\mathrm{NO_2} + \mathrm{F_2} \longrightarrow 2\,\mathrm{NO_2F} \quad \text{rate} = k[\mathrm{NO_2}][\mathrm{F_2}]$$

$$2\,\mathrm{NO_2Cl} \longrightarrow 2\,\mathrm{NO_2} + \mathrm{Cl_2} \quad \text{rate} = k[\mathrm{NO_2Cl}]$$

> *It is important to note that rate laws are determined by experiment only and are not reliably predicted by reaction stoichiometry.*

Reaction orders also play a role in determining the units for the rate constant *k*. In Example 4.4.2, a second-order reaction, we found the units for *k* to be $\mathrm{L\ mol^{-1}\ s^{-1}}$, whereas in Example 4.4.3, a third order reaction, we found the units for *k* to be $\mathrm{mol^{-2}\ L^2/s}$. More generally speaking, the units for the rate constant for a reaction of order $(m+n)$ are $\mathrm{mol}^{1-(m+n)}\mathrm{L}^{(m+n)-1}\mathrm{s}^{-1}$. Table 4.4.1 summarizes the rate constant units for common reaction orders.

Table 4.4.1: Rate Constants for Common Reaction Orders

Reaction Order	Units of *k*
$(m+n)$	$\mathrm{mol}^{1-(m+n)}\,\mathrm{L}^{(m+n)-1}\,\mathrm{s}^{-1}$
zero	mol/L/s
first	$\mathrm{s^{-1}}$
second	L/mol/s
third	$\mathrm{mol^{-2}\ L^2\ s^{-1}}$

Note that the units in the table can also be expressed in terms of molarity (*M*) instead of mol/L. Also, units of time other than the second (such as minutes, hours, days) may be used, depending on the situation.

Summary

Rate laws provide a mathematical description of how changes in the amount of a substance affect the rate of a chemical reaction. Rate laws are determined experimentally and cannot be predicted by reaction stoichiometry. The order of reaction describes how much a change in the amount of each substance affects the overall rate, and the overall order of a reaction is the sum of the orders for each substance present in the reaction. Reaction orders are typically first order, second order, or zero order, but fractional and even negative orders are possible.

Glossary

method of initial rates
use of a more explicit algebraic method to determine the orders in a rate law

overall reaction order
sum of the reaction orders for each substance represented in the rate law

rate constant (*k*)
proportionality constant in the relationship between reaction rate and concentrations of reactants

rate law
(also, rate equation) mathematical equation showing the dependence of reaction rate on the rate constant and the concentration of one or more reactants

reaction order
value of an exponent in a rate law, expressed as an ordinal number (for example, zero order for 0, first order for 1, second order for 2, and so on)

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4.5: Integrated Rate Laws

Learning Objectives

- Explain the form and function of an integrated rate law
- Perform integrated rate law calculations for zero-, first-, and second-order reactions
- Define half-life and carry out related calculations
- Identify the order of a reaction from concentration/time data

The rate laws we have seen thus far relate the rate and the concentrations of reactants. We can also determine a second form of each rate law that relates the concentrations of reactants and time. These are called integrated rate laws. We can use an integrated rate law to determine the amount of reactant or product present after a period of time or to estimate the time required for a reaction to proceed to a certain extent. For example, an integrated rate law is used to determine the length of time a radioactive material must be stored for its radioactivity to decay to a safe level.

Using calculus, the differential rate law for a chemical reaction can be integrated with respect to time to give an equation that relates the amount of reactant or product present in a reaction mixture to the elapsed time of the reaction. This process can either be very straightforward or very complex, depending on the complexity of the differential rate law. For purposes of discussion, we will focus on the resulting integrated rate laws for first-, second-, and zero-order reactions.

4.5.1: First-Order Reactions

An equation relating the rate constant k to the initial concentration $[A]_0$ and the concentration $[A]_t$ present after any given time t can be derived for a first-order reaction and shown to be:

$$ln\left(\frac{[A]_t}{[A]_0}\right) = -kt \tag{4.5.1}$$

or alternatively

$$\ln\left(\frac{[A]_0}{[A]_t}\right) = kt$$

or

$$[A] = [A]_0 e^{-kt}$$

Example 4.5.1: The Integrated Rate Law for a First-Order Reaction

The rate constant for the first-order decomposition of cyclobutane, C_4H_8 at 500 °C is 9.2×10^{-3} s^{-1}:

$$C_4H_8 \longrightarrow 2\,C_2H_4$$

How long will it take for 80.0% of a sample of C_4H_8 to decompose?

Solution

We use the integrated form of the rate law to answer questions regarding time:

$$\ln\left(\frac{[A]_0}{[A]}\right) = kt$$

There are four variables in the rate law, so if we know three of them, we can determine the fourth. In this case we know $[A]_0$, $[A]$, and k, and need to find t.

The initial concentration of C_4H_8, $[A]_0$, is not provided, but the provision that 80.0% of the sample has decomposed is enough information to solve this problem. Let x be the initial concentration, in which case the concentration after 80.0% decomposition is 20.0% of x or 0.200x. Rearranging the rate law to isolate t and substituting the provided quantities yields:

$$\begin{aligned} t &= \ln \frac{[x]}{[0.200x]} \times \frac{1}{k} \\ &= \ln \frac{0.100 \text{ mol L}^{-1}}{0.020 \text{ mol L}^{-1}} \times \frac{1}{9.2 \times 10^{-3} \text{ s}^{-1}} \\ &= 1.609 \times \frac{1}{9.2 \times 10^{-3} \text{ s}^{-1}} \\ &= 1.7 \times 10^{2} \text{ s} \end{aligned}$$

? Exercise 4.5.1

Iodine-131 is a radioactive isotope that is used to diagnose and treat some forms of thyroid cancer. Iodine-131 decays to xenon-131 according to the equation:

$$\text{I-131} \longrightarrow \text{Xe-131} + \text{electron}$$

The decay is first-order with a rate constant of 0.138 d^{-1}. All radioactive decay is first order. How many days will it take for 90% of the iodine−131 in a 0.500 *M* solution of this substance to decay to Xe-131?

Answer

16.7 days

We can use integrated rate laws with experimental data that consist of time and concentration information to determine the order and rate constant of a reaction. The integrated rate law can be rearranged to a standard linear equation format:

$$ln[A] = (-k)(t) + \ln[A]_0 \tag{4.5.2}$$

$$y = mx + b$$

A plot of $ln[A]$ versus t for a first-order reaction is a straight line with a slope of $-k$ and an intercept of $ln[A]_0$. If a set of rate data are plotted in this fashion but do *not* result in a straight line, the reaction is not first order in A.

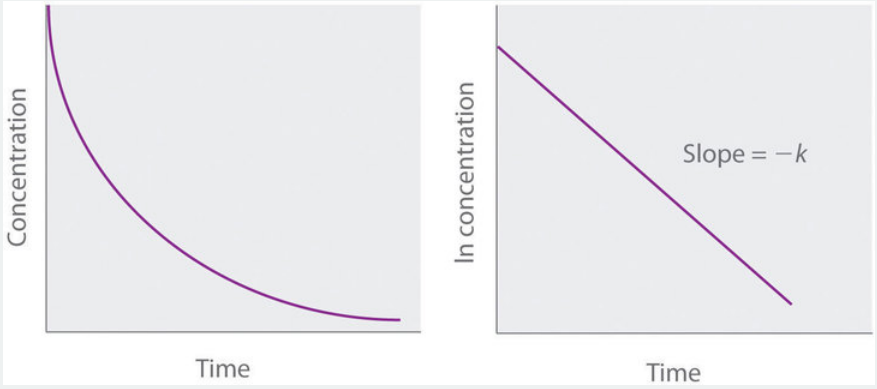


Figure 4.5.1: Graphs of a first-order reaction. The expected shapes of the curves for plots of reactant concentration versus time (left) and the natural logarithm of reactant concentration versus time (right) for a first-order reaction.

✓ Example 4.5.2: Determination of Reaction Order by Graphing

Show that the data below can be represented by a first-order rate law by graphing $\ln[H_2O_2]$ versus time. Determine the rate constant for the rate of decomposition of H_2O_2 from this data.

Trial	Time (h)	$[H_2O_2]$ (M)	$\ln[H_2O_2]$
1	0	1.000	0.0
2	6.00	0.500	−0.693
3	12.00	0.250	−1.386
4	18.00	0.125	−2.079
5	24.00	0.0625	−2.772

Solution

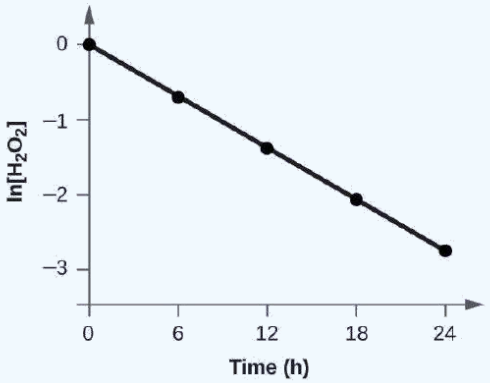


Figure 4.5.2: The linear relationship between the $\ln[H_2O_2]$ and time shows that the decomposition of hydrogen peroxide is a first-order reaction.

The plot of $\ln[H_2O_2]$ versus time is linear, thus we have verified that the reaction may be described by a first-order rate law.

The rate constant for a first-order reaction is equal to the negative of the slope of the plot of $\ln[H_2O_2]$ versus time where:

$$\text{slope} = \frac{\text{change in } y}{\text{change in } x} = \frac{\Delta y}{\Delta x} = \frac{\Delta \ln[H_2O_2]}{\Delta t}$$

In order to determine the slope of the line, we need two values of $\ln[H_2O_2]$ at different values of t (one near each end of the line is preferable). For example, the value of $\ln[H_2O_2]$ when t is 6.00 h is −0.693; the value when t = 12.00 h is −1.386:

$$\begin{aligned} \text{slope} &= \frac{-1.386-(-0.693)}{12.00\ \text{h}-6.00\ \text{h}} \\ &= \frac{-0.693}{6.00\ \text{h}} \\ &= -1.155\times10^{-2}\ \text{h}^{-1} \\ k &= -\text{slope} = -(-1.155\times10^{-1}\ \text{h}^{-1}) = 1.155\times10^{-1}\ \text{h}^{-1} \end{aligned}$$

Exercise 4.5.2

Graph the following data to determine whether the reaction $A \longrightarrow B + C$ is first order.

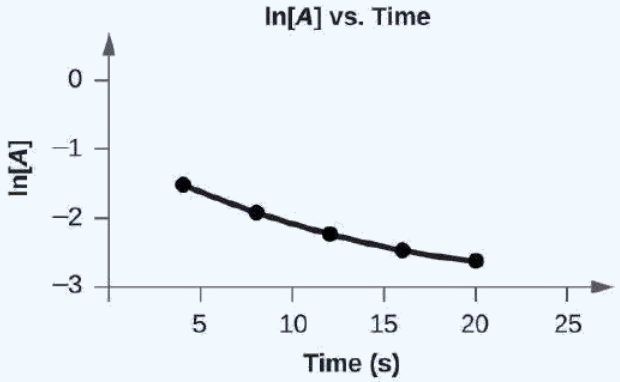
Data for the reaction $A \longrightarrow B + C$

Trial	Time (s)	[A]
1	4.0	0.220
2	8.0	0.144
3	12.0	0.110

Trial	Time (s)	[A]
4	16.0	0.088
5	20.0	0.074

Answer

The plot of ln[A] vs. t is not a straight line. The equation is not first order:



4.5.2: Second-Order Reactions

The equations that relate the concentrations of reactants and the rate constant of second-order reactions are fairly complicated. We will limit ourselves to the simplest second-order reactions, namely, those with rates that are dependent upon just one reactant's concentration and described by the differential rate law:

$$\text{Rate} = k[A]^2$$

For these second-order reactions, the integrated rate law is:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0} \tag{4.5.3}$$

where the terms in the equation have their usual meanings as defined earlier.

Example 4.5.3: The Integrated Rate Law for a Second-Order Reaction

The reaction of butadiene gas (C_4H_6) with itself produces C_8H_{12} gas as follows:

$$2\,C_4H_6(g) \longrightarrow C_8H_{12}(g)$$

The reaction is second order with a rate constant equal to 5.76×10^{-2} L/mol/min under certain conditions. If the initial concentration of butadiene is 0.200 *M*, what is the concentration remaining after 10.0 min?

Solution

We use the integrated form of the rate law to answer questions regarding time. For a second-order reaction, we have:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

We know three variables in this equation: $[A]_0$ = 0.200 mol/L, $k = 5.76 \times 10^{-2}$ L/mol/min, and t = 10.0 min. Therefore, we can solve for [*A*], the fourth variable:

$$\frac{1}{[A]} = (5.76 \times 10^{-2}\ \text{L mol}^{-1}\ \text{min}^{-1})(10\ \text{min}) + \frac{1}{0.200\ \text{mol}^{-1}}$$

$$\frac{1}{[A]} = (5.76 \times 10^{-1}\ \text{L mol}^{-1}) + 5.00\ \text{L mol}^{-1}$$

$$\frac{1}{[A]} = 5.58\ \text{L mol}^{-1}$$

$$[A] = 1.79 \times 10^{-1}\ \text{mol L}^{-1}$$

Therefore 0.179 mol/L of butadiene remain at the end of 10.0 min, compared to the 0.200 mol/L that was originally present.

? Exercise 4.5.3

If the initial concentration of butadiene is 0.0200 *M*, what is the concentration remaining after 20.0 min?

Answer

0.0196 mol/L

The integrated rate law for our second-order reactions has the form of the equation of a straight line:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

$$y = mx + b$$

A plot of $\frac{1}{[A]}$ versus *t* for a second-order reaction is a straight line with a slope of *k* and an intercept of $\frac{1}{[A]_0}$. If the plot is not a straight line, then the reaction is not second order.

✓ Example 4.5.4: Determination of Reaction Order by Graphing

Test the data given to show whether the dimerization of C_4H_6 is a first- or a second-order reaction.

Solution

Solutions to Example 12.4.4

Trial	Time (s)	$[C_4H_6]$ (*M*)
1	0	1.00×10^{-2}
2	1600	5.04×10^{-3}
3	3200	3.37×10^{-3}
4	4800	2.53×10^{-3}
5	6200	2.08×10^{-3}

In order to distinguish a first-order reaction from a second-order reaction, we plot $\ln[C_4H_6]$ versus *t* and compare it with a plot of $\frac{1}{[C_4H_6]}$ versus *t*. The values needed for these plots follow.

Time (s)	$\frac{1}{[C_4H_6]}$ (M^{-1})	$\ln[C_4H_6]$
0	100	−4.605
1600	198	−5.289
3200	296	−5.692

Time (s)	$\frac{1}{[C_4H_6]}\ (M^{-1})$	$\ln[C_4H_6]$
4800	395	−5.978
6200	481	−6.175

The plots are shown in Figure 4.5.3. As you can see, the plot of $\ln[C_4H_6]$ versus t is not linear, therefore the reaction is not first order. The plot of $\frac{1}{[C_4H_6]}$ versus t is linear, indicating that the reaction is second order.

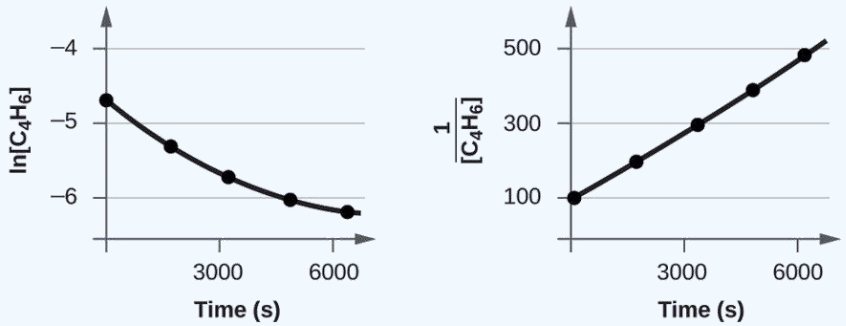


Figure 4.5.3: These two graphs show first- and second-order plots for the dimerization of C_4H_6. Since the first-order plot (left) is not linear, we know that the reaction is not first order. The linear trend in the second-order plot (right) indicates that the reaction follows second-order kinetics.

Exercise 4.5.4

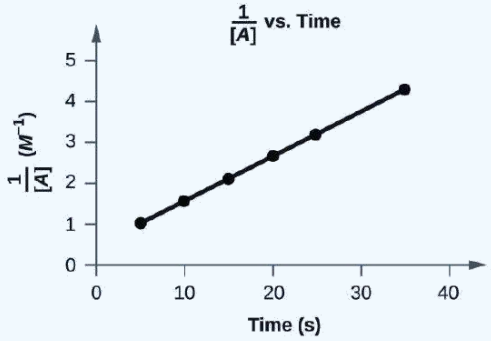
Does the following data fit a second-order rate law?

Data for second-order rate law

Trial	Time (s)	[A] (M)
1	5	0.952
2	10	0.625
3	15	0.465
4	20	0.370
5	25	0.308
6	35	0.230

Answer

Yes. The plot of $\frac{1}{[A]}$ vs. t is linear:



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4.5.3: Zero-Order Reactions

For zero-order reactions, the differential rate law is:

$$\text{Rate} = k[A]^0 = k$$

A zero-order reaction thus exhibits a constant reaction rate, regardless of the concentration of its reactants.

The integrated rate law for a zero-order reaction also has the form of the equation of a straight line:

$$[A] = -kt + [A]_0 \tag{4.5.4}$$

$$y = mx + b$$

A plot of $[A]$ versus t for a zero-order reaction is a straight line with a slope of $-k$ and an intercept of $[A]_0$.

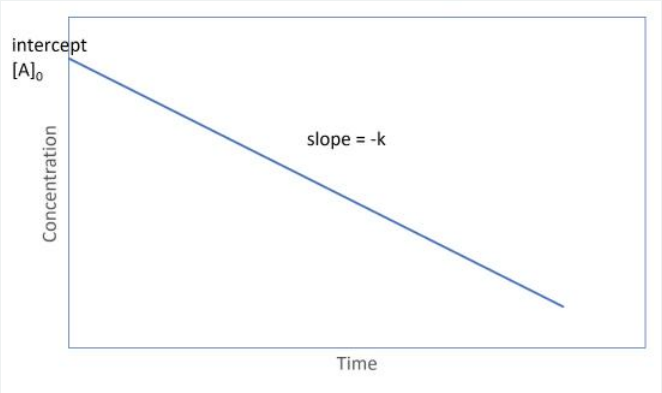


Figure 4.5.4 shows a plot of concentration versus time for a zero order reaction.

Figure 4.5.5 shows a plot of [NH_3] versus *t* for the decomposition of ammonia on a hot tungsten wire and for the decomposition of ammonia on hot quartz (SiO_2). The decomposition of NH_3 on hot tungsten is zero order; the plot is a straight line. The decomposition of NH_3 on hot quartz is not zero order (it is first order). From the slope of the line for the zero-order decomposition, we can determine the rate constant:

$$\text{slope} = -k = 1.3110^{-6}\ \text{mol/L/s}$$

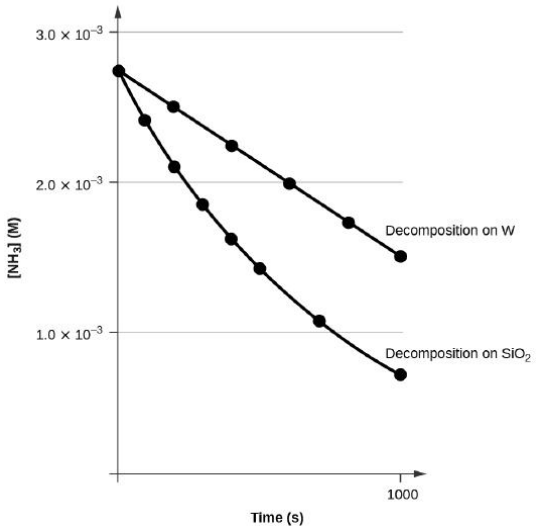


Figure 4.5.5: The decomposition of NH_3 on a tungsten (W) surface is a zero-order reaction, whereas on a quartz (SiO_2) surface, the reaction is first order.

4.5.4: The Half-Life of a Reaction

The half-life of a reaction ($t_{1/2}$) is the time required for one-half of a given amount of reactant to be consumed. In each succeeding half-life, half of the remaining concentration of the reactant is consumed.

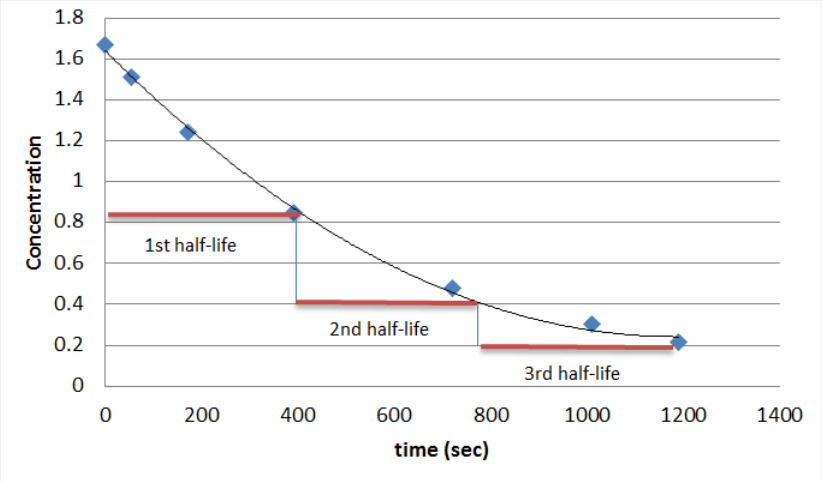


Figure 4.5.6: A plot of concentration versus time for a first order reaction shows a curve which decreases exponentially. The time it takes teh concentration to decrease by half is constant and is labeled as successive half-lives on the graph.

Using the decomposition of hydrogen peroxide as an example (see data in above Example 4.5.2), we find that during the first half-life (from 0.00 hours to 6.00 hours), the concentration of H_2O_2 decreases from 1.000 *M* to 0.500 *M*. During the second half-life (from 6.00 hours to 12.00 hours), it decreases from 0.500 *M* to 0.250 *M*; during the third half-life, it decreases from 0.250 *M* to 0.125 *M*. The concentration of H_2O_2 decreases by half during each successive period of 6.00 hours. The decomposition of hydrogen peroxide is a first-order reaction, and, as can be shown, the half-life of a first-order reaction is independent of the concentration of the reactant. However, half-lives of reactions with other orders depend on the concentrations of the reactants.

4.5.4.1: First-Order Reactions

We can derive an equation for determining the half-life of a first-order reaction from the alternate form of the integrated rate law as follows:

$$\ln \frac{[A]_0}{[A]} = kt$$

$$t = \ln \frac{[A]_0}{[A]} \times \frac{1}{k}$$

If we set the time *t* equal to the half-life, $t_{1/2}$, the corresponding concentration of *A* at this time is equal to one-half of its initial concentration. Hence, when $t = t_{1/2}$, $[A] = \frac{1}{2}[A]_0$.

Therefore:

$$t_{1/2} = \ln \frac{[A]_0}{\frac{1}{2}[A]_0} \times \frac{1}{k}$$

$$= \ln 2 \times \frac{1}{k} = 0.693 \times \frac{1}{k}$$

Thus:

$$t_{1/2} = \frac{0.693}{k}$$

We can see that the half-life of a first-order reaction is inversely proportional to the rate constant *k*. A fast reaction (shorter half-life) will have a larger *k*; a slow reaction (longer half-life) will have a smaller *k*.

Example 4.5.5: Calculation of a First-order Rate Constant using Half-Life

Calculate the rate constant for the first-order decomposition of hydrogen peroxide in water at 40 °C, using the data given in Figure 4.5.4.



Figure 4.5.7: The decomposition of H_2O_2 $(2\,H_2O_2 \longrightarrow 2\,H_2O + O_2)$ *at 40 °C is illustrated. The intensity of the color symbolizes the concentration of* H_2O_2 *at the indicated times;* H_2O_2 *is actually colorless.*

Solution The half-life for the decomposition of H_2O_2 is 2.16×10^4 s:

$$t_{1/2} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.16 \times 10^4\ \text{s}} = 3.21 \times 10^{-5}\ \text{s}^{-1}$$

Exercise 4.5.1

The first-order radioactive decay of iodine-131 exhibits a rate constant of 0.138 d^{-1}. What is the half-life for this decay?

Answer

5.02 d.

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4.5.4.2: Second-Order Reactions

We can derive the equation for calculating the half-life of a second order as follows:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

or

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

If

$$t = t_{1/2}$$

then

$$[A] = \frac{1}{2}[A]_0$$

and we can write:

$$\frac{1}{\frac{1}{2}[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$

$$2[A]_0 - \frac{1}{[A]_0} = kt_{1/2}$$

$$\frac{1}{[A]_0} = kt_{1/2}$$

Thus:

$$t_{1/2} = \frac{1}{k[A]_0}$$

For a second-order reaction, $t_{1/2}$ is inversely proportional to the concentration of the reactant, and the half-life increases as the reaction proceeds because the concentration of reactant decreases. Consequently, we find the use of the half-life concept to be more complex for second-order reactions than for first-order reactions. Unlike with first-order reactions, the rate constant of a second-order reaction cannot be calculated directly from the half-life unless the initial concentration is known.

4.5.4.3: Zero-Order Reactions

We can derive an equation for calculating the half-life of a zero order reaction as follows:

$$[A] = -kt + [A]_0$$

When half of the initial amount of reactant has been consumed $t = t_{1/2}$ and $[A] = \frac{[A]_0}{2}$. Thus:

$$\frac{[A]_0}{2} = -kt_{1/2} + [A]_0$$

$$kt_{1/2} = \frac{[A]_0}{2}$$

and

$$t_{1/2} = \frac{[A]_0}{2k}$$

The half-life of a zero-order reaction increases as the initial concentration increases. Equations for both differential and integrated rate laws and the corresponding half-lives for zero-, first-, and second-order reactions are summarized in Table $4.5.1$.

Table 4.5.1: Summary of Rate Laws for Zero-, First-, and Second-Order Reactions

	Zero-Order	First-Order	Second-Order
rate law	rate = k	rate = $k[A]$	rate = $k[A]^2$
units of rate constant	M s^{-1}	s^{-1}	M^{-1} s^{-1}
integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \left(\frac{1}{[A]_0}\right)$
plot needed for linear fit of rate data	$[A]$ vs. t	$\ln[A]$ vs. t	$\frac{1}{[A]}$ vs. t
relationship between slope of linear plot and rate constant	k = −slope	k = −slope	k = +slope
half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{[A]_0 k}$

Summary

Differential rate laws can be determined by the method of initial rates or other methods. We measure values for the initial rates of a reaction at different concentrations of the reactants. From these measurements, we determine the order of the reaction in each reactant. Integrated rate laws are determined by integration of the corresponding differential rate laws. Rate constants for those rate laws are determined from measurements of concentration at various times during a reaction.

The half-life of a reaction is the time required to decrease the amount of a given reactant by one-half. The half-life of a zero-order reaction decreases as the initial concentration of the reactant in the reaction decreases. The half-life of a first-order reaction is independent of concentration, and the half-life of a second-order reaction decreases as the concentration increases.

4.5.5: Key Equations

- integrated rate law for zero-order reactions (Equation ???):

$$[A] = -kt + [A]_0 \quad \text{with } t_{1/2} = \frac{[A]_0}{2k}$$

- integrated rate law for first-order reactions (Equation ???):

$$\ln[A] = -kt + \ln[A]_0 \quad \text{with } t_{1/2} = \frac{0.693}{k}$$

- integrated rate law for second-order reactions (Equation 4.5.3):

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0} \quad \text{with } t_{1/2} = \frac{1}{[A]_0 k}$$

Glossary

half-life of a reaction ($t_{1/2}$)
time required for half of a given amount of reactant to be consumed

integrated rate law
equation that relates the concentration of a reactant to elapsed time of reaction

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4.6: Collision Theory

Learning Objectives

- Use the postulates of collision theory to explain the effects of physical state, temperature, and concentration on reaction rates
- Define the concepts of activation energy and transition state
- Use the Arrhenius equation in calculations relating rate constants to temperature

We should not be surprised that atoms, molecules, or ions must collide before they can react with each other. Atoms must be close together to form chemical bonds. This simple premise is the basis for a very powerful theory that explains many observations regarding chemical kinetics, including factors affecting reaction rates. Collision theory is based on the following postulates:

Postulates of Collision theory

1. The rate of a reaction is proportional to the rate of reactant collisions:

$$\text{reaction rate} \propto \frac{\#\,\text{collisions}}{\text{time}}$$

2. The reacting species must collide in an orientation that allows contact between the atoms that will become bonded together in the product.
3. The collision must occur with adequate energy to permit mutual penetration of the reacting species' valence shells so that the electrons can rearrange and form new bonds (and new chemical species).

We can see the importance of the two physical factors noted in postulates 2 and 3, the orientation and energy of collisions, when we consider the reaction of carbon monoxide with oxygen:

$$2\,CO(g) + O_2(g) \longrightarrow 2\,CO_2(g)$$

Carbon monoxide is a pollutant produced by the combustion of hydrocarbon fuels. To reduce this pollutant, automobiles have catalytic converters that use a catalyst to carry out this reaction. It is also a side reaction of the combustion of gunpowder that results in muzzle flash for many firearms. If carbon monoxide and oxygen are present in sufficient quantity, the reaction is spontaneous at high temperature and pressure.

The first step in the gas-phase reaction between carbon monoxide and oxygen is a collision between the two molecules:

$$CO(g) + O_2(g) \longrightarrow CO_2(g) + O(g)$$

Although there are many different possible orientations the two molecules can have relative to each other, consider the two presented in Figure 4.6.1. In the first case, the oxygen side of the carbon monoxide molecule collides with the oxygen molecule. In the second case, the carbon side of the carbon monoxide molecule collides with the oxygen molecule. The second case is clearly more likely to result in the formation of carbon dioxide, which has a central carbon atom bonded to two oxygen atoms (O=C=O). This is a rather simple example of how important the orientation of the collision is in terms of creating the desired product of the reaction.

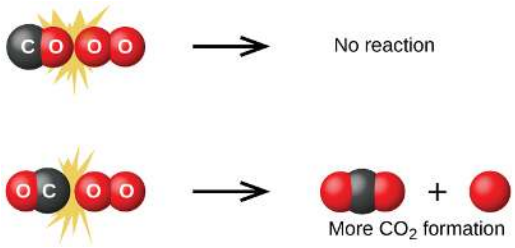


Figure 4.6.1: Illustrated are two collisions that might take place between carbon monoxide and oxygen molecules. The orientation of the colliding molecules partially determines whether a reaction between the two molecules will occur.

If the collision does take place with the correct orientation, there is still no guarantee that the reaction will proceed to form carbon dioxide. Every reaction requires a certain amount of activation energy for it to proceed in the forward direction, yielding an

appropriate activated complex along the way. As Figure 4.6.2 demonstrates, even a collision with the correct orientation can fail to form the reaction product. In the study of reaction mechanisms, each of these three arrangements of atoms is called a proposed activated complex or transition state.

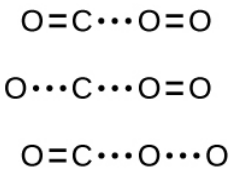


Figure 4.6.2: Possible transition states (activated complexes) for carbon monoxide reacting with oxygen to form carbon dioxide. Solid lines represent covalent bonds, while dotted lines represent unstable orbital overlaps that may, or may not, become covalent bonds as product is formed. In the first two examples in this figure, the O=O double bond is not impacted; therefore, carbon dioxide cannot form. The third proposed transition state will result in the formation of carbon dioxide if the third "extra" oxygen atom separates from the rest of the molecule.

In most circumstances, it is impossible to isolate or identify a transition state or activated complex. In the reaction between carbon monoxide and oxygen to form carbon dioxide, activated complexes have only been observed spectroscopically in systems that utilize a heterogeneous catalyst. The gas-phase reaction occurs too rapidly to isolate any such chemical compound.

Collision theory explains why most reaction rates increase as concentrations increase. With an increase in the concentration of any reacting substance, the chances for collisions between molecules are increased because there are more molecules per unit of volume. More collisions mean a faster reaction rate, assuming the energy of the collisions is adequate.

4.6.1: Activation Energy and the Arrhenius Equation

The minimum energy necessary to form a product during a collision between reactants is called the activation energy (E_a). The kinetic energy of reactant molecules plays an important role in a reaction because the energy necessary to form a product is provided by a collision of a reactant molecule with another reactant molecule. (In single-reactant reactions, activation energy may be provided by a collision of the reactant molecule with the wall of the reaction vessel or with molecules of an inert contaminant.) If the activation energy is much larger than the average kinetic energy of the molecules, the reaction will occur slowly: Only a few fast-moving molecules will have enough energy to react. If the activation energy is much smaller than the average kinetic energy of the molecules, the fraction of molecules possessing the necessary kinetic energy will be large; most collisions between molecules will result in reaction, and the reaction will occur rapidly.

Figure 4.6.3 shows the energy relationships for the general reaction of a molecule of A with a molecule of B to form molecules of C and D:

$$A + B \longrightarrow C + D$$

The figure shows that the energy of the transition state is higher than that of the reactants A and B by an amount equal to E_a, the activation energy. Thus, the sum of the kinetic energies of A and B must be **equal to or greater** than E_a to reach the transition state. After the transition state has been reached, and as C and D begin to form, the system loses energy until its total energy is lower than that of the initial mixture. This lost energy is transferred to other molecules, giving them enough energy to reach the transition state. The forward reaction (that between molecules A and B) therefore tends to take place readily once the reaction has started. In Figure 4.6.3, ΔH represents the difference in enthalpy between the reactants (A and B) and the products (C and D). The sum of E_a and ΔH represents the activation energy for the reverse reaction:

$$C + D \longrightarrow A + B$$

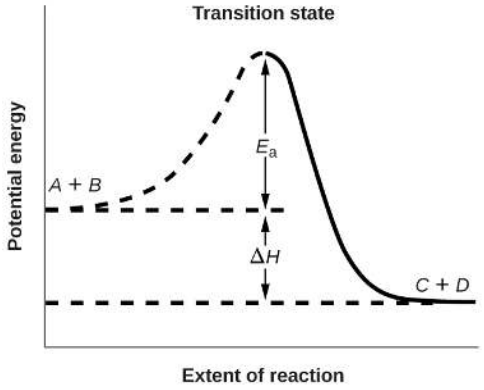


Figure 4.6.3: This graph shows the potential energy relationships for the reaction $A + B \longrightarrow C + D$. The dashed portion of the curve represents the energy of the system with a molecule of A and a molecule of B present, and the solid portion the energy of the system with a molecule of C and a molecule of D present. The activation energy for the forward reaction is represented by E_a. The activation energy for the reverse reaction is greater than that for the forward reaction by an amount equal to ΔH. The curve's peak represents the transition state.

We can use the Arrhenius equation to relate the activation energy and the rate constant, *k*, of a given reaction:

$$k = Ae^{-E_a/RT} \tag{4.6.1}$$

In this equation,

- R is the ideal gas constant, which has a value 8.314 J/mol/K,
- T is temperature on the Kelvin scale,
- E_a is the activation energy in joules per mole,
- e is the constant 2.7183, and
- A is a constant called the frequency factor, which is related to the frequency of collisions and the orientation of the reacting molecules.

Both postulates of the collision theory of reaction rates are accommodated in the Arrhenius equation. The frequency factor *A* is related to the rate at which collisions having the correct *orientation* occur. The exponential term, $e^{-E_a/RT}$, is related to the fraction of collisions providing adequate *energy* to overcome the activation barrier of the reaction.

At one extreme, the system does not contain enough energy for collisions to overcome the activation barrier. In such cases, no reaction occurs. At the other extreme, the system has so much energy that every collision with the correct orientation can overcome the activation barrier, causing the reaction to proceed. In such cases, the reaction is nearly instantaneous.

The Arrhenius equation (Equation 4.6.1) describes quantitatively much of what we have already discussed about reaction rates. For two reactions at the same temperature, the reaction with the higher activation energy has the lower rate constant and the slower rate. The larger value of E_a results in a smaller value for $e^{-E_a/RT}$, reflecting the smaller fraction of molecules with enough energy to react. Alternatively, the reaction with the smaller E_a has a larger fraction of molecules with enough energy to react. This will be reflected as a larger value of $e^{-E_a/RT}$, a larger rate constant, and a faster rate for the reaction.

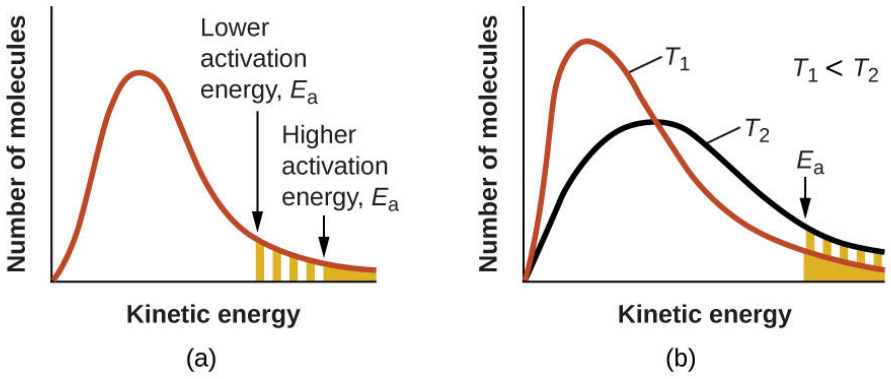


Figure 4.6.4: (a) As the activation energy of a reaction decreases, the number of molecules with at least this much energy increases, as shown by the shaded areas. (b) At a higher temperature, T2, more molecules have kinetic energies greater than Ea, as shown by the yellow shaded area.

An increase in temperature has the same effect as a decrease in activation energy. A larger fraction of molecules has the necessary energy to react (Figure 4.6.4), as indicated by an increase in the value of $e^{-E_a/RT}$. The rate constant is also directly proportional to the frequency factor, A. Hence a change in conditions or reactants that increases the number of collisions with a favorable orientation for reaction results in an increase in A and, consequently, an increase in k.

A convenient approach to determining E_a for a reaction involves the measurement of k at different temperatures and using of an alternate version of the Arrhenius equation that takes the form of linear equation:

$$\ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$$
$$y = mx + b$$

Thus, a plot of $\ln k$ versus $\frac{1}{T}$ gives a straight line with the slope $\frac{-E_a}{R}$, from which E_a may be determined. The intercept gives the value of $\ln A$. This is sometimes call an Arrhenius Plot.

Example 4.6.1

Determination of E_a The variation of the rate constant with temperature for the decomposition of HI(g) to $H_2(g)$ and $I_2(g)$ is given here. What is the activation energy for the reaction?

$$2\,HI(g) \longrightarrow H_2(g) + I_2(g)$$

variation of the rate constant with temperature for the decomposition of HI(g) to H2(g) and I2(g)

T (K)	k (L/mol/s)
555	3.52×10^{-7}
575	1.22×10^{-6}
645	8.59×10^{-5}
700	1.16×10^{-3}
781	3.95×10^{-2}

Solution

Values of $\frac{1}{T}$ and ln k are:

Solutions to Example 12.5.1

$\frac{1}{T}$ (K^{-1})	ln k

$\frac{1}{T}$ (K^{-1})	ln *k*
1.80×10^{-3}	−14.860
1.74×10^{-3}	−13.617
1.55×10^{-3}	−9.362
1.43×10^{-3}	−6.759
1.28×10^{-3}	−3.231

Figure 4.6.5 is a graph of ln *k* versus $\frac{1}{T}$. To determine the slope of the line, we need two values of ln *k*, which are determined from the line at two values of $\frac{1}{T}$ (one near each end of the line is preferable). For example, the value of ln *k* determined from the line when $\frac{1}{T} = 1.25 \times 10^{-3}$ is −2.593; the value when $\frac{1}{T} = 1.78 \times 10^{-3}$ is −14.447.

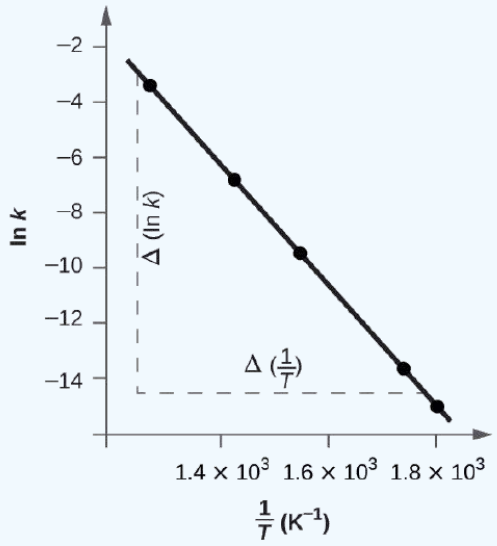


Figure 4.6.5: This graph shows the linear relationship between ln *k* and $\frac{1}{T}$ for the reaction $2\,HI \longrightarrow H_2 + I_2$ according to the Arrhenius equation.

The slope of this line is given by the following expression:

$$\begin{aligned} \text{Slope} &= \frac{\Delta(\ln k)}{\Delta\left(\frac{1}{T}\right)} \\ &= \frac{(-14.447) - (-2.593)}{(1.78 \times 10^{-3}\ \text{K}^{-1}) - (1.25 \times 10^{-3}\ \text{K}^{-1})} \\ &= \frac{-11.854}{0.53 \times 10^{-3}\ \text{K}^{-1}} = 2.2 \times 10^{4}\ \text{K} \\ &= -\frac{E_a}{R} \end{aligned}$$

Thus:

$$\begin{aligned} E_a &= -\text{slope} \times R = -(-2.2 \times 10^{4}\ \text{K} \times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}) \\ &= 1.8 \times 10^{5}\ \text{J mol}^{-1} \end{aligned}$$

In many situations, it is possible to obtain a reasonable estimate of the activation energy without going through the entire process of constructing the Arrhenius plot. The Arrhenius equation:

$$\ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$$

can be rearranged as shown to give:

$$\frac{\Delta(\ln k)}{\Delta\left(\frac{1}{T}\right)} = -\frac{E_a}{R}$$

or

$$\ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

This equation can be rearranged to give a one-step calculation to obtain an estimate for the activation energy:

$$E_a = -R\left(\frac{\ln k_2 - \ln k_1}{\left(\frac{1}{T_2}\right) - \left(\frac{1}{T_1}\right)}\right)$$

Using the experimental data presented here, we can simply select two data entries. For this example, we select the first entry and the last entry:

First and Last Entry

T (K)	k (L/mol/s)	$\frac{1}{T}$ (K^{-1})	ln k
555	3.52×10^{-7}	1.80×10^{-3}	−14.860
781	3.95×10^{-2}	1.28×10^{-3}	−3.231

After calculating $\frac{1}{T}$ and ln *k*, we can substitute into the equation:

$$E_a = -8.314\ \text{J mol}^{-1}\ \text{K}^{-1}\left(\frac{-3.231 - (-14.860)}{1.28 \times 10^{-3}\ \text{K}^{-1} - 1.80 \times 10^{-3}\ \text{K}^{-1}}\right)$$

and the result is E_a = 185,900 J/mol.

This method is very effective, especially when a limited number of temperature-dependent rate constants are available for the reaction of interest.

Exercise 4.6.1

The rate constant for the rate of decomposition of N_2O_5 to NO and O_2 in the gas phase is 1.66 L/mol/s at 650 K and 7.39 L/mol/s at 700 K:

$$2\,N_2O_5(g) \longrightarrow 4\,NO(g) + 3\,O_2(g)$$

Assuming the kinetics of this reaction are consistent with the Arrhenius equation, calculate the activation energy for this decomposition.

Answer

113,000 J/mol

Summary

Chemical reactions require collisions between reactant species. These reactant collisions must be of proper orientation and sufficient energy in order to result in product formation. Collision theory provides a simple but effective explanation for the effect

of many experimental parameters on reaction rates. The Arrhenius equation describes the relation between a reaction's rate constant and its activation energy, temperature, and dependence on collision orientation.

4.6.2: Key Equations

- $k = Ae^{-E_a/RT}$
- $\ln k = \left(\frac{-E_\text{a}}{R}\right)\left(\frac{1}{T}\right) + \ln A$
- $\ln \frac{k_1}{k_2} = \frac{E_\text{a}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

Glossary

activated complex
(also, transition state) unstable combination of reactant species representing the highest energy state of a reaction system

activation energy (E_a)
energy necessary in order for a reaction to take place

Arrhenius equation
mathematical relationship between the rate constant and the activation energy of a reaction

collision theory
model that emphasizes the energy and orientation of molecular collisions to explain and predict reaction kinetics

frequency factor (A)
proportionality constant in the Arrhenius equation, related to the relative number of collisions having an orientation capable of leading to product formation

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4.7: Reaction Mechanisms

Learning Objectives

- Distinguish net reactions from elementary reactions (steps)
- Identify the molecularity of elementary reactions
- Write a balanced chemical equation for a process given its reaction mechanism
- Derive the rate law consistent with a given reaction mechanism

A balanced equation for a chemical reaction indicates what is reacting and what is produced, but it reveals nothing about how the reaction actually takes place. The reaction mechanism (or reaction path) is the process, or pathway, by which a reaction occurs. A chemical reaction often occurs in steps, although it may not always be obvious to an observer. The decomposition of ozone, for example, appears to follow a mechanism with two steps:

$$\begin{aligned} \mathrm{O_3}(g) &\longrightarrow \mathrm{O_2}(g) + \mathrm{O} \\ \mathrm{O} + \mathrm{O_3}(g) &\longrightarrow 2\,\mathrm{O_2}(g) \end{aligned} \tag{4.7.1}$$

We call each step in a reaction mechanism an elementary reaction. Elementary reactions occur exactly as they are written and cannot be broken down into simpler steps. Elementary reactions add up to the overall reaction, which, for the decomposition, is:

$$2\,\mathrm{O_3}(g) \longrightarrow 3\,\mathrm{O_2}(g) \tag{4.7.2}$$

Notice that the oxygen atom produced in the first step of this mechanism is consumed in the second step and therefore does not appear as a product in the overall reaction. Species that are produced in one step and consumed in a subsequent step are called intermediates.

While the overall reaction equation for the decomposition of ozone indicates that two molecules of ozone react to give three molecules of oxygen, the mechanism of the reaction does not involve the collision and reaction of two ozone molecules. Rather, it involves a molecule of ozone decomposing to an oxygen molecule and an intermediate oxygen atom; the oxygen atom then reacts with a second ozone molecule to give two oxygen molecules. These two elementary reactions occur exactly as they are shown in the reaction mechanism.

4.7.0.0.1: Unimolecular Elementary Reactions

The molecularity of an elementary reaction is the number of reactant species (atoms, molecules, or ions). For example, a unimolecular reaction involves the rearrangement of a *single* reactant species to produce one or more molecules of product:

$$A \longrightarrow \text{products} \tag{4.7.3}$$

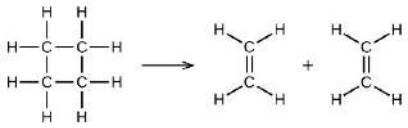
The rate equation for a unimolecular reaction is:

$$\text{rate} = k[A] \tag{4.7.4}$$

A unimolecular reaction may be one of several elementary reactions in a complex mechanism. For example, the reaction:

$$\mathrm{O_3} \longrightarrow \mathrm{O_2} + \mathrm{O} \tag{4.7.5}$$

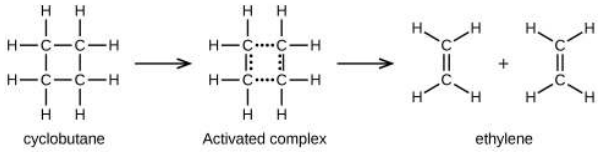
illustrates a unimolecular elementary reaction that occurs as one part of a two-step reaction mechanism. However, some unimolecular reactions may have only a single reaction in the reaction mechanism. (In other words, an elementary reaction can also be an overall reaction in some cases.) For example, the gas-phase decomposition of cyclobutane, $\mathrm{C_4H_8}$, to ethylene, $\mathrm{C_2H_4}$, occurs via a unimolecular, single-step mechanism:



In this figure, structural formulas are used to illustrate a chemical reaction. On the left, a structural formula for cyclobutane is shown. This structure is composed of 4 C atoms connected with single bonds in a square shape. Each C atom is bonded to two other C atoms in the structure, leaving two bonds for H atoms pointing outward above, below, left, and right. An arrow points right to two identical ethane molecules with a plus symbol between them. Each of these molecules contains two C atoms connected with a double bond oriented vertically between them. The C atom at the top of these molecules has H atoms bonded above to the right and left. Similarly, the lower C atom has two H atoms bonded below to the right and left.

For these unimolecular reactions to occur, all that is required is the separation of parts of single reactant molecules into products.

Chemical bonds do not simply fall apart during chemical reactions. Energy is required to break chemical bonds. The activation energy for the decomposition of $\mathrm{C_4H_8}$, for example, is 261 kJ per mole. This means that it requires 261 kilojoules to distort one mole of these molecules into activated complexes that decompose into products:



In this figure, structural formulas are used to illustrate a chemical reaction, including an intermediate step. On the left, a structural formula for cyclobutane is shown. This structure is composed of 4 C atoms connected with single bonds in a square shape. Each C atom is bonded to two other C atoms in the structure, leaving two bonds for H atoms pointing outward above, below, left, and right. This structure is labeled, “Cyclohexane.” An arrow points right to a similar structure which has the upper and lower bonds replaced by rows of 4 dots. Similarly, columns of 3 dots appear just inside the line segments indicating the vertically oriented single bonds in the structure. The label “Activated complex” appears beneath this structure. A second arrow points right to two identical ethane molecules with a plus symbol between them. Each of these molecules contains two C atoms connected with a double bond oriented vertically between them. The C atom at the top of these molecules has H atoms bonded above to the right and left. Similarly, the lower C atom has two H atoms bonded below to the right and left. Below these two molecules appears the label “Ethylene.”

In a sample of $\mathrm{C_4H_8}$, a few of the rapidly moving $\mathrm{C_4H_8}$ molecules collide with other rapidly moving molecules and pick up additional energy. When the $\mathrm{C_4H_8}$ molecules gain enough energy, they can transform into an activated complex, and the formation of ethylene molecules can occur. In effect, a particularly energetic collision knocks a $\mathrm{C_4H_8}$ molecule into the geometry of the activated complex. However, only a small fraction of gas molecules travel at sufficiently high speeds with large enough kinetic energies to accomplish this. Hence, at any given moment, only a few molecules pick up enough energy from collisions to react.

The rate of decomposition of $\mathrm{C_4H_8}$ is directly proportional to its concentration. Doubling the concentration of $\mathrm{C_4H_8}$ in a sample gives twice as many molecules per liter. Although the fraction of molecules with enough energy to react remains the same, the total number of such molecules is twice as great. Consequently, there is twice as much $\mathrm{C_4H_8}$ per liter, and the reaction rate is twice as fast:

$$\text{rate} = -\frac{\Delta[\mathrm{C_4H_8}]}{\Delta t} = k[\mathrm{C_4H_8}] \tag{4.7.6}$$

A similar relationship applies to any unimolecular elementary reaction; the reaction rate is directly proportional to the concentration of the reactant, and the reaction exhibits first-order behavior. The proportionality constant is the rate constant for the particular unimolecular reaction.

4.7.1: Bimolecular Elementary Reactions

The collision and combination of two molecules or atoms to form an activated complex in an elementary reaction is called a bimolecular reaction. There are two types of bimolecular elementary reactions:

$$A + B \longrightarrow \text{products} \tag{4.7.7}$$

and

$$2A \longrightarrow \text{products} \tag{4.7.8}$$

For the first type, in which the two reactant molecules are different, the rate law is first-order in *A* and first order in *B*:

$$\text{rate} = k[A][B] \tag{4.7.9}$$

For the second type, in which two identical molecules collide and react, the rate law is second order in *A*:

$$\text{rate} = k[A][A] = k[A]^2 \tag{4.7.10}$$

Some chemical reactions have mechanisms that consist of a single bimolecular elementary reaction. One example is the reaction of nitrogen dioxide with carbon monoxide:

$$\mathrm{NO_2}(g) + \mathrm{CO}(g) \longrightarrow \mathrm{NO}(g) + \mathrm{CO_2}(g) \tag{4.7.11}$$

(see Figure 4.7.1)

Figure 4.7.1: The probable mechanism for the reaction between $\mathrm{NO_2}$ and CO to yield NO and $\mathrm{CO_2}$.

This figure provides an illustration of a reaction between two H I molecules using space filling models. H atoms are shown as white spheres, and I atoms are shown as purple spheres. On the left, two H I molecules are shownwith a small white sphere bonded to a much larger purple sphere. The label, “Two H I molecules,” appears below. An arrow points right to a similar structure in which the two molecules appear pushed together, so that the purple spheres of the two molecules are touching. Below appears the label, “Transition state.” Following another arrow, two white spheres are shown vertically oriented and bonded together with the label, “H subscript 2” above. The H subscript 2 molecule is followed by a plus sign and two purple spheres bonded together with the label, “I subscript 2” above. Below these structures is the label, “Hydrogen iodide molecules decompose to produce hydrogen H subscript 2 and iodine I subscript 2.”

Bimolecular elementary reactions may also be involved as steps in a multistep reaction mechanism. The reaction of atomic oxygen with ozone is one example:

$$\mathrm{O}(g) + \mathrm{O_3}(g) \longrightarrow 2\,\mathrm{O_2}(g) \tag{4.7.12}$$

4.7.1.0.1: Termolecular Elementary Reactions

An elementary termolecular reaction involves the simultaneous collision of three atoms, molecules, or ions. Termolecular elementary reactions are uncommon because the probability of three particles colliding simultaneously is less than one one-thousandth of the probability of two particles colliding. There are, however, a few established termolecular elementary reactions. The reaction of nitric oxide with oxygen appears to involve termolecular steps:

$$2\,\mathrm{NO} + \mathrm{O_2} \longrightarrow 2\,\mathrm{NO_2} \tag{4.7.13}$$
$$\text{rate} = k[\mathrm{NO}]^2[\mathrm{O_2}]$$

Likewise, the reaction of nitric oxide with chlorine appears to involve termolecular steps:

$$2\,\mathrm{NO} + \mathrm{Cl_2} \longrightarrow 2\,\mathrm{NOCl} \tag{4.7.14}$$
$$\text{rate} = k[\mathrm{NO}]^2[\mathrm{Cl_2}]$$

4.7.1.0.1: Relating Reaction Mechanisms to Rate Laws

It's often the case that one step in a multistep reaction mechanism is significantly slower than the others. Because a reaction cannot proceed faster than its slowest step, this step will limit the rate at which the overall reaction occurs. The slowest step is therefore called the rate-limiting step (or rate-determining step) of the reaction Figure 4.7.2.



Figure 4.7.2: A cattle chute is a nonchemical example of a rate-determining step. Cattle can only be moved from one holding pen to another as quickly as one animal can make its way through the chute. (credit: Loren Kerns)

A photo is shown of cattle passing through a narrow chute into a holding pen. A person directs them through the gate with a long white and red pole.

As described earlier, rate laws may be derived directly from the chemical equations for elementary reactions. This is not the case, however, for ordinary chemical reactions. The balanced equations most often encountered represent the overall change for some chemical system, and very often this is the result of some multistep reaction mechanisms. In every case, we must determine the overall rate law from experimental data and deduce the mechanism from the rate law (and sometimes from other data). The reaction of $\mathrm{NO_2}$ and CO provides an illustrative example:

$$\mathrm{NO_2}(g) + \mathrm{CO}(g) \longrightarrow \mathrm{CO_2}(g) + \mathrm{NO}(g)$$

For temperatures above 225 °C, the rate law has been found to be:

$$\text{rate} = k[\mathrm{NO_2}][\mathrm{CO}]$$

The reaction is first order with respect to $\mathrm{NO_2}$ and first-order with respect to CO. This is consistent with a single-step bimolecular mechanism and it is *possible* that this is the mechanism for this reaction at high temperatures.

At temperatures below 225 °C, the reaction is described by a rate law that is second order with respect to $\mathrm{NO_2}$:

$$\text{rate} = k[\mathrm{NO_2}]^2$$

This is consistent with a mechanism that involves the following two elementary reactions, the first of which is slower and is therefore the rate-determining step:

$$NO_2(g) + NO_2(g) \longrightarrow NO_3(g) + NO(g) \text{ (slow)}$$
$$NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g) \text{ (fast)}$$

The rate-determining step gives a rate law showing second-order dependence on the NO_2 concentration, and the sum of the two equations gives the net overall reaction.

In general, when the rate-determining (slower) step is the first step in a mechanism, the rate law for the overall reaction is the same as the rate law for this step. However, when the rate-determining step is preceded by a step involving an *equilibrium* reaction, the rate law for the overall reaction may be more difficult to derive.

An elementary reaction is at equilibrium when it proceeds in both the forward and reverse directions at equal rates. Consider the dimerization of NO to N_2O_2, with k_1 used to represent the rate constant of the forward reaction and k_{-1} used to represent the rate constant of the reverse reaction:

$$NO + NO \rightleftharpoons N_2O_2$$
$$\text{rate}_{\text{forward}} = \text{rate}_{\text{reverse}}$$
$$k_1[NO]^2 = k_{-1}[N_2O_2]$$

If N_2O_2 was an intermediate in a mechanism, this expression could be rearranged to represent the concentration of N_2O_2 in the overall rate law expression using algebraic manipulation:

$$\left(\frac{k_1[NO]^2}{k_{-1}}\right) = [N_2O_2]$$

However, once again, intermediates cannot be listed as part of the overall rate law expression, though they can be included in an individual elementary reaction of a mechanism. Example 4.7.1 will illustrate how to derive overall rate laws from mechanisms involving equilibrium steps preceding the rate-determining step.

Example 4.7.1: Deriving the Overall Rate Law Expression for a Multistep Reaction

Mechanism Nitryl chloride (NO_2Cl) decomposes to nitrogen dioxide (NO_2) and chlorine gas (Cl_2) according to the following mechanism:

1. $2\,NO_2Cl(g) \rightleftharpoons ClO_2(g) + N_2O(g) + ClO(g)$ (fast, k_1 represents the rate constant for the forward reaction and k_{-1} the rate constant for the reverse reaction)
2. $N_2O(g) + ClO_2(g) \rightleftharpoons NO_2(g) + NOCl(g)$ (fast, k_2 for the forward reaction, k_{-2} for the reverse reaction)
3. $NOCl + ClO \longrightarrow NO_2 + Cl_2$ (slow, k_3 the rate constant for the forward reaction)

Determine the overall reaction, write the rate law expression for each elementary reaction, identify any intermediates, and determine the overall rate law expression.

Solution

For the overall reaction, simply sum the three steps, cancel intermediates, and combine like formulas:

$$2\,NO_2Cl(g) \longrightarrow 2\,NO_2(g) + Cl_2(g)$$

Next, write the rate law expression for each elementary reaction. Remember that for elementary reactions that are part of a mechanism, the rate law expression can be derived directly from the stoichiometry:

$$k_1[NO_2Cl]_2 = k_{-1}[ClO_2][N_2O][ClO]$$
$$k_2[N_2O][ClO_2] = k_{-2}[NO_2][NOCl]$$
$$\text{Rate} = k_3[NOCl][ClO]$$

The third step, which is the slow step, is the rate-determining step. Therefore, the overall rate law expression could be written as Rate = k_3 [NOCl][ClO]. However, both NOCl and ClO are intermediates. Algebraic expressions must be used to represent [NOCl] and [ClO] such that no intermediates remain in the overall rate law expression.

- Using elementary reaction 1, $[ClO] = \dfrac{k_1[NO_2Cl]^2}{k_{-1}[ClO_2][N_2O]}$.
- Using elementary reaction 2, $[NOCl] = \dfrac{k_2[N_2O][ClO_2]}{k_{-2}[NO_2]}$.

Now substitute these algebraic expressions into the overall rate law expression and simplify:

$$\text{rate} = k_3\left(\frac{k_2[N_2O][ClO_2]}{k_{-2}[NO_2]}\right)\left(\frac{k_1[NO_2Cl]^2}{k_{-1}[ClO_2][N_2O]}\right)$$
$$\text{rate} = \frac{k_3k_2k_1[NO_2Cl]^2}{k_{-2}k_{-1}[NO_2]}$$

Notice that this rate law shows an *inverse* dependence on the concentration of one of the product species, consistent with the presence of an equilibrium step in the reaction mechanism.

Exercise 4.7.1

Atomic chlorine in the atmosphere reacts with ozone in the following pair of elementary reactions:

$$Cl + O_3(g) \longrightarrow ClO(g) + O_2(g) \quad \text{(rate constant } k_1\text{)}$$
$$ClO(g) + O \longrightarrow Cl(g) + O_2(g) \quad \text{(rate constant } k_2\text{)}$$

Determine the overall reaction, write the rate law expression for each elementary reaction, identify any intermediates, and determine the overall rate law expression.

Answer

- overall reaction: $O_3(g) + O \longrightarrow 2\,O_2(g)$
- $\text{rate}_1 = k_1[O_3][Cl]$; $\text{rate}_2 = k_2[ClO][O]$
- intermediate: ClO(g)
- overall rate = $k_2k_1[O_3][Cl][O]$

Summary

The sequence of individual steps, or elementary reactions, by which reactants are converted into products during the course of a reaction is called the reaction mechanism. The overall rate of a reaction is determined by the rate of the slowest step, called the rate-determining step. Unimolecular elementary reactions have first-order rate laws, while bimolecular elementary reactions have second-order rate laws. By comparing the rate laws derived from a reaction mechanism to that determined experimentally, the mechanism may be deemed either incorrect or plausible.

4.7.1.1: Footnotes

1. This question is taken from the Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

4.7.1.2: Glossary

bimolecular reaction
elementary reaction involving the collision and combination of two reactant species

elementary reaction
reaction that takes place precisely as depicted in its chemical equation

intermediate
molecule or ion produced in one step of a reaction mechanism and consumed in another

molecularity
number of reactant species (atoms, molecules or ions) involved in an elementary reaction

rate-determining step
(also, rate-limiting step) slowest elementary reaction in a reaction mechanism; determines the rate of the overall reaction

reaction mechanism
stepwise sequence of elementary reactions by which a chemical change takes place

termolecular reaction
elementary reaction involving the simultaneous collision and combination of three reactant species

unimolecular reaction
elementary reaction involving the rearrangement of a single reactant species to produce one or more molecules of product

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4.8: Catalysis

Learning Objectives

- Explain the function of a catalyst in terms of reaction mechanisms and potential energy diagrams
- List examples of catalysis in natural and industrial processes

We have seen that the rate of many reactions can be accelerated by catalysts. A catalyst speeds up the rate of a reaction by lowering the activation energy; in addition, the catalyst is regenerated in the process. Several reactions that are thermodynamically favorable in the absence of a catalyst only occur at a reasonable rate when a catalyst is present. One such reaction is catalytic hydrogenation, the process by which hydrogen is added across an alkene C=C bond to afford the saturated alkane product. A comparison of the reaction coordinate diagrams (also known as energy diagrams) for catalyzed and uncatalyzed alkene hydrogenation is shown in Figure 4.8.1.

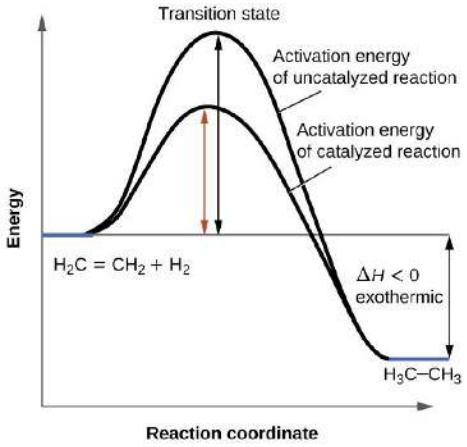


Figure 4.8.1: This graph compares the reaction coordinates for catalyzed and uncatalyzed alkene hydrogenation.

Catalysts function by providing an alternate reaction mechanism that has a lower activation energy than would be found in the absence of the catalyst. In some cases, the catalyzed mechanism may include additional steps, as depicted in the reaction diagrams shown in Figure 4.8.2 This lower activation energy results in an increase in rate as described by the Arrhenius equation. Note that a catalyst decreases the activation energy for both the forward and the reverse reactions and hence *accelerates both the forward and the reverse reactions*. Consequently, the presence of a catalyst will permit a system to reach equilibrium more quickly, but it has no effect on the position of the equilibrium as reflected in the value of its equilibrium constant (see the later chapter on chemical equilibrium).

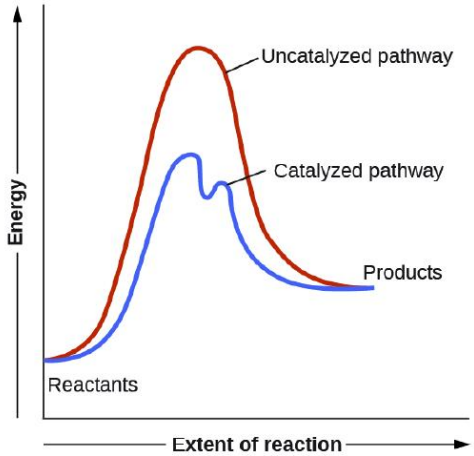
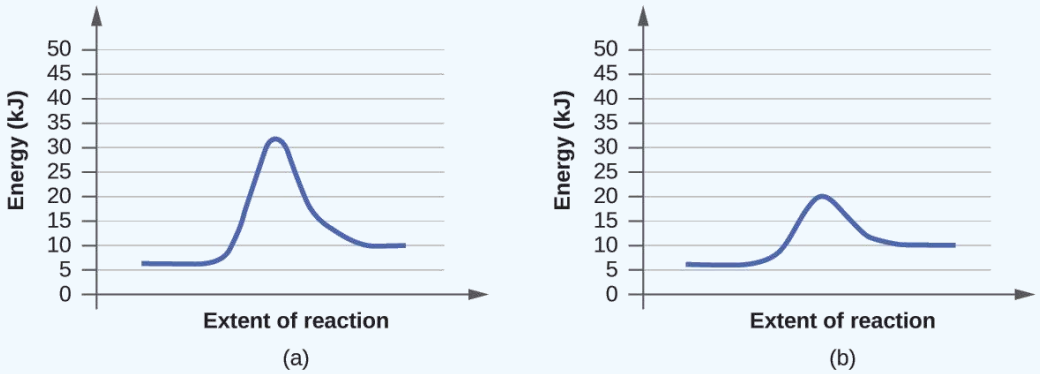


Figure 4.8.2: This potential energy diagram shows the effect of a catalyst on the activation energy. The catalyst provides a different reaction path with a lower activation energy. As shown, the catalyzed pathway involves a two-step mechanism (note the presence of two transition states) and an intermediate species (represented by the valley between the two transitions states).

Example 4.8.1: Using Reaction Diagrams to Compare Catalyzed Reactions

The two reaction diagrams here represent the same reaction: one without a catalyst and one with a catalyst. Identify which diagram suggests the presence of a catalyst, and determine the activation energy for the catalyzed reaction:



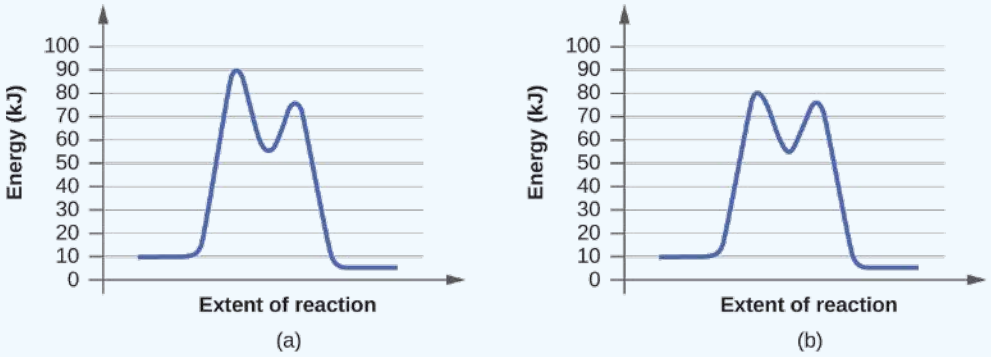
Solution

A catalyst does not affect the energy of reactant or product, so those aspects of the diagrams can be ignored; they are, as we would expect, identical in that respect. There is, however, a noticeable difference in the transition state, which is distinctly lower in diagram (b) than it is in (a). This indicates the use of a catalyst in diagram (b). The activation energy is the difference between the energy of the starting reagents and the transition state—a maximum on the reaction coordinate diagram. The reagents are at 6 kJ and the transition state is at 20 kJ, so the activation energy can be calculated as follows:

$$E_a = 20\ \text{kJ} - 6\ \text{kJ} = 14\ \text{kJ} \tag{4.8.1}$$

Exercise 4.8.1

Determine which of the two diagrams here (both for the same reaction) involves a catalyst, and identify the activation energy for the catalyzed reaction:



Answer

Diagram (b) is a catalyzed reaction with an activation energy of about 70 kJ.

4.8.1: Homogeneous Catalysts

A homogeneous catalyst is present in the same phase as the reactants. It interacts with a reactant to form an intermediate substance, which then decomposes or reacts with another reactant in one or more steps to regenerate the original catalyst and form product. As an important illustration of homogeneous catalysis, consider the earth's ozone layer. Ozone in the upper atmosphere, which protects the earth from ultraviolet radiation, is formed when oxygen molecules absorb ultraviolet light and undergo the reaction:

$$3\,O_2(g) \xrightarrow{h\nu} 2\,O_3(g) \tag{4.8.2}$$

Ozone is a relatively unstable molecule that decomposes to yield diatomic oxygen by the reverse of this equation. This decomposition reaction is consistent with the following mechanism:

$$\begin{aligned} \mathrm{O_3} &\longrightarrow \mathrm{O_2 + O} \\ \mathrm{O + O_3} &\longrightarrow \mathrm{2\,O_2} \end{aligned} \tag{4.8.3}$$

The presence of nitric oxide, NO, influences the rate of decomposition of ozone. Nitric oxide acts as a catalyst in the following mechanism:

$$\begin{aligned} \mathrm{NO}(g) + \mathrm{O_3}(g) &\longrightarrow \mathrm{NO_2}(g) + \mathrm{O_2}(g) \\ \mathrm{O_3}(g) &\longrightarrow \mathrm{O_2}(g) + \mathrm{O}(g) \\ \mathrm{NO_2}(g) + \mathrm{O}(g) &\longrightarrow \mathrm{NO}(g) + \mathrm{O_2}(g) \end{aligned} \tag{4.8.4}$$

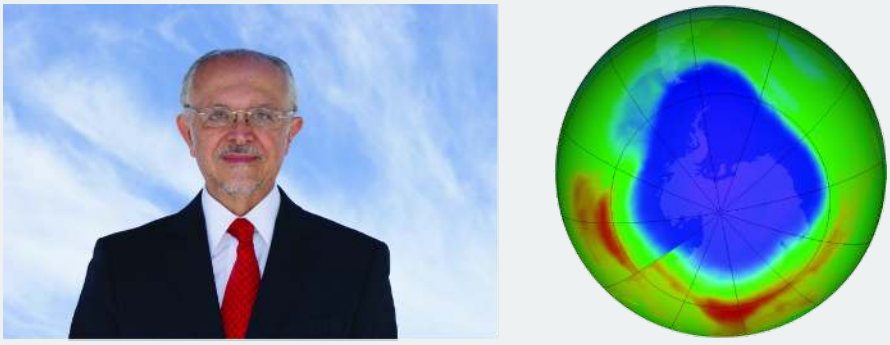
The overall chemical change for the catalyzed mechanism is the same as:

$$\mathrm{2\,O_3}(g) \longrightarrow \mathrm{3\,O_2}(g) \tag{4.8.5}$$

The nitric oxide reacts and is regenerated in these reactions. It is not permanently used up; thus, it acts as a catalyst. The rate of decomposition of ozone is greater in the presence of nitric oxide because of the catalytic activity of NO. Certain compounds that contain chlorine also catalyze the decomposition of ozone.

Mario J. Molina

The 1995 Nobel Prize in Chemistry was shared by Paul J. Crutzen, Mario J. Molina (Figure 4.8.3), and F. Sherwood Rowland “for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone." Molina, a Mexican citizen, carried out the majority of his work at the Massachusetts Institute of Technology (MIT).



(a) (b)

Figure 4.8.3: (a) Mexican chemist Mario Molina (1943 –) shared the Nobel Prize in Chemistry in 1995 for his research on (b) the Antarctic ozone hole. (credit a: courtesy of Mario Molina; credit b: modification of work by NASA)

In 1974, Molina and Rowland published a paper in the journal *Nature* (one of the major peer-reviewed publications in the field of science) detailing the threat of chlorofluorocarbon gases to the stability of the ozone layer in earth’s upper atmosphere. The ozone layer protects earth from solar radiation by absorbing ultraviolet light. As chemical reactions deplete the amount of ozone in the upper atmosphere, a measurable “hole” forms above Antarctica, and an increase in the amount of solar ultraviolet radiation— strongly linked to the prevalence of skin cancers—reaches earth’s surface. The work of Molina and Rowland was instrumental in the adoption of the Montreal Protocol, an international treaty signed in 1987 that successfully began phasing out production of chemicals linked to ozone destruction.

Molina and Rowland demonstrated that chlorine atoms from human-made chemicals can catalyze ozone destruction in a process similar to that by which NO accelerates the depletion of ozone. Chlorine atoms are generated when chlorocarbons or chlorofluorocarbons—once widely used as refrigerants and propellants—are photochemically decomposed by ultraviolet light or react with hydroxyl radicals. A sample mechanism is shown here using methyl chloride:

\[\ce{CH3Cl + OH ⟶ Cl + other\: products} \nonumber \]

Chlorine radicals break down ozone and are regenerated by the following catalytic cycle:

$$\mathrm{Cl} + \mathrm{O_3} \longrightarrow \mathrm{ClO} + \mathrm{O_2}$$
$$\mathrm{ClO} + \mathrm{O} \longrightarrow \mathrm{Cl} + \mathrm{O_2}$$
$$\text{overall Reaction: } \mathrm{O_3} + \mathrm{O} \longrightarrow 2\,\mathrm{O_2}$$

A single monatomic chlorine can break down thousands of ozone molecules. Luckily, the majority of atmospheric chlorine exists as the catalytically inactive forms Cl_2 and $ClONO_2$.

4.8.2: Glucose-6-Phosphate Dehydrogenase Deficiency

Enzymes in the human body act as catalysts for important chemical reactions in cellular metabolism. As such, a deficiency of a particular enzyme can translate to a life-threatening disease. G6PD (glucose-6-phosphate dehydrogenase) deficiency, a genetic condition that results in a shortage of the enzyme glucose-6-phosphate dehydrogenase, is the most common enzyme deficiency in humans. This enzyme, shown in Figure 4.8.4, is the rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells (FIgure 4.8.5).

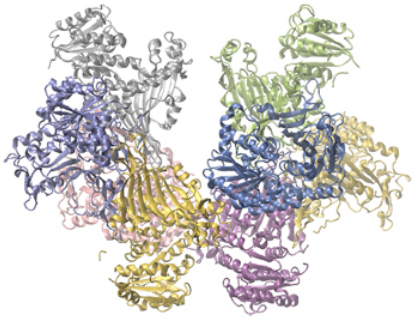


Figure **4.8.4:** Glucose-6-phosphate dehydrogenase is a rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells.

A disruption in this pathway can lead to reduced glutathione in red blood cells; once all glutathione is consumed, enzymes and other proteins such as hemoglobin are susceptible to damage. For example, hemoglobin can be metabolized to bilirubin, which leads to jaundice, a condition that can become severe. People who suffer from G6PD deficiency must avoid certain foods and medicines containing chemicals that can trigger damage their glutathione-deficient red blood cells.

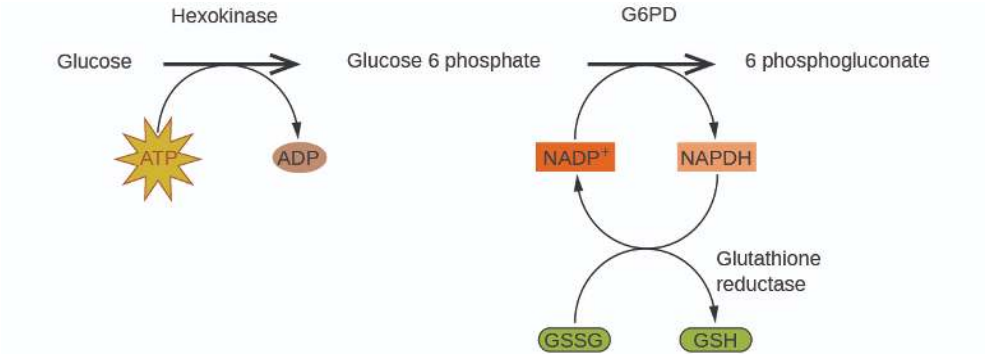


Figure 4.8.5: In the mechanism for the pentose phosphate pathway, G6PD catalyzes the reaction that regulates NAPDH, a co-enzyme that regulates glutathione, an antioxidant that protects red blood cells and other cells from oxidative damage.

4.8.3: Heterogeneous Catalysts

A heterogeneous catalyst is a catalyst that is present in a different phase (usually a solid) than the reactants. Such catalysts generally function by furnishing an active surface upon which a reaction can occur. Gas and liquid phase reactions catalyzed by heterogeneous catalysts occur on the surface of the catalyst rather than within the gas or liquid phase.

Heterogeneous catalysis has at least four steps:

1. Adsorption of the reactant onto the surface of the catalyst
2. Activation of the adsorbed reactant
3. Reaction of the adsorbed reactant
4. Diffusion of the product from the surface into the gas or liquid phase (desorption).

Any one of these steps may be slow and thus may serve as the rate determining step. In general, however, in the presence of the catalyst, the overall rate of the reaction is faster than it would be if the reactants were in the gas or liquid phase.

Figure 4.8.6 illustrates the steps that chemists believe to occur in the reaction of compounds containing a carbon–carbon double bond with hydrogen on a nickel catalyst. Nickel is the catalyst used in the hydrogenation of polyunsaturated fats and oils (which contain several carbon–carbon double bonds) to produce saturated fats and oils (which contain only carbon–carbon single bonds).

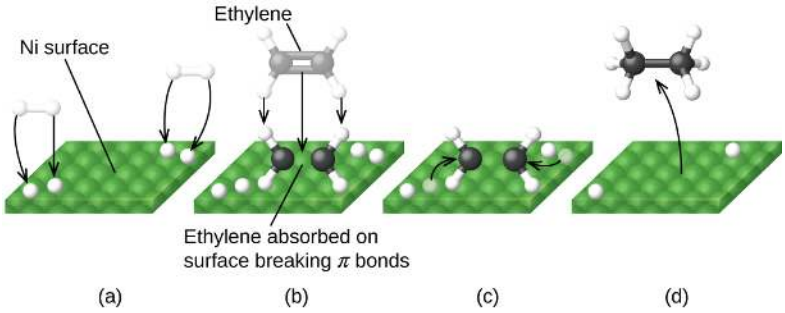


Figure 4.8.6: There are four steps in the catalysis of the reaction $C_2H_4 + H_2 \longrightarrow C_2H_6$ *by nickel. (a) Hydrogen is adsorbed on the surface, breaking the H–H bonds and forming Ni–H bonds. (b) Ethylene is adsorbed on the surface, breaking the π-bond and forming Ni–C bonds. (c) Atoms diffuse across the surface and form new C–H bonds when they collide. (d)* C_2H_6 *molecules escape from the nickel surface, since they are not strongly attracted to nickel.*

Other significant industrial processes that involve the use of heterogeneous catalysts include the preparation of sulfuric acid, the preparation of ammonia, the oxidation of ammonia to nitric acid, and the synthesis of methanol, CH_3OH. Heterogeneous catalysts are also used in the catalytic converters found on most gasoline-powered automobiles (Figure 4.8.7).

Automobile Catalytic Converters

Scientists developed catalytic converters to reduce the amount of toxic emissions produced by burning gasoline in internal combustion engines. Catalytic converters take advantage of all five factors that affect the speed of chemical reactions to ensure that exhaust emissions are as safe as possible.

By utilizing a carefully selected blend of catalytically active metals, it is possible to effect complete combustion of all carbon-containing compounds to carbon dioxide while also reducing the output of nitrogen oxides. This is particularly impressive when we consider that one step involves adding more oxygen to the molecule and the other involves removing the oxygen (Figure 4.8.6).

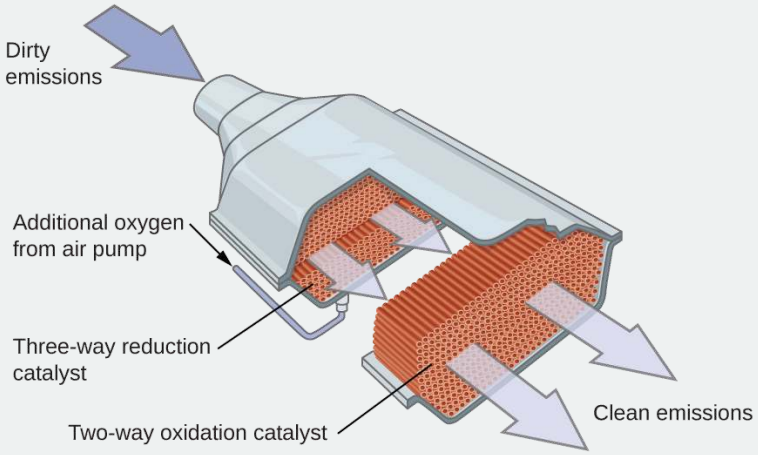


Figure 4.8.6: A catalytic converter allows for the combustion of all carbon-containing compounds to carbon dioxide, while at the same time reducing the output of nitrogen oxide and other pollutants in emissions from gasoline-burning engines.

Most modern, three-way catalytic converters possess a surface impregnated with a platinum-rhodium catalyst, which catalyzes the conversion nitric oxide into dinitrogen and oxygen as well as the conversion of carbon monoxide and hydrocarbons such as octane into carbon dioxide and water vapor:

$$2\,NO_2(g) \longrightarrow N_2(g) + 2\,O_2(g)$$
$$[5pt] 2\,CO(g) + O_2(g) \longrightarrow 2\,CO_2(g)$$
$$[5pt] 2\,C_8H_{18}(g) + 25\,O_2(g) \longrightarrow 16\,CO_2(g) + 18\,H_2O(g)$$

In order to be as efficient as possible, most catalytic converters are preheated by an electric heater. This ensures that the metals in the catalyst are fully active even before the automobile exhaust is hot enough to maintain appropriate reaction temperatures.

4.8.4: Enzyme Structure and Function

The study of enzymes is an important interconnection between biology and chemistry. Enzymes are usually proteins (polypeptides) that help to control the rate of chemical reactions between biologically important compounds, particularly those that are involved in cellular metabolism. Different classes of enzymes perform a variety of functions, as shown in Table 4.8.1.

ATP hydrolysis.”" data-quail-id="131">

Table 4.8.1: Classes of Enzymes and Their Functions

Class	Function
oxidoreductases	redox reactions
transferases	transfer of functional groups
hydrolases	hydrolysis reactions
lyases	group elimination to form double bonds
isomerases	isomerization
ligases	bond formation with ATP hydrolysis

Enzyme molecules possess an active site, a part of the molecule with a shape that allows it to bond to a specific substrate (a reactant molecule), forming an enzyme-substrate complex as a reaction intermediate. There are two models that attempt to explain how this active site works. The most simplistic model is referred to as the lock-and-key hypothesis, which suggests that the molecular shapes of the active site and substrate are complementary, fitting together like a key in a lock. The induced fit hypothesis, on the other hand, suggests that the enzyme molecule is flexible and changes shape to accommodate a bond with the substrate. This is not to suggest that an enzyme’s active site is completely malleable, however. Both the lock-and-key model and the induced fit model account for the fact that enzymes can only bind with specific substrates, since in general a particular enzyme only catalyzes a particular reaction (Figure 4.8.7).

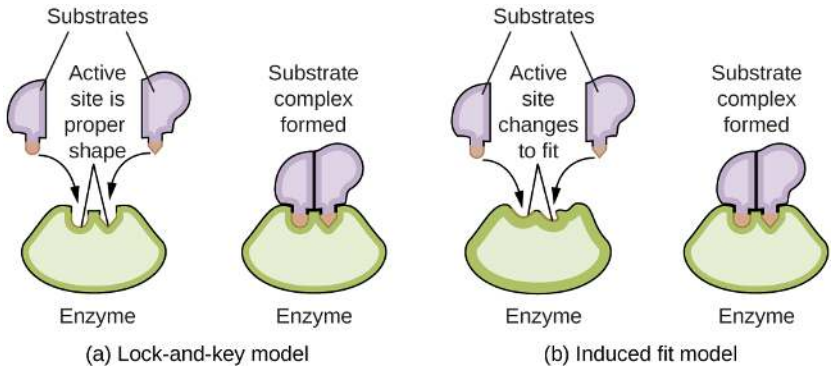


Figure 4.8.7: (a) According to the lock-and-key model, the shape of an enzyme’s active site is a perfect fit for the substrate. (b) According to the induced fit model, the active site is somewhat flexible, and can change shape in order to bond with the substrate.

Summary

Catalysts affect the rate of a chemical reaction by altering its mechanism to provide a lower activation energy. Catalysts can be homogenous (in the same phase as the reactants) or heterogeneous (a different phase than the reactants).

Footnotes

1. “The Nobel Prize in Chemistry 1995,” Nobel Prize.org, accessed February 18, 2015, Nobel Prizes Chemistry [www.nobelprize.org].

Glossary

heterogeneous catalyst

catalyst present in a different phase from the reactants, furnishing a surface at which a reaction can occur

homogeneous catalyst

catalyst present in the same phase as the reactants

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4.E: Kinetics (Exercises)

4.2 Chemical Reaction Rates

Q 4.1

What is the difference between average rate, initial rate, and instantaneous rate?

Solution

First, a general reaction rate must be defined to know what any variation of a rate is. The reaction rate is defined as the measure of the change in concentration of the reactants or products per unit time. The rate of a chemical reaction is not a constant and rather changes continuously, and can be influenced by temperature. Rate of a reaction can be defined as the disappearance of any reactant or appearance of any product. Thus, an average rate is the average reaction rate over a given period of time in the reaction, the instantaneous rate is the reaction rate at a specific given moment during the reaction, and the initial rate is the instantaneous rate at the very start of the reaction (when the product begins to form).

The instantaneous rate of a reaction can be denoted as

$$\lim_{\Delta t \to 0} \frac{\Delta [concentration]}{\Delta t}$$

Q 4.2

Ozone decomposes to oxygen according to the equation $2\,O_3(g) \longrightarrow 3\,O_2(g)$. Write the equation that relates the rate expressions for this reaction in terms of the disappearance of O_3 and the formation of oxygen.

Solution

For the general reaction, aA ---> bB, the rate of the reaction can be expressed in terms of the disappearance of A or the appearance of B over a certain time period as follows.

$$-\frac{1}{a}\frac{\Delta [A]}{\Delta t} = -\frac{1}{b}\frac{\Delta [B]}{\Delta t} = \frac{1}{c}\frac{\Delta [C]}{\Delta t} = \frac{1}{d}\frac{\Delta [D]}{\Delta t} \tag{4.E.1}$$

We want the rate of a reaction to be positive, but the change in the concentration of a reactant, A, will be negative because it is being used up to be transformed into product, B. Therefore, when expressing the rate of the reaction in terms of the change in the concentration of A, it is important to add a negative sign in front to ensure the overall rate positive.

Lastly, the rate must be normalized according to the stoichiometry of the reaction. In the decomposition of ozone to oxygen, two moles of ozone form three moles of oxygen gas. This means that the increase in oxygen gas will be 1.5 times as great as the decrease in ozone. Because the rate of the reaction should be able to describe both species, we divide the change in concentration by its stoichiometric coefficient in the balanced reaction equation to deal with this issue.

Therefore, the rate of the reaction of the decomposition of ozone into oxygen gas can be described as follows:

$$Rate = -\frac{\Delta [O3]}{2\Delta T} = \frac{\Delta [O2]}{3\Delta T} \tag{4.E.2}$$

Answer

$Rate=-\frac{Δ[O3]}{2ΔT}=\frac{Δ[O2]}{3ΔT}\]

Q 4.3

In the nuclear industry, chlorine trifluoride is used to prepare uranium hexafluoride, a volatile compound of uranium used in the separation of uranium isotopes. Chlorine trifluoride is prepared by the reaction $Cl_2(g) + 3\,F_2(g) \longrightarrow 2\,ClF_3(g)$. Write the equation that relates the rate expressions for this reaction in terms of the disappearance of Cl_2 and F_2 and the formation of ClF_3.

Solution

In this problem we are asked to write the equation that relates rate expressions in terms of disappearance of the reactants of the equation and in terms of the formation of the product. A reaction rate gives insight to how rate is affected as a function of

concentration of the substances in the equation. Rates can often be expressed on graphs of concentration vs time expressed in change (Δ) of concentration and time and in a short enough time interval, the instantaneous rate can be approximated. If we were to analyze the reaction given, the graph would demonstrate that Cl_2 decreases, that F_2 decreases 3 times as quickly, and then ClF_3 increases at a rate doubles. The reactants are being used and converted to product so they decrease while products increase.

For this problem, we can apply the general formula of a rate to the specific aspects of a problem where the general form follows:

$$aA + bB \longrightarrow cC + dD$$

.

And the rate can then be written as $rate = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$. Here the negative signs are used to keep the convention of expressing rates as positive numbers.

In this specific case we use the stoichiometry to get the specific rates of disappearance and formation (back to what was said in the first paragraph). So, the problem just involves referring the to the equation and its balanced coefficients. Based upon the equation we see that Cl_2 is a reactant and has no coefficient, F_2 has a coefficient of 3 and is also used up, and then ClF_3 is a product that increases two-fold with a coefficient of 2. So, the rate here can be written as:

$$rate = -\frac{\Delta[Cl_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[F_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[ClF_3]}{\Delta t}$$

Answer

$$\text{rate} = +\frac{1}{2}\frac{\Delta[\text{ClF}_3]}{\Delta t} = -\frac{\Delta[\text{Cl}_2]}{\Delta t} = -\frac{1}{3}\frac{\Delta[\text{F}_2]}{\Delta t}$$

Q 4.4

A study of the rate of dimerization of C_4H_6 gave the data shown in the table:

$$2\,\text{C}_4\text{H}_6 \longrightarrow \text{C}_8\text{H}_{12}$$

Time (s)	0	1600	3200	4800	6200
[C_4H_6] (*M*)	1.00×10^{-2}	5.04×10^{-3}	3.37×10^{-3}	2.53×10^{-3}	2.08×10^{-3}

a. Determine the average rate of dimerization between 0 s and 1600 s, and between 1600 s and 3200 s.
b. Estimate the instantaneous rate of dimerization at 3200 s from a graph of time versus [C_4H_6]. What are the units of this rate?
c. Determine the average rate of formation of C_8H_{12} at 1600 s and the instantaneous rate of formation at 3200 s from the rates found in parts (a) and (b).

Solution

1.) The average rate of dimerization is the change in concentration of a reactant per unit time. In this case it would be:

$$rate\ of\ dimerization = -\frac{\Delta[C_4H_6]}{\Delta t}$$

Rate of dimerization between 0 s and 1600 s:

$$rate\ of\ dimerization = -\frac{5.04\times10^{-3}M - 1.00\times10^{-2}M}{1600s - 0s}$$

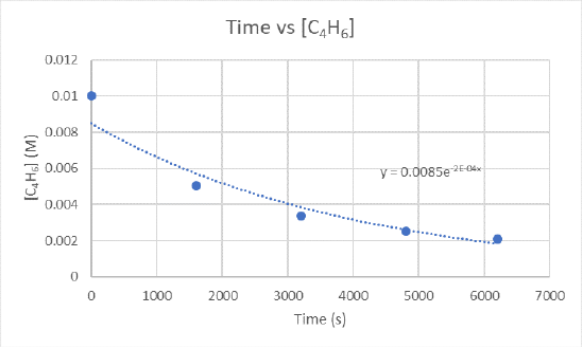
$$rate\ of\ dimerization = 3.10 \times 10^{-6}\,\frac{M}{s}$$

Rate of dimerization between 1600 s and 3200 s:

$$rate\ of\ dimerization = -\frac{3.37\times10^{-3}M - 5.04\times10^{-3}M}{3200s - 1600s}$$

$$rate\ of\ dimerization = 1.04 \times 10^{-6}\,\frac{M}{s}$$

2.) The instantaneous rate of dimerization at 3200 s can be found by graphing time versus [C_4H_6].



Because you want to find the rate of dimerization at 3200 s, you need to find the slope between 1600 s and 3200 s and also 3200 s and 4800 s.

For the slope between 1600 s and 3200 s use the points (1600 s, 5.04 x 10^{-3} M) and (3200 s, 3.37 x 10^{-3} M)

$$\frac{3.37\times10^{-3}M-5.04\times10^{-3}M}{3200s-1600s}$$

$$\frac{-0.00167M}{1600s}$$

$$-1.04\times10^{-6}\,\frac{M}{s}$$

For the slope between 3200 s and 4800 s use the points (3200s, 3.37 x 10^{-3} M) and (4800s, 2.53 x 10^{-3} M)

$$\frac{2.53\times10^{-3}M-3.37\times10^{-3}M}{4800s-3200s}$$

$$\frac{-8.4\times10^{-4}M}{1600s}$$

$$-5.25\times10^{-7}\,\frac{M}{s}$$

Take the two slopes you just found and find the average of them to get the instantaneous rate of dimerization.

$$\frac{-1.04\times10^{-6}\frac{M}{s}+-5.25\times x10^{-7}\frac{M}{s}}{2}$$

$$\frac{-1.565\times10^{-6}\frac{M}{s}}{2}$$

$$-7.83\times10^{-}7\frac{M}{s}$$

The instantaneous rate of dimerization is $-7.83\times10^{-}7\frac{M}{s}$ and the units of this rate is $\frac{M}{s}$.

3.) The average rate of formation of C_8H_{12} at 1600 s and the instantaneous rate of formation at 3200 s can be found by using our answers from part a and b. If you look back up at the original equation, you could see that C_4H_6 and C_8H_{12} are related in a two to one ratio. For every two moles of C_4H_6 used, there is one mole of C_8H_{12} produced.

For this reaction, the average rate of dimerization and the average rate of formation can be linked through this equation:

$$\frac{-1}{2}\frac{\Delta[C_4H_6]}{\Delta t}=\frac{\Delta[C_8H_{12}]}{\Delta t}$$

Notice that reactant side is negative because the reactants are being used up in the reaction.

So, for the average rate of formation of C_8H_{12} at 1600 s, use the rate of dimerization between 0 s and 1600 s we found earlier and plug into the equation:

$$\frac{-1}{2}\times3.10\times10^{-6}\,\frac{M}{s}=\frac{\Delta[C_8H_{12}]}{\Delta t}$$

$$\frac{\Delta[C_8H_{12}]}{\Delta t}=1.55\times10^{-6}\,\frac{M}{s}$$

The average rate of formation for C_8H_{12} at 1600 s is $1.55\times10^{-6}\,\frac{M}{s}$. The rate of formation will be positive because products are being formed.

The instantaneous rate of formation for C_8H_{12} can be linked to the instantaneous rate of dimerization by this equation:

$$\frac{-1}{2}\frac{d[C_4H_6]}{dt} = \frac{d[C_8H_{12}]}{dt}$$

So, for the instantaneous rate of formation for C_8H_{12} at 3200 s, use the value of instantaneous rate of dimerization at 3200 s found earlier and plug into the equation:

$$\frac{-1}{2} \times -7.83 \times 10^-7 \frac{M}{s} = \frac{d[C_8H_{12}]}{dt}$$

$$\frac{d[C_8H_{12}]}{dt} = -3.92 \times 10^{-7}\,\frac{M}{s}$$

The instantaneous rate of formation for C_8H_{12} at 3200 s is $-3.92 \times 10^-7 \frac{M}{s}$

Answer

a. $3.10 \times 10^{-6}\,\frac{M}{s}$ and $1.04 \times 10^{-6}\,\frac{M}{s}$
b. $-7.83 \times 10^-7 \frac{M}{s}$ and $\frac{M}{s}$
c. $-3.92 \times 10^-7 \frac{M}{s}$

Q 4.5

A study of the rate of the reaction represented as $2A \longrightarrow B$ gave the following data:

Time (s)	0.0	5.0	10.0	15.0	20.0	25.0	35.0
[A] (M)	1.00	0.952	0.625	0.465	0.370	0.308	0.230

a. Determine the average rate of disappearance of *A* between 0.0 s and 10.0 s, and between 10.0 s and 20.0 s.
b. Estimate the instantaneous rate of disappearance of *A* at 15.0 s from a graph of time versus [*A*]. What are the units of this rate?
c. Use the rates found in parts (a) and (b) to determine the average rate of formation of *B* between 0.00 s and 10.0 s, and the instantaneous rate of formation of *B* at 15.0 s.

Solution

Equations: $\frac{-\triangle A}{\triangle time}$ and Rate=$\frac{-\triangle A}{2\triangle time} = \frac{\triangle B}{time}$

Solve: 1.)The change in A from 0s to 10s is .625-1=-.375 so $\frac{-\triangle A}{\triangle time}$ =.375/10= **0.0374 M/s**

Similarly, the change in A from 10 to 20 seconds is .370-.625=-.255 so $\frac{-\triangle A}{\triangle time}$ =.255/20-10= **0.0255M/s**

2.) We can estimate the rate law graphing the points against different order equations to determine the right order.

Zero Order:

$$\frac{d[A]}{dt} = -k$$

$$\int_{A_\circ}^{A} d[A] = -k\int_{0}^{t} dt$$

$$[A] = -kt + [A_\circ]$$

First Order:

$$\frac{d[A]}{dt} = -k[A]$$

$$\int_{A_\circ}^{A} \frac{d[A]}{[A]} = -kdt$$

$$Ln(A) = -kt + Ln(A_\circ)$$

Second Order:

$$\frac{d[A]}{dt} = -k[A]^2$$

$$\int_{A\circ}^{A} \frac{d[A]}{[A]^2} = -k\int_0^t dt$$

$$\frac{1}{[A]} = kt + \frac{1}{[A_\circ]}$$

Now that we have found the linear from of each order we will plot the points vs an [A] y-axis, a Ln(A) y-axis, and a 1/[A] y-axis. whichever of the plots has the most linear points will give us a good idea of the order and the slope will be the k value.



Here we notice that the second order is most linear so we conclude the Rate to be..

$$\frac{-d[A]}{2dt} = k[A]^2$$

At 15 seconds [A]=.465 and from the slope of the graph we find k=.116.so if we plug this data in and multiply both sides by 2 to get rid of the 2 in the denominator on the left side of the equation we find that the rate of disappearance of A is .05 M/s where the units are equivalent to [mol*L^{-1}*s^{-1}]

3.) Using the equation $\frac{-\triangle A}{2\triangle time} = \frac{\triangle B}{time}$ we divide the rates in part a and b in half to get .0188 M/s from 0 to 10 seconds and .025 M/s for the estimated instantaneous rate at 15s.

Answer

(a) average rate, 0 − 10 s = 0.0375 mol L^{-1} s^{-1}; average rate, 12 − 18 s = 0.0225 mol L^{-1} s^{-1}; (b) instantaneous rate, 15 s = 0.0500 mol L^{-1} s^{-1}; (c) average rate for B formation = 0.0188 mol L^{-1} s^{-1}; instantaneous rate for B formation = 0.0250 mol L^{-1} s^{-1}

Q 4.6

Consider the following reaction in aqueous solution:

$$5\,\mathrm{Br}^-(aq) + \mathrm{BrO}_3^-(aq) + 6\,\mathrm{H}^+(aq) \longrightarrow 3\,\mathrm{Br}_2(aq) + 3\,\mathrm{H}_2\mathrm{O}(l)$$

If the rate of disappearance of $Br^-(aq)$ at a particular moment during the reaction is $3.5 \times 10^{-4}\ M\ s^{-1}$, what is the rate of appearance of $Br_2(aq)$ at that moment?

Solution

Step 1. Define the rate of the reaction.

Recall:

For the general reaction: aA + bB → cC+ dD

$rate = -\frac{\Delta[A]}{a\Delta t} = -\frac{\Delta[B]}{b\Delta t} = \frac{\Delta[C]}{c\Delta t} = \frac{\Delta[D]}{d\Delta t}$

So, for the reaction: $5Br^-(aq) + BrO_3^-(aq) + 6H^+ \rightarrow 3Br_2(aq) + 3H_2O(l)$

The rate would be: $rate = -\frac{\Delta[Br^-]}{5\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = -\frac{\Delta[H^+]}{6\Delta t} = \frac{\Delta[Br_2]}{3\Delta t} = \frac{H_2O}{3\Delta t}$

https://chem.libretexts.org/@go/page/412080

Step 2. Since we are given the rate for the disappearance of Br^-(aq) is $3.5x10^-4Ms^{-1}$, and we want to find the rate of appearance of Br_2(aq). Therefore we set the two rates equal to each other.

$$rate = -\frac{\Delta[Br^-]}{5\Delta t} = \frac{\Delta[Br_2]}{3\Delta t}$$

$$\text{And,} -\frac{\Delta[Br^-]}{\Delta t} = -3.5x10^{-4}Ms^{-1}$$

$$\text{So, } 3.5x10^{-4}Ms^{-1} = \frac{5}{3}\frac{\Delta[Br_2]}{\Delta t}$$

Step 3. Now solve the equation.

$$\frac{(3.5x10^{-4})(3)}{5} = \frac{\Delta[Br_2]}{\Delta t}$$

$$\frac{\Delta[Br_2]}{\Delta t} = 2.1x10^{-4}Ms^{-1}$$

Answer

$$\frac{\Delta[Br_2]}{\Delta t} = 2.1x10^{-4}Ms^{-1}$$

4.3 Factors Affecting Reaction Rates

Q 4.7

Describe the effect of each of the following on the rate of the reaction of magnesium metal with a solution of hydrochloric acid: the molarity of the hydrochloric acid, the temperature of the solution, and the size of the pieces of magnesium.

Solution

Molarity of Hydrochloric Acid

- Reaction rates are affected by the frequency at which molecules collide. High Molarity=High Concentration which means more molecules are available to collide thus a faster reaction that one with a low molarity of HCl at a fixed volume.

Temperature of Solution

- Higher temperatures increase the rate of reaction because molecules move faster thus colliding more frequently
- increasing temperatures allows for more particles to move past activation energy barrier to start the reaction

Size of pieces of Magnesium

- reaction rate is dependent on solid reactant size; smaller pieces increases the chance of collision because they enable a greater surface area thus faster reaction rate

Q 4.8

Go to the PhET Reactions & Rates interactive. Use the Single Collision tab to represent how the collision between monatomic oxygen (O) and carbon monoxide (CO) results in the breaking of one bond and the formation of another. Pull back on the red plunger to release the atom and observe the results. Then, click on “Reload Launcher” and change to “Angled shot” to see the difference.

a. What happens when the angle of the collision is changed?
b. Explain how this is relevant to rate of reaction.

Solution

According to the collision theory, there are many factors that cause a reaction to happen, with three of the factors being how often the molecules or atoms collide, the molecules' or atoms' orientations, and if there is sufficient energy for the reaction to happen. So, if the angle of the plunger is changed, the atom that is shot (a lone Oxygen atom in this case) will hit the other molecule (CO in this case) at a different spot and at a different angle, therefore changing the orientation and the number of proper collisions will most likely not cause for a reaction to happen. Thanks to the simulation, we can see that this is true: depending on the angle selected, the atom may take a long time to collide with the molecule and, when a collision does occur, it may not result in the breaking of the bond and the forming of the other (no reaction happens).

In this particular case, the rate of the reaction will decrease because, by changing the angle, the molecules or atoms won't collide with the correct orientation or as often with the correct orientation.

Q 4.9

In the PhET Reactions & Rates interactive, use the “Many Collisions” tab to observe how multiple atoms and molecules interact under varying conditions. Select a molecule to pump into the chamber. Set the initial temperature and select the current amounts of each reactant. Select “Show bonds” under Options. How is the rate of the reaction affected by concentration and temperature?

S 4.9

Based on the Collision Theory, a reaction will only occur if the molecules collide with proper orientation and with sufficient energy required for the reaction to occur. The minimum energy the molecules must collide with is called the activation energy (energy of transition state).

Increasing the concentration of reactants increases the probability that reactants will collide in the correct orientation since there are more reactants in the same volume of space. Therefore, increasing the concentration of reactants would increase the rate of the reaction. Decreasing the concentration of reactants would decrease the rate of reaction because the overall number of possible collisions would decrease.

Temperature is directly related the the kinetic energy of molecules and activation energy E_a is the minimum energy required for a reaction to occur and doesn't change for a reaction. Increasing the temperature increases the kinetic energy of the reactants meaning the reactants will move faster and collide with each other more frequently. Therefore, increasing the temperature increase the rate of the reaction. Decreasing the temperature decreases the rate of reaction since the molecules will have less kinetic energy, move slower, and therefore collide with each other less frequently.

Q 4.10

In the PhET Reactions & Rates interactive, on the Many Collisions tab, set up a simulation with 15 molecules of A and 10 molecules of BC. Select “Show Bonds” under Options.

a. Leave the Initial Temperature at the default setting. Observe the reaction. Is the rate of reaction fast or slow?
b. Click “Pause” and then “Reset All,” and then enter 15 molecules of A and 10 molecules of BC once again. Select “Show Bonds” under Options. This time, increase the initial temperature until, on the graph, the total average energy line is completely above the potential energy curve. Describe what happens to the reaction.

Solution

a. On the simulation, we select the default setting and the reaction A+BC. In the default setting, we see frequent collisions, a low initial temperature, and a total average energy lower than the energy of activation. The collision theory states that the rate of a reaction is directly proportional to (the fraction of molecules with required orientation), (fractions of collisions with required energy), and (collision frequency). Although we see moving and frequently colliding reactants, the rate of the forward reaction is actually slow because it takes a long time for the products, AB and C, to start appearing. This is mainly because the fractions of collisions with required energy is low, coming from the average energy of the molecules being lower than the energy of activation.

b. The reaction proceeds at an even faster rate. Again, the collision theory states that the rate of a reaction is directly proportional to (the fraction of molecules with required orientation), (fractions of collisions with required energy), and (collision frequency). Because molecules have a higher amount of energy, they have more kinetic energy. With an increased kinetic energy, the molecules not only collide more but also increase in the fraction of collision. However, the forward reaction and the backward reaction both proceed at a fast rate, so both happen almost simultaneously. It takes a shorter time for both reactions to happen. With both of the reactions adding up together overall, there is eventually a state of equilibrium. The process at which equilibrium is reached, however, is faster. Therefore, the amount of products of A+BC stays the same after a while.

4.4 Rate Laws

Q 4.11

How do the rate of a reaction and its rate constant differ?

S 4.11

The rate of a reaction or reaction rate is the change in the concentration of either the reactant or the product over a period of time. If the concentrations change, the rate also changes.

Rate for A → B:

$$rate = \frac{\Delta[B]}{\Delta t} = -\frac{\Delta[A]}{\Delta t}$$

The rate constant (k) is a proportionality constant that relates the reaction rates to reactants. If the concentrations change, the rate constant does not change.

For a reaction with the general equation: $aA + bB \rightarrow cC + dD$

the experimentally determined rate law usually has the following form:

$$rate = k[A]^m[B]^n$$

Q 4.12

Doubling the concentration of a reactant increases the rate of a reaction four times. With this knowledge, answer the following questions:

a. What is the order of the reaction with respect to that reactant?
b. Tripling the concentration of a different reactant increases the rate of a reaction three times. What is the order of the reaction with respect to that reactant?

Solution

(a) 2; (b) 1

Q 4.13

Tripling the concentration of a reactant increases the rate of a reaction nine times. With this knowledge, answer the following questions:

a. What is the order of the reaction with respect to that reactant?
b. Increasing the concentration of a reactant by a factor of four increases the rate of a reaction four times. What is the order of the reaction with respect to that reactant?

Q 4.14

How much and in what direction will each of the following affect the rate of the reaction: $\mathrm{CO}(g) + \mathrm{NO_2}(g) \longrightarrow \mathrm{CO_2}(g) + \mathrm{NO}(g)$ if the rate law for the reaction is $\text{rate} = k[\mathrm{NO_2}]^2$?

a. Decreasing the pressure of NO_2 from 0.50 atm to 0.250 atm.
b. Increasing the concentration of CO from 0.01 *M* to 0.03 *M*.

Solution

(a) The process reduces the rate by a factor of 4. (b) Since CO does not appear in the rate law, the rate is not affected.

Q 4.15

How will each of the following affect the rate of the reaction: $\mathrm{CO}(g) + \mathrm{NO_2}(g) \longrightarrow \mathrm{CO_2}(g) + \mathrm{NO}(g)$ if the rate law for the reaction is $\text{rate} = k[\mathrm{NO_2}][\mathrm{CO}]$?

a. Increasing the pressure of NO_2 from 0.1 atm to 0.3 atm
b. Increasing the concentration of CO from 0.02 *M* to 0.06 *M*.

Q 4.16

Regular flights of supersonic aircraft in the stratosphere are of concern because such aircraft produce nitric oxide, NO, as a byproduct in the exhaust of their engines. Nitric oxide reacts with ozone, and it has been suggested that this could contribute to depletion of the ozone layer. The reaction $\mathrm{NO} + \mathrm{O_3} \longrightarrow \mathrm{NO_2} + \mathrm{O_2}$ is first order with respect to both NO and O_3 with a rate

constant of 2.20×10^7 L/mol/s. What is the instantaneous rate of disappearance of NO when [NO] = 3.3×10^{-6} *M* and [O_3] = 5.9×10^{-7} *M*?

Solution

4.3×10^{-5} mol/L/s

Q 4.17

Radioactive phosphorus is used in the study of biochemical reaction mechanisms because phosphorus atoms are components of many biochemical molecules. The location of the phosphorus (and the location of the molecule it is bound in) can be detected from the electrons (beta particles) it produces:

$$^{32}_{15}\mathrm{P} \longrightarrow ^{32}_{16}\mathrm{S} + \mathrm{e}^-$$

Rate = $4.85 \times 10^{-2}\ \mathrm{day}^{-1}\ [^{32}\mathrm{P}]$

What is the instantaneous rate of production of electrons in a sample with a phosphorus concentration of 0.0033 *M*?

Q 4.18

The rate constant for the radioactive decay of ^{14}C is 1.21×10^{-4} year^{-1}. The products of the decay are nitrogen atoms and electrons (beta particles):

$$^{6}_{14}\mathrm{C} \longrightarrow ^{6}_{14}\mathrm{N} + \mathrm{e}^-$$

$$\text{rate} = k[^{6}_{14}\mathrm{C}]$$

What is the instantaneous rate of production of N atoms in a sample with a carbon-14 content of 6.5×10^{-9} *M*?

Solution

7.9×10^{-13} mol/L/year

Q 4.19

What is the instantaneous rate of production of N atoms Q12.3.8 in a sample with a carbon-14 content of 1.5×10^{-9} *M*?

Q 4.20

The decomposition of acetaldehyde is a second order reaction with a rate constant of 4.71×10^{-8} L/mol/s. What is the instantaneous rate of decomposition of acetaldehyde in a solution with a concentration of 5.55×10^{-4} *M*?

Q 4.21

Alcohol is removed from the bloodstream by a series of metabolic reactions. The first reaction produces acetaldehyde; then other products are formed. The following data have been determined for the rate at which alcohol is removed from the blood of an average male, although individual rates can vary by 25–30%. Women metabolize alcohol a little more slowly than men:

[C_2H_5OH] (*M*)	4.4×10^{-2}	3.3×10^{-2}	2.2×10^{-2}
Rate (mol/L/h)	2.0×10^{-2}	2.0×10^{-2}	2.0×10^{-2}

Determine the rate equation, the rate constant, and the overall order for this reaction.

Solution

rate = *k*; *k* = 2.0×10^{-2} mol/L/h (about 0.9 g/L/h for the average male); The reaction is zero order.

Q 4.22

Under certain conditions the decomposition of ammonia on a metal surface gives the following data:

[NH_3] (*M*)	1.0×10^{-3}	2.0×10^{-3}	3.0×10^{-3}
Rate (mol/L/h[1])	1.5×10^{-6}	1.5×10^{-6}	1.5×10^{-6}

Determine the rate equation, the rate constant, and the overall order for this reaction.

Q 4.23

Nitrosyl chloride, NOCl, decomposes to NO and Cl_2.

$$2\,NOCl(g) \longrightarrow 2\,NO(g) + Cl_2(g)$$

Determine the rate equation, the rate constant, and the overall order for this reaction from the following data:

[NOCl] (*M*)	0.10	0.20	0.30
Rate (mol/L/h)	8.0×10^{-10}	3.2×10^{-9}	7.2×10^{-9}

Solution

Before we can figure out the rate constant first we must first determine the basic rate equation and rate order. The basic rate equation for this reaction, where n is the rate order of NOCl and k is the rate constant, is

$$rate = k[NOCl]^n$$

since NOCl is the reactant in the reaction.

In order to figure out the order of the reaction we must find the order of [NOCl] as it is the only reactant in the reaction. To do this we must examine how the rate of the reaction changes as the concentration of NOCl changes.

As [NOCl] doubles in concentration from 0.10 M to 0.20 M the rate goes from 8.0 x 10^{-10} to 3.2 x 10^{-9}

(3.2 x 10^{-9}(mol/L/h))/(8.0 x 10^{-10}(mol/L/h)) = 4

so we conclude that as [NOCl] doubles, the rate goes up by 4. Since 2^2= 4 we can say that the order of [NOCl] is 2 so our updated rate law is

$$rate = k[NOCl]^2$$

Now that we have the order, we can substitute the first experimental values from the given table to find the rate constant, k

(8.0 x 10^{-10}(mol/L/h)) = k(0.10 M)^2 so

$$k = \frac{8.0 \times 10^{-10}}{(0.10\,M)^2} = 8 \times 10^{-8}\,M^{-1}\,sec^{-1}$$

We were able to find the units of k using rate order, when the rate order is 2 units of k are M^{-1} x sec^{-1}

So the rate equation is: rate = k[NOCl]^2, it is second order, and k = 8 x 10^{-8} M^{-1} x sec^{-1}

Overall rate law :

$$rate = \underbrace{(8 \times 10^{-8})}_{1/(\text{M x sec})}[NOCl]^2$$

Answer

rate = *k*[NOCl]^2; *k* = 8.0×10^{-8} L/mol/s; second order

Q 4.24

From the following data, determine the rate equation, the rate constant, and the order with respect to *A* for the reaction $A \longrightarrow 2C$.

[A] (*M*)	1.33×10^{-2}	2.66×10^{-2}	3.99×10^{-2}
Rate (mol/L/h)	3.80×10^{-7}	1.52×10^{-6}	3.42×10^{-6}

Solution

A. Using the experimental data, we can compare the effects of changing [A] on the rate of reaction by relating ratios of [A] to ratios of rates

$$\frac{2.66 \times 10^{-2}}{1.33 \times 10^{-2}} = 2$$

and

$$\frac{1.52 \times 10^{-6}}{3.8 \times 10^{-7}} = 4$$

B. From this we know that doubling the concentration of A will result in quadrupling the rate of reaction. The order of this reaction is 2.

C. We can now write the rate equation since we know the order:

$$rate = k[A]^2$$

D. By plugging in one set of experimental data into our rate equation we can solve for the rate constant, k:

$$3.8 \times 10^{-7} = k \times (1.33 \times 10^{-2})^2$$

$$k = \frac{3.8 \times 10^{-7}}{1.769 \times 10^{-4}}$$

$$k = .00215 M^{-1} s^{-1}$$

Answer

$k = .00215 M^{-1} s^{-1}$

2nd Order

Q 4.25

Nitrogen(II) oxide reacts with chlorine according to the equation:

$$2\,\mathrm{NO}(g) + \mathrm{Cl_2}(g) \longrightarrow 2\,\mathrm{NOCl}(g)$$

The following initial rates of reaction have been observed for certain reactant concentrations:

[NO] (mol/L^1)	[Cl_2] (mol/L)	Rate (mol/L/h)
0.50	0.50	1.14
1.00	0.50	4.56
1.00	1.00	9.12

What is the rate equation that describes the rate's dependence on the concentrations of NO and Cl_2? What is the rate constant? What are the orders with respect to each reactant?

Solution

For the general equation,

$aA + bB \rightarrow cC + dD$

The rate can be written as

$rate = k[A]^m[B]^n$ where k is the rate constant, and m and n are the reaction orders.

For our equation

$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$

the $rate = k[NO]^m[Cl_2]^n$

Now, we need to find the reaction orders. Reaction orders can only be found through experimental values. We can compare two reactions where one of the reactants has the same concentration for both trials, and solve for the reaction order.

$$\frac{rate_1}{rate_2} = \frac{[NO]_1^m[Cl_2]_1^n}{[NO]_2^m[Cl_2]_2^n}$$

We can use the data in the table provided. If we plug in the values for rows 1 and 2, we see that the values for the concentration of Cl will cancel, leaving just the rates and the concentrations of NO.

$$\frac{1.14}{4.56} = \frac{[0.5]^m}{[1.0]^m}$$

We can now solve for m, and we find that m =2. This means that the reaction order for [NO] is 2.

Now we must find the value of n. To do so, we can use the same equation but with the values from rows 2 and 3. This time, the concentration of NO will cancel out.

$$\frac{4.56}{9.12} = \frac{[0.5]^n}{[1.0]^n}$$

When we solve for n, we find that n = 1. This means that the reaction order for [Cl_2] is 1.

We are one step closer to finishing our rate equation.

$$rate = k[NO]^2[Cl_2]$$

Finally, we can solve for the rate constant. To do this, we can use one of the trials of the experiment, and plug in the values for the rate, and concentrations of reactants, then solve for k.

$$1.14 mol/L/h = k[0.5 mol/L]^2[0.5 mol/L]$$

$$k = 9.12 L^2 mol^{-2} h^{-1}$$

So, our final rate equation is:

$$rate = (9.12 L^2 mol^{-2} h^{-1})[NO]^2[Cl_2]$$

*A common mistake is forgetting units. Make sure to track your units throughout the process of determining your rate constant. Be careful because the units will change relative to the reaction order.

Answer

rate = k[NO]^2[Cl]$_2$; k = 9.12 L^2 mol^{-2} h^{-1}; second order in NO; first order in Cl_2

Q 4.26

Hydrogen reacts with nitrogen monoxide to form dinitrogen monoxide (laughing gas) according to the equation:

$$\mathrm{H_2}(g) + 2\,\mathrm{NO}(g) \longrightarrow \mathrm{N_2O}(g) + \mathrm{H_2O}(g)$$

Determine the rate equation, the rate constant, and the orders with respect to each reactant from the following data:

[NO] (*M*)	0.30	0.60	0.60
[H_2] (*M*)	0.35	0.35	0.70
Rate (mol/L/s)	2.835 × 10^{-3}	1.134 × 10^{-2}	2.268 × 10^{-2}

Solution

Determine the rate equation, the rate constant, and the orders with respect to each reactant.

The rate constant and the orders can be determined through the differential rate law. The general form of the differential rate law is given below:

aA + bB + cC ==> products

rate = - d[A]/dt = k[A]^n[B]^m[C]^p

where A, B, and C are the concentrations of the reactants, k is the rate constant, and n,m, and p refer to the order of each reactant.

To find the orders of each reactant, we see that when [NO] doubles but [H_2] doesn't change, the rate quadruples, meaning that [NO] is a second order reaction ([NO]^2). When [H_2] doubles but [NO] doesn't change, the rate doubles, meaning that [H_2] is a first order reaction. So the rate law would look something like this:

$$\text{Rate} = k[NO]^2[H_2]$$

We can use this rate law to determine the value of the rate constant. Plug in the data for reactant concentration and rate from one of the trials to solve for k the rate constant. In this case, we chose to use the data from trial 1 from the second column of the data table.

$$2.835 \times 10^{-3} = k[0.3]^2[0.35]$$

$$k = .09\ M^{-2}/s^{-1}$$

Q 4.27

For the reaction $A \longrightarrow B + C$, the following data were obtained at 30 °C:

[*A*] (*M*)	0.230	0.356	0.557
Rate (mol/L/s)	4.17×10^{-4}	9.99×10^{-4}	2.44×10^{-3}

a. What is the order of the reaction with respect to [*A*], and what is the rate equation?
b. What is the rate constant?

Solution

1. The rate equation for an n order reaction is given as $\frac{dr}{dt} = k[A]^n$. Where $[A]$ is the concentration in M, and $\frac{dr}{dt}$ is the rate in M/s.

We can then use each set of data points, plug its values into the rate equation and solve for n. Note you can use any of the data points as long as the concentration corresponds to its rate.

Rate equation 1: $4.17 \times 10^{-4} = k[0.230]^n$

Rate equation 2: $9.99 \times 10^{-4} = k[0.356]^n$

We divide Rate equation 1 by Rate equation 2 in order to cancel out k, the rate constant.

$\frac{4.17 \times 10^{-4}}{9.99 \times 10^{-4}} = \frac{k[0.230]^n}{k[0.356]^n}$

$0.417 = 0.646^n$

Now the only unknown we have is n. Using logarithm rules one can solve for it.

$ln\ 0.417 = n \cdot ln\ 0.646$

$\frac{ln\ 0.417}{ln\ 0.646} = n = 2$

The rate equation is second order with respect to A and is written as $\frac{dr}{dt} = k[A]^2$.

2. We can solve for k by plugging in any data point into our rate equation $\frac{dr}{dt} = k[A]^2$.

Using the first data points for instance $[A] = 0.230\ \frac{mol}{L}$ and $\frac{dr}{dt} = 4.17 \times 10^{-4}\ \frac{mol}{L \cdot s}$] we get the equation $4.17 \times 10^{-4}\ \frac{mol}{L \cdot s} = k[0.230\ \frac{mol}{L}]^2$

Which solves for $k = 7.88 \times 10^{-3}\ \frac{L}{mol \cdot s}$

Since we know this is a second order reaction the appropriate units for k can also be written as $\frac{1}{M \cdot s}$

Answer

(a) The rate equation is second order in A and is written as rate = $k[A]^2$. (b) k = 7.88×10^{-13} L mol^{-1} s^{-1}

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Q 4.28

For the reaction $Q \longrightarrow W + X$, the following data were obtained at 30 °C:

$[Q]_{initial}$ (M)	0.170	0.212	0.357
Rate (mol/L/s)	6.68×10^{-3}	1.04×10^{-2}	2.94×10^{-2}

a. What is the order of the reaction with respect to [Q], and what is the rate equation?
b. What is the rate constant?

Solution

What is the order of the reaction with respect to [Q], and what is the rate equation?

- Order reaction: 2 because when you use the ratio trial 3:2, it will look like this:
- $(\frac{2.94 * 10^{-2}}{1.04 * 10^{-2}}) = (\frac{0.357^{x}}{0.212^{x}})$
- $2.82 = 1.7^{x}$
- x = 2 so the order of reaction is 2
- Rate reaction equation: Rate=k[Q]^2

What is the rate constant?

- To find the rate constant (k) simply plug and calculate one of the trials into the rate equation
- 1.04 x 10^{-2}=k[0.212]^2
- k=0.231 $M^{-1}s^{-1}$

Answer

Order: 2

k=0.231 $M^{-1}s^{-1}$

Q 4.29

The rate constant for the first-order decomposition at 45 °C of dinitrogen pentoxide, N_2O_5, dissolved in chloroform, $CHCl_3$, is 6.2×10^{-4} min^{-1}.

$$2\,N_2O_5 \longrightarrow 4\,NO_2 + O_2$$

What is the rate of the reaction when [N_2O_5] = 0.40 M?

Solution

Step 1: The first step is to write the rate law. We know the general formula for for a first-order rate law. It is as follows: Rate=k[A]

Step 2: We now plug in [N_2O_5] in for [A] in our general rate law. We also plug in our rate constant (k), which was given to us. Now our equation looks as follows:

Rate=($6.2x10^{-4}$ min^{-1})[N_2O_5]

Step 3: We now plug in our given molarity. [N_2O_5]=0.4 M. Now our equation looks as follows:

Rate=($6.2x10^{-4}$ min^{-1})(0.4 M)

Step 4: We now solve our equation. Rate=($6.2x10^{-4}$ min^{-1})(0.4 M)= $2.48x10^{-4}$ M/min.
Step 5: Use significant figures and unit conversion to round $2.48x10^{-4}$ M/min to 2.5×10^{-4} (moles)$L^{-1}min^{-1}$

Answer

(a) 2.5×10^{-4} mol/L/min

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Q 4.30

The annual production of HNO_3 in 2013 was 60 million metric tons Most of that was prepared by the following sequence of reactions, each run in a separate reaction vessel.

a. $4\,NH_3(g) + 5\,O_2(g) \longrightarrow 4\,NO(g) + 6\,H_2O(g)$
b. $2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)$
c. $3\,NO_2(g) + H_2O(l) \longrightarrow 2\,HNO_3(aq) + NO(g)$

The first reaction is run by burning ammonia in air over a platinum catalyst. This reaction is fast. The reaction in equation (c) is also fast. The second reaction limits the rate at which nitric acid can be prepared from ammonia. If equation (b) is second order in NO and first order in O_2, what is the rate of formation of NO_2 when the oxygen concentration is 0.50 *M* and the nitric oxide concentration is 0.75 *M*? The rate constant for the reaction is 5.8×10^{-6} $L^2/mol^2/s$.

Solution

To determine the rate law for an equation we need to look at its slow step. Since both equation a and c are fast, equation b can be considered the slow step of the reaction. The slow step is also considered the rate determining step of the system.

Hence, The rate determining step is the second step because it's the slow step.

rate of production of $NO_2 = k[A]^m[B]^n$

$rate = k[NO]^2[O_2]^1\ M/s$

$rate = (5.8 * 10^{-6})[0.75]^2[0.5]^1\ M/s$

$rate = 1.6 * 10^{-6}\ M/s$

Answer

$rate = 1.6 * 10^{-6}\ M/s$

Q 4.31

The following data have been determined for the reaction:

$$I^- + OCl^- \longrightarrow IO^- + Cl^-$$

	1	2	3
$[I^-]_{initial}$ (*M*)	0.10	0.20	0.30
$[OCl^-]_{initial}$ (*M*)	0.050	0.050	0.010
Rate (mol/L/s)	3.05×10^{-4}	6.20×10^{-4}	1.83×10^{-4}

Determine the rate equation and the rate constant for this reaction.

Solution

Using the reactants, we can form the rate law of the reaction: $ r=k[OCl^-]^n[I^-]^m \]

From there, we need to use the data to determine the order of both $[OCl^-]$ and $[I^-]$. In doing so, we need to compare r_1 to r_2 such that:

$$\frac{r_1}{r_2} = \frac{(0.10^m)(0.050^n)}{(0.20^m)(0.050^n)} = \frac{3.05 \times 10^{-4}}{6.20 \times 10^{-4}} \tag{4.E.3}$$

$$0.5^m = 0.5 \tag{4.E.4}$$

$$m = 1 \tag{4.E.5}$$

We can "cross out" the concentration of $[OCl^-]$ because it has the same concentration in both of the trials used.

Now that we know m ($[I^-]$) has a first order of 1.

We cannot "cross out" $[I^-]$ to find $[OCl^-]$ because no two trials have the same concentration. In order to solve for n we will plug in 1 for m.

$$\frac{r_1}{r_3} = \frac{(0.10^1)(0.050^n)}{(0.30^1)(0.010^n)} = \frac{3.05 \times 10^{-4}}{1.83 \times 10^{-4}} \tag{4.E.6}$$

$$\frac{1}{3}(5^n) = 1.6666667 \tag{4.E.7}$$

$$5^n = 5 \tag{4.E.8}$$

$$n = 1 \tag{4.E.9}$$

Since we know that orders of both n and m are equal to one, we can not substitute them into the rate law equation along with the respective concentrations (from either the first, second, or third reaction) and solve for the rate constant, k.

$$r = k[OCl^-]^n[I^-]^m \tag{4.E.10}$$

$$3.05 * 10^{-4} = k[0.05]^1[0.10]^1 \tag{4.E.11}$$

$$k = 6.1 * 10^{-2} \frac{L}{mol \times s} \tag{4.E.12}$$

Thus the overall rate law is: $ r = (6.1 * 10^{-2} \frac {L}{mol \times s})[OCl^-][I^-] \]

The units for K depend on the overall order of the reaction. To find the overall order we add m and n together. By doing this we find an overall order of 2. This is why the units for K are $ \frac {L}{mol \times s} \]

Answer

rate = k[I$^-$][OCl^{-1}]; k = 6.1 × 10^{-2} L mol $^{-1}$ s^{-1}

Q 4.32

In the reaction

$$2NO + Cl_2 \rightarrow 2NOCl$$

the reactants and products are gases at the temperature of the reaction. The following rate data were measured for three experiments:

Initial p{NO}$	Initial p{Cl$_2$}$	Initial rate
(atm)	(atm)	(moles of A consumed atm sec^{-1})
0.50	0.50	5.1 x 10^{-3}
1.0	1.0	4.0 x 10^{-2}
0.50	1.0	1.0 x 10^{-2}

a. From these data, write the rate equation for this gas reaction. What order is the reaction in NO, Cl_2, and overall?
b. Calculate the specific rate constant for this reaction.

Solution

a. The rate equation can be determined by designing experiments that measure the concentration(s) of one or more reactants or products as a function of time. For the reaction $A + B \rightarrow products$, for example, we need to determine k and the exponents m and n in the following equation:

$$rate = k[A]^m[B]^n$$

To do this, the initial concentration of B can be kept constant while varying the initial concentration of A and calculating the initial reaction rate. This information would deduce the reaction order with respect to A. The same process can be done to find

the reaction order with respect to B.
In this particular example,

$$\frac{rate_2}{rate_3} = \frac{k[A_2]^m[B_2]^n}{k[A_3]^m[B_3]^n}$$

So taking the values from the table,

$$\frac{4.0*10^{-2}}{1.0*10^{-2}} = \frac{k[1.0]^m[1.0]^n}{k[0.5]^m[1.0]^n}$$

and by canceling like terms, you are left with

$$\frac{4.0*10^{-2}}{1.0*10^{-2}} = \frac{[1.0]^m}{[0.5]^m}$$

Now, solve for m

$4 = 2^m \Longrightarrow m = 2$ Because m=2, the reaction with respect to NO is 2. NO **is second order.**

You can repeat the same process to find n.

$$\frac{rate_3}{rate_1} = \frac{k[A_3]^m[B_3]^n}{k[A_1]^m[B_1]^n}$$

Taking the values from the table,

$$\frac{1.0*10^{-2}}{5.1*10^{-3}} = \frac{k[0.5]^m[1.0]^n}{k[0.5]^m[0.5]^n}$$

and by canceling like terms, you are left with

$$\frac{1.0*10^{-2}}{5.1*10^{-3}} = \frac{[1.0]^n}{[0.5]^n}$$

Now this time, solve for n

$2 = 2^n \Longrightarrow n = 1$

Because n=1, the reaction with respect to Cl_2 is 1. Cl_2 **is first order.**

So the rate equation is

$$rate = k[NO]^2[Cl_2]^1$$

To find the overall rate order, you simply add the orders together. Second order + first order makes the **overall reaction third order.**

b. The rate constant is calculated by inserting the data from any row of the table into the experimentally determined rate law and solving for k. For a third order reaction, the units of k are $frac1atm^2 * sec$. Using Experiment 1,

$$rate = k[NO]^2[Cl_2]^1 \Longrightarrow 5.1 * 10^{-3} \frac{atm}{sec} = k[0.5matm]^2[0.5atm]^1$$

$$k = 0.0408 \frac{1}{atm^2 * sec}$$

Answer

NO is second order.

Cl_2 is first order.

Overall reaction order is three.

b)

$k = 0.0408\ atm^{-2} * sec^{-1}$

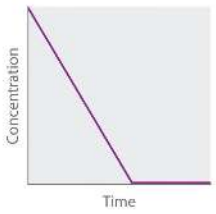
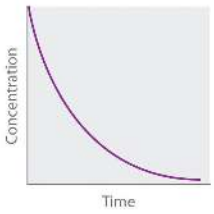
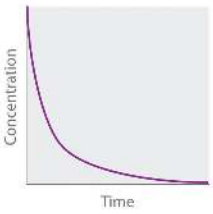
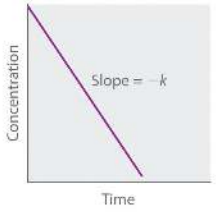
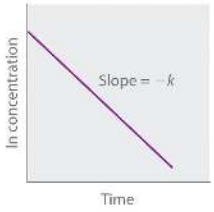
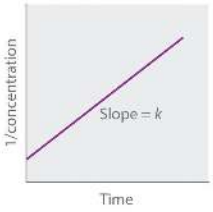
4.5 Integrated Rate Laws

Q 4.33

Describe how graphical methods can be used to determine the order of a reaction and its rate constant from a series of data that includes the concentration of *A* at varying times.

Solution

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	Zeroth Order	First Order	Second Order
Differential rate law	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$
Concentration vs. time			
Integrated rate law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$ or $\ln[A] = \ln[A]_0 - kt$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$
Straight-line plot to determine rate constant			
Relative rate vs. concentration	[A], *M* / Rate, M/s 1 / 1 2 / 1 3 / 1	[A], *M* / Rate, M/s 1 / 1 2 / 2 3 / 3	[A], *M* / Rate, M/s 1 / 1 2 / 4 3 / 9
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$
Units of *k*, rate constant	M/s	1/s	$M^{-1}\cdot s^{-1}$

To determine the order of a reaction when given the data series, one must graph the data how it is, graph it as natural log of [A], and graph it as 1/[A]. Whichever method yields a straight line will determine the order. Respective of the methods of graphing above, if a straight line is yielded by the first graphing method its a 0 order, if by the second method it's a 1st order, and the third graphing method its a 2nd order. When the order of the graph is known, a series of equations, given in the above image, can be used with the various points on the graph to determine the value of k. We can see that we need an initial value of A and a final value of A, and both of these would be given by the data.

Zeroth order when plotting initial concentrating versus final concentration you have a negative linear slope.

$$[A] = [A]_0 - kt$$

First order when plotting ln[initial concentration] versus ln[final concentration] you have a negative linear slope.

$$\ln[A] = \ln[A]_0 - kt$$

Second order when plotting the 1/[initial concentration] versus 1/[final concentration] you have a positive linear slope.

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

Q 4.34

Use the data provided to graphically determine the order and rate constant of the following reaction: $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$

Time (s)	0	5.00×10^3	1.00×10^4	1.50×10^4	2.50×10^4	3.00×10^4	4.00×10^4

$[SO_2Cl_2]$ (M)	0.100	0.0896	0.0802	0.0719	0.0577	0.0517	0.0415

Solution

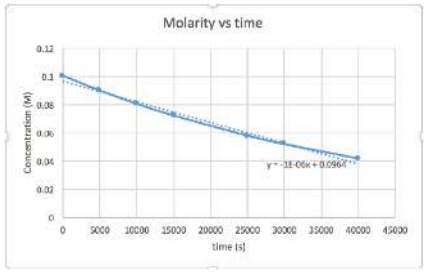
Use the data to graphically determine the order and rate constant of the following reaction.

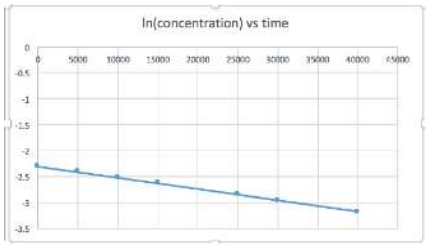
In order to determine the rate law for a reaction from a set of data consisting of concentration (or the values of some function of concentration) versus time, make three graphs of the data based on the integrated rate laws of each order reaction.

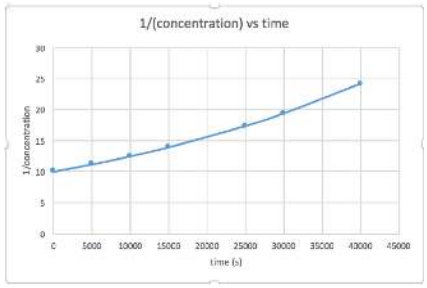
[concentration] versus time (linear for a zero order reaction) ln [concentration] versus time (linear for a 1^{st} order reaction) 1 / [concentration] versus time (linear for a 2^{nd} order reaction)

slope= -2.0 x 10^{-5}

k = 2.0 x 10^{-5}





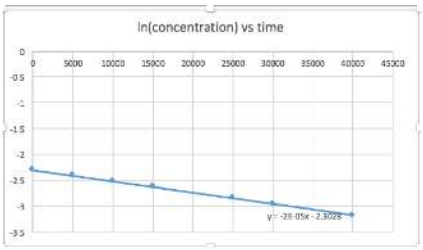


The graph that is linear indicates the order of the reaction. Then, you can find the correct rate equation:

zero order reaction	rate = k	(k = - slope of line)
1^{st} order reaction	rate = k[A]	(k = - slope of line)
2^{nd} order reaction	rate = $k[A]^2$	(k = slope of line)

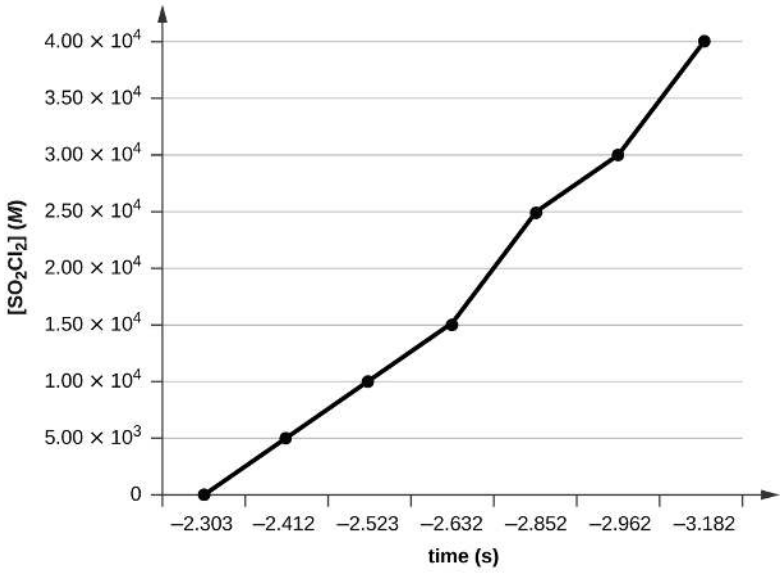
In this graph, ln(concentration) vs time is linear, indicating that the **reaction is first order**.

k=-slope of line



Answer

Plotting a graph of $\ln[SO_2Cl_2]$ versus t reveals a linear trend; therefore we know this is a first-order reaction:



$k = -2.20 \times 10^5\ s^{-1}$

Q 4.35

Use the data provided in a graphical method to determine the order and rate constant of the following reaction:

$$2P \longrightarrow Q + W$$

Time (s)	9.0	13.0	18.0	22.0	25.0
[P] (*M*)	1.077×10^{-3}	1.068×10^{-3}	1.055×10^{-3}	1.046×10^{-3}	1.039×10^{-3}

Q 4.36

Pure ozone decomposes slowly to oxygen, $2\,O_3(g) \longrightarrow 3\,O_2(g)$. Use the data provided in a graphical method and determine the order and rate constant of the reaction.

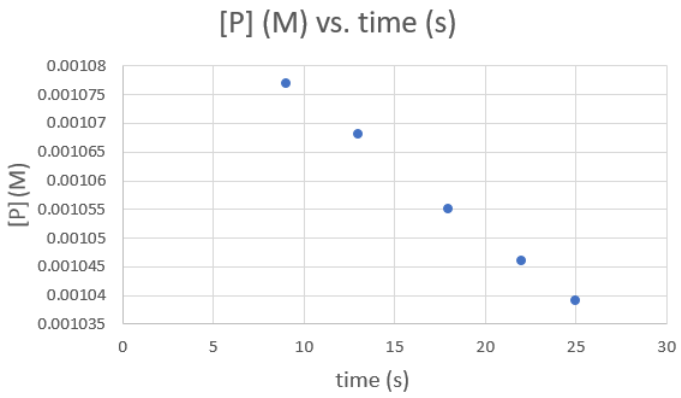
Time (h)	0	2.0×10^3	7.6×10^3	1.23×10^4	1.70×10^4	1.70×10^4
[O_3] (*M*)	1.00×10^{-5}	4.98×10^{-6}	2.07×10^{-6}	1.39×10^{-6}	1.22×10^{-6}	1.05×10^{-6}

Solution

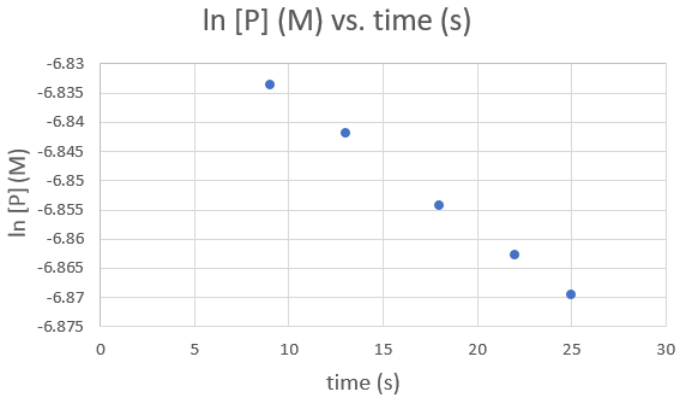
To determine the order and rate constant, you need to graph the data for zero order, first order, and second order by plotting concentration versus time- [A] vs. time, natural logarithm (ln) of [A] vs. time, and 1/[A] vs. time respectively. The order of the

reaction is determined by identifying which of these three graphs produces a straight line. The rate constant *k* is represented by the slope of the graph. The graphs with their respective data values would be

Time (s)	9.0	13.0	18.0	22.0	25.0
[P] (*M*)	1.077 × 10−3	1.068 × 10−3	1.055 × 10−3	1.046 × 10−3	1.039 × 10−3

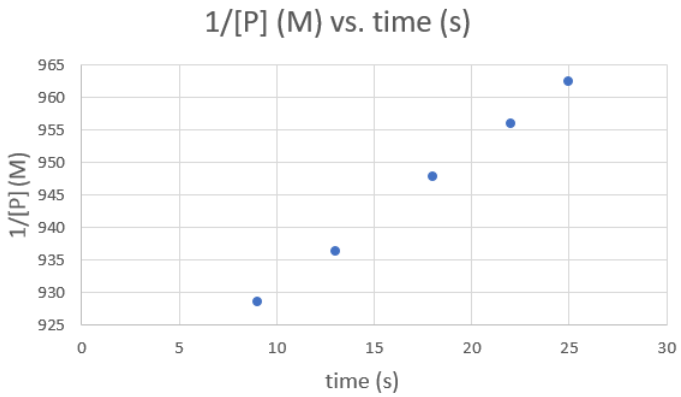


Time (s)	9.0	13.0	18.0	22.0	25.0
ln [P] (*M*)	-6.83358	-6.84197	-6.85421	-6.86278	-6.8695



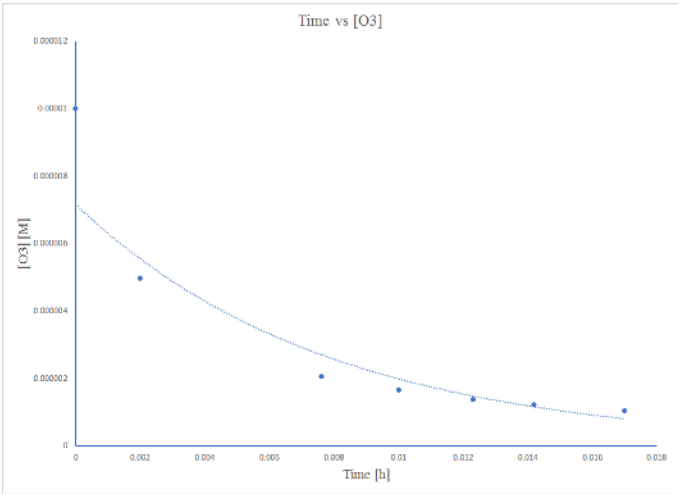
Time (s)	9.0	13.0	18.0	22.0	25.0
1/[P] (*M*)	928.5051	936.3296	947.8673	956.0229	962.4639

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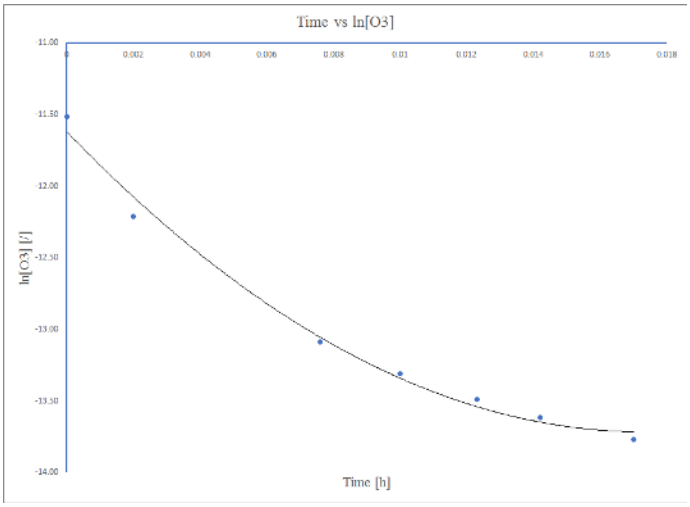


Since each graph yields a straight line **the order and rate constant of the reaction cannot be determined**.

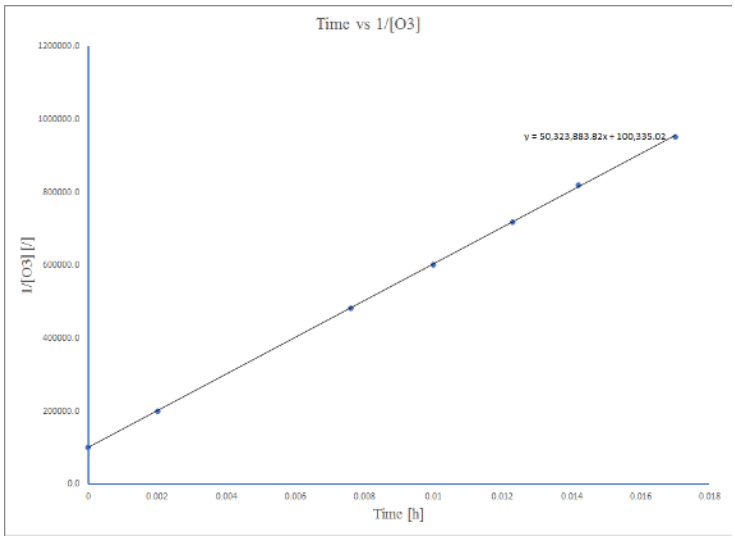
To identify how the concentrations changes a function of time, requires solving the appropriate differential equation (i.e., the differential rate law).
The zero-order rate law predicts in a linear decay of concentration with time
The 1st-order rate law predicts in an exponential decay of concentration with time
The 2nd-order rate law predicts in an reciprocal decay of concentration with time



The plot is not linear, so the reaction is not zero order.



The plot is not linear, so the reaction is not first order.



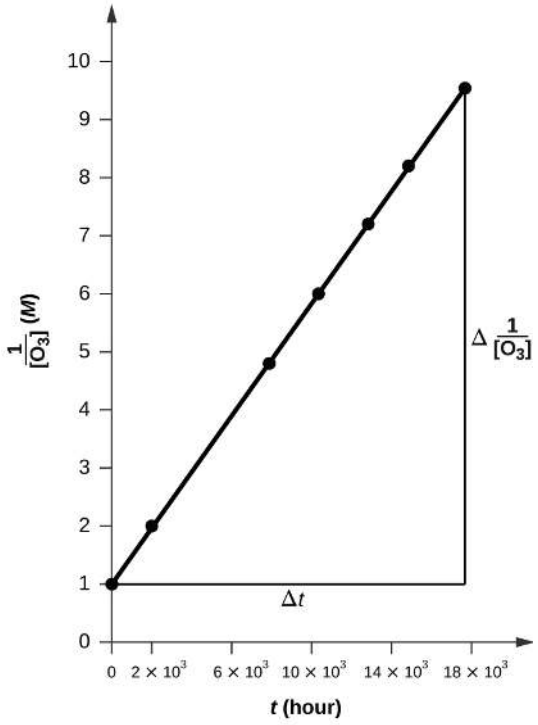
The plot is nicely linear, so the reaction is second order.

To a second order equation, $1/[A] = k*t+1/[A_0]$

Thus, the value of K is the slope of the graph Time vs $\frac{1}{O_3}$,

k = 50.3*10^6 L mol^{-1} h^{-1}

Answer



The plot is nicely linear, so the reaction is second order.

k = 50.1 L mol^{-1} h^{-1}

Q 4.37

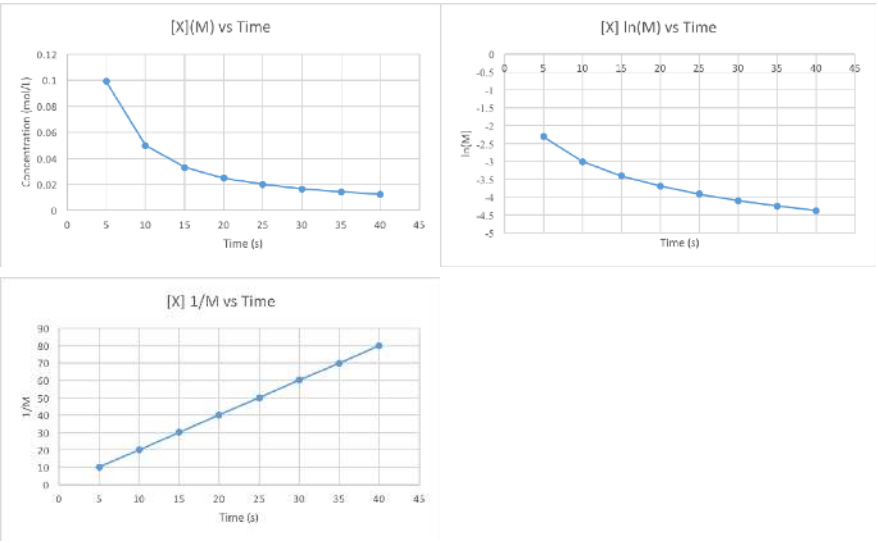
From the given data, use a graphical method to determine the order and rate constant of the following reaction:

$$2X \longrightarrow Y + Z \tag{4.E.13}$$

Time (s)	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0
[*X*] (*M*)	0.0990	0.0497	0.0332	0.0249	0.0200	0.0166	0.0143	0.0125

Solution

In order to determine the order of the reaction we need to plot the data using three different graphs. All three graphs will have time in seconds as the x-axis, but the y-axis is what will differ. One graph will plot concentration versus time, the second will plot natural log of concentration versus time, and the other will plot 1/concentration versus times. Whichever graph results in a line, we know that must be the order of the reaction. If we get a line using the first graph, it will be zero order, if it is a line for the second graph it will be first order, and if it is a line for the third graph it will be a second order reaction. Now lets plot the data to determine the order.



We can clearly see that the third graph, which plots 1/M versus time, is a straight line while the other two are slightly curved. Therefore, we can determine that the rate of this reaction is second order. This also tells us that the units of the rate constant which should be $M^{-2}s^{-1}$ for a second order reaction.

To determine the rate constant, called k, we simple need to figure out the slope of the third graph since that is the order of this reaction. To find the slope of the line, we take two points and subtract the y values and then divide them by the difference of the x values. This is how to do it:

Use the points (5, 10.101) and (40, 80).

Now use these to get the slop, aka the rate constant: (80-10.101)/(40-5) = 1.997 = k

So the rate constant for this second order reaction is 1.997 $M^{-1}s^{-1}$.

Q 4.38

What is the half-life for the first-order decay of phosphorus-32? $\left({}^{32}_{15}\mathrm{P} \longrightarrow {}^{32}_{16}\mathrm{S} + \mathrm{e}^{-}\right)$ The rate constant for the decay is 4.85×10^{-2} day^{-1}.

Solution

This is a first order reaction, so we can use our half life equation below:

$$t_{1/2} = \frac{0.693}{k}$$

The rate constant is given to us in units per day. All we have to do, is to plug it into the equation.

$$t_{1/2} = \frac{0.693}{4.85 * 10^{-2}}$$

$$= 14.3\ days$$

Q 4.39

What is the half-life for the first-order decay of carbon-14? $\left({}^{6}_{14}\mathrm{C} \longrightarrow {}^{7}_{14}\mathrm{N} + \mathrm{e}^{-}\right)$ The rate constant for the decay is 1.21 × 10^{-4} $year^{-1}$.

Solution

To find the half life, we need to use the first-order half-life equation. All half life reactions undergo first order reactions.

The half-life equation for first order is

$$t_{1/2} = ln2/k$$

with k being the rate constant. The rate constant for carbon-14 was given as $1.21 \times 10^{-4} year^{-1}$.

Plug it in the equation.

$$t_{1/2} = ln2/(1.21 \times 10^{-4} year^{-1})$$

and solve for $t_{1/2}$.

When you calculate it, the half life for carbon-14 is 5.73*10^{3}

Answer

The half-life for carbon-14 is calculated to be 5.73*10^{3}

Q 4.40

What is the half-life for the decomposition of NOCl when the concentration of NOCl is 0.15 *M*? The rate constant for this second-order reaction is 8.0 × 10^{-8} L/mol/s.

Solution

The half-life of a reaction, $t_{1/2}$, is the amount of time that is required for a reactant concentration to decrease by half compared to its initial concentration. When solving for the half-life of a reaction, we should first consider the order of reaction to determine it's rate law. In this case, we are told that this reaction is second-order, so we know that the integrated rate law is given as:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

Isolating for time, we find that:

$$t_{1/2} = \frac{1}{k[A]_0}$$

Now it is just a matter of substituting the information we have been given to calculate $t_{1/2}$, where the rate constant, k, is equal to 8.0 × 10^{-8} L/mol/s and initial concentration, $[A]_0$, is equal to 0.15*M*:

$$t_{1/2} = \frac{1}{(8.0 \times 10^{-8})(0.15)} = 8.33 \times 10^{7}\, seconds$$

Answer

8.33 × 10^{7} s

Q 4.41

What is the half-life for the decomposition of O_3 when the concentration of O_3 is 2.35 × 10^{-6} *M*? The rate constant for this second-order reaction is 50.4 L/mol/h.

Solution

Since the reaction is second order, its half-life is

$$t_{\frac{1}{2}} = \frac{1}{k[\mathrm{A}]_0}$$

$$t_{1/2} = \frac{1}{(50.4 M^{-1}/h)[2.35 \times 10^{-6} M]}$$

So, half-life is 8443 hours.

Q 4.42

The reaction of compound *A* to give compounds *C* and *D* was found to be second-order in *A*. The rate constant for the reaction was determined to be 2.42 L/mol/s. If the initial concentration is 0.500 mol/L, what is the value of $t_{1/2}$?

Solution

As mentioned in the question the reaction of compound *A* will result in the formation of compounds C and D. This reaction was found to be second-order in *A*. Therefore, we should use the second order equation for half-life which relates the rate constant and initial concentrations to the half-life:

$$t_{\frac{1}{2}} = \frac{1}{k[A]_0}$$

Since we were given *k* (rate constant) and Initial concentration of A, we have everything needed to calculate the half life of A.

$$k = 0.5 \frac{\frac{L}{mol}}{s}$$

$$[A]_0 = 2.42 \frac{mol}{L}$$

When we plug in the given information notice that the units cancel out to seconds.

$$t_{\frac{1}{2}} = \frac{1}{\frac{2.42 L mol^{-}}{s}[0.500 \frac{mol}{L}]} = 0.826 s$$

Answer

0.826 s

Q 4.43

The half-life of a reaction of compound *A* to give compounds *D* and *E* is 8.50 minutes when the initial concentration of *A* is 0.150 mol/L. How long will it take for the concentration to drop to 0.0300 mol/L if the reaction is (a) first order with respect to *A* or (b) second order with respect to *A*?

Solution

Organize the given variables:

(half-life of *A*) $t_{1/2} = 8.50 min$
(initial concentration of *A*) $[A]_0 = 0.150 mol/L$
(target concentration of *A*) $[A] = 0.0300 mol/L$

Find the the rate constant k, using the half-life formulas for each respective order. After finding k, use the integrated rate law respective to each order and the initial and target concentrations of *A* to find the time it took for the concentration to drop.

(a) first order with respect to *A*

(half-life) $t_{1/2} = \frac{ln(2)}{k} = \frac{0.693}{k}$
(rearranged for k) $k = \frac{0.693}{t_{1/2}}$
(plug in $t_{1/2}$ = 8.50 min) $k = \frac{0.693}{8.50min} = 0.0815min^{-1}$
(integrated rate law) $ln[A] = -kt + ln[A]_0$
(rearranged for t) $ln(\frac{[A]}{[A]_0}) = -kt$
$-ln(\frac{[A]}{[A]_0}) = kt$
$ln(\frac{[A]}{[A]_0})^{-1} = kt$
$ln(\frac{[A]_0}{[A]}) = kt$
$t = \frac{ln(\frac{[A]_0}{[A]})}{k}$
(plug in variables) $t = \frac{ln(\frac{0.150mol/L}{0.0300mol/L})}{0.0815min^{-1}} = \frac{ln(5.00)}{0.0815min^{-1}} = 19.7min$

(b) second order with respect to *A*

(half-life) $t_{1/2} = \frac{1}{k[A]_0}$
(rearranged for k) $k = \frac{1}{t_{1/2}[A]_0}$
(plug in variables) $k = \frac{1}{(8.50min)(0.150mol/L)} = \frac{1}{1.275min \cdot mol/L} = 0.784L/mol \cdot min$
(integrated rate law) $\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
(rearranged for t) $\frac{1}{[A]} - \frac{1}{[A]_0} = kt$
$t = \frac{1}{k}(\frac{1}{[A]} - \frac{1}{[A]_0})$
(plug in variables) $t = \frac{1}{0.784L/mol \cdot min}(\frac{1}{0.0300mol/L} - \frac{1}{0.150mol/L}) = \frac{1}{0.784L/mol \cdot min}(\frac{80}{3}L/mol) = 34.0min$

Answer

a) 19.7 min

b) 34.0 min

Q 4.44

Some bacteria are resistant to the antibiotic penicillin because they produce penicillinase, an enzyme with a molecular weight of 3 × 10^4 g/mol that converts penicillin into inactive molecules. Although the kinetics of enzyme-catalyzed reactions can be complex, at low concentrations this reaction can be described by a rate equation that is first order in the catalyst (penicillinase) and that also involves the concentration of penicillin. From the following data: 1.0 L of a solution containing 0.15 µg (0.15 × 10^{-6} g) of penicillinase, determine the order of the reaction with respect to penicillin and the value of the rate constant.

[Penicillin] (*M*)	**Rate (mol/L/min)**
2.0 × 10^{-6}	1.0 × 10^{-10}
3.0 × 10^{-6}	1.5 × 10^{-10}
4.0 × 10^{-6}	2.0 × 10^{-10}

Solution

The first step is to solve for the order or the reaction. This can be done by setting up two expressions which equate the rate to the rate constant times the molar concentration of penicillin raised to the power of it's order. Once we have both expressions set up, we can divide them to cancel out k (rate constant) and use a basic logarithm to solve for the exponent, which is the order. It will look like this.

$$\text{rate(mol/L/min)} = k[M]^x$$

$$(1.0 \times 10^{-10}) = k[2.0 \times 10^{-6}]^x$$

$$(1.5 \times 10^{-10}) = k[3.0 \times 10^{-6}]^x$$

Dividing the two equations results in the expression:

$$(2/3) = (2/3)^x$$

*A single ratio equation can also be set up to solve for the reaction order:

*

$$\frac{rate_1}{rate_2} = \frac{k[Penicillin]_1^x}{k[Penicillin]_2^x}$$

*We then solve for x in a similar fashion.

*

$$\frac{1.0x10^{-10}}{1.5x10^{-10}} = \frac{[2.0x10^{-6}]^x}{[3.0x10^{-6}]^x}$$

We can now use the natural logarithm to solve for x, or simply and intuitively see that in order for the equation to work, **x must be equal to one. Thus, the reaction is of the first order.**

Now that we have the order of the reaction, we can proceed to solve for the value of the rate constant. Substituting x=1 into our first equation yields the expression:

$$(1 \times 10^{-10}) = k[2.0 \times 10^{-6}]^1$$

$$k = (1 \times 10^{-10})/(2 \times 10^{-6})$$

$$k = (5 \times 10^{-5})\ min^{-1}$$

We have a unit of min^{-1} because we divided (mol/L/min) by molarity, which is in (mol/L), yielding a unit of min^{-1}.

We were given two important pieces of information to finish the problem. It is stated that the enzyme has a molecular weight of 3×10^4 g/mol, and that we have a one liter solution that contains (0.15×10^{-6}) g) of penicillinase. Dividing the amount of grams by the molecular weight yields **5×10^{-12} moles**.

$$(0.15 \times 10^{-6})\ g\ /\ (3 \times 10^4)\ g/mol = (5 \times 10^{-12})\ mol$$

Now that we have the amount of moles, we can divide our rate constant by this value.

$$(5 \times 10^{-5})\ min^{-1}\ /\ (5 \times 10^{-12})\ mol = \mathbf{(1 \times 10^7)\ mol^{-1}\ min^{-1}}$$

Answer

The reaction is first order with $k = 1.0 \times 10^7\ mol^{-1}\ min^{-1}$

Q 4.45

Both technetium-99 and thallium-201 are used to image heart muscle in patients with suspected heart problems. The half-lives are 6 h and 73 h, respectively. What percent of the radioactivity would remain for each of the isotopes after 2 days (48 h)?

Solution

This problem is asking us for the percentage of radioactivity remaining after a certain time for both isotopes after 48 hours. We must identify an equation that will help us solve this and we can determine that we can determine this information using the first order equation.

This equation $Ln(N/N_o) = -kt$ tells that the Natural log of the fraction remaining is equal to the rate constant times time. To determine the rate constant, we can also compute .693 over the half-life given in the information.

For Technetium-99 we can determine the rate constant by plugging into the second equation: .693/6 hrs= .1155 h^{-1}

Now that we have the rate constant we can plug in : $Ln(N/N_o)=-(.1155h^{-1})(48h)$ so $Ln(N/N_o)=-5.544$ and if we take the inverse of the natural log, we get $(N/N_o)=3.9x10^{-3}$ and if we multiply this by 100, we get .39% remaining.

We can do this same process for Thallium-201 and plugin: .693/73 hrs= .009493151 h^{-1} and when we plug this into the first order equation we get:

$Ln(N/N_o)=-(.009493h^{-1})(48h)$ so $Ln(N/N_o)=-.45567248$ and when we take the inverse of the natural log, we get $(N/N_o)=.6340$ and when multiplied by 100, we get 63.40% remaining which makes sense since its half-life is 73 hours and only 48 hours have passed, half of the amount has yet to be consumed.

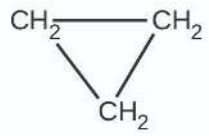
Answer

Technetium-99: 0.39%

Thallium-201: 63.40%

Q 4.46

There are two molecules with the formula C_3H_6. Propene, $CH_3CH{=}CH_2$, is the monomer of the polymer polypropylene, which is used for indoor-outdoor carpets. Cyclopropane is used as an anesthetic:



When heated to 499 °C, cyclopropane rearranges (isomerizes) and forms propene with a rate constant of $5.95 \times 10^{-4}\ s^{-1}$. What is the half-life of this reaction? What fraction of the cyclopropane remains after 0.75 h at 499 °C?

Solution

Use the equation

$$t_{1/2} = \frac{ln2}{k}$$

since this is a first-order reaction. You can tell that this is a **first order reaction** due to the units of measurement of the rate constant, which is s^{-1}. Different orders of reactions lead to different rate constants, and a rate constant of s^{-1} will always be first order.

Plug into the equation, and you get half life = 1164.95 seconds. To convert this to hours, we would divide this number by 3600 seconds/hour, to get **0.324 hours**.

Use the integrated first order rate law

$$ln\frac{[A]}{[A]_0} = -kt$$

. In this equation, $[A]_0$ represents the initial amount of compound present at time 0, while [A] represents the amount of compound that is left after the reaction has occurred. Therefore, the fraction

$$\frac{[A]}{[A]_0}$$

is equal to the fraction of cyclopropane that remains after a certain amount of time, in this case, 0.75 hours.

Substitute x for the fraction of

$$\frac{[A]}{[A]_0}$$

into the integrated rate law:

$$ln\frac{[A]}{[A]_0} = -kt$$

$$ln(x) = -5.95x10^{-4}(0.75)$$

$$x = e^{(-0.000595)(0.75)}$$

= 0.20058 = 20%.

So, the half life is 0.324 hours, and 20% of the cyclopropane will remain as 80% will have formed propene.

Answer

0.324 hours. ; 20% remains

Q 4.47

Fluorine-18 is a radioactive isotope that decays by positron emission to form oxygen-18 with a half-life of 109.7 min. (A positron is a particle with the mass of an electron and a single unit of positive charge; the nuclear equation is $^{18}_{9}\mathrm{F} \longrightarrow {}^{18}_{8}\mathrm{O} + {}^{0}_{1}\mathrm{e}^{+}$.) Physicians use ^{18}F to study the brain by injecting a quantity of fluoro-substituted glucose into the blood of a patient. The glucose accumulates in the regions where the brain is active and needs nourishment.

a. What is the rate constant for the decomposition of fluorine-18?
b. If a sample of glucose containing radioactive fluorine-18 is injected into the blood, what percent of the radioactivity will remain after 5.59 h?
c. How long does it takFe for 99.99% of the ^{18}F to decay?

Solution

a) The nuclear decay of an isotope of an element is represented by the first order equation:

$$\ln(N/N0) = -kt$$

Where t is time, N0 is the initial amount of the substance, N is the amount of the substance after time t, and k is the rate constant. We can rearrange the equation and isolate k so that we could solve for the rate constant:

$$k = [-\ln(N/N0)] / t$$

We are given that fluorine-18 has a half-life of 109.7 minutes. Since we have the half-life, we can choose an arbitrary value for N_0 and use half of that value for N. In this case, we choose 100 for N_0 and 50 for N. Now we can plug in those values into the equation above and solve for k.

$$k = [-\ln(50/100)] / 109.7$$

$$k = 0.6931 / 109.7 = 0.006319\ \text{min}^{-1}$$

The rate constant for this reaction is 0.006319 min^{-1}.

b) For this problem, we are able to use the same equation from part a:

$$\ln(N/N0) = -kt$$

However, this time we are given the amount of time elapsed instead of the half-life, and we are asked to determine the percent of fluorine-18 radioactivity remaining after that time. In this problem, we must plug in values for N0, k (determined from part a), and t.

But first, since we are given the elapsed time in hours, we must convert it into minutes:

$$5.59\ \text{hours} \times (60\ \text{minutes} / 1\ \text{hours}) = 335.4\ \text{minutes}$$

This gives us the value for t. We also have values for k (0.006319 min^{-1}) and N_0 (again an arbitrary number.) Now we can plug values into the original equation, giving us:

$$\ln(N/100) = -(0.006319)(335.4)$$

We solve this equation by taking the exponential of both sides:

$$e^{\ln(N/100)} = e^{-(0.006319)(335.4)}$$

where e^{ln} equals 1 and now we can just solve for N:

$$N/100 = e^{-(0.006319)(335.4)}$$

$$N = [e^{-(0.006319)(335.4)}] \times 100 = 12.0$$

Since 100 was used as the initial amount and 12.0 was determined as the remaining amount, 12.0 can be used as the percentage of remaining amount of radioactivity of fluorine-18. **Thus the percent of fluorine-18 radioactivity remaining after 5.59 hours is 12.0%.**

c) This part of the question is much like the previous two parts, but this time we are given the initial amount of radioactivity, the final amount of radioactivity and we are asked do determine how long it took for that amount of radioactivity to decay. We are able to use the same equation:

$$\ln(N/N0) = -kt$$

However, now we are given N and N_0 and we have already determined k from before. We are told that 99.99% of the radioactivity has decayed, so we can use 100 and 0.01 for N_0 and N respectively. We plug these values in to the equation, solve for t, and get

$$\ln(0.01/1000) = -0.006319t$$

$$-9.21 = -0.006319t$$

$$t = 1458 \text{ minutes}$$

Therefore, its takes 1458 minutes for 99.99% of the radioactivity to decay.

Answer

a) 0.006319 min^{-1}

b) 12.0%

c) 1458 minutes

Q 4.48

Suppose that the half-life of steroids taken by an athlete is 42 days. Assuming that the steroids biodegrade by a first-order process, how long would it take for $\frac{1}{64}$ of the initial dose to remain in the athlete's body?

Solution

252 days

for first order reaction: $t_{1/2} = 0.693 / k$

$k = 0.693 / 42$

$k = 0.0165$

for first order reaction: $[A] = [A]_0 e^{-kt}$

1/64 initial means that: $[A] = 1/64 [A]_0$

therefore: $1/64 [A]_0 = [A]_0 e^{-0.0165t}$

$t = 252$ days

Q 4.49

Recently, the skeleton of King Richard III was found under a parking lot in England. If tissue samples from the skeleton contain about 93.79% of the carbon-14 expected in living tissue, what year did King Richard III die? The half-life for carbon-14 is 5730 years.

Solution

In order to find out what year King Richard III died, set [A]/[A_0] (the percent of carbon-14 still contained) equal to $0.5^{\text{time(t)/half life } (t_{1/2})}$ or use the equation $N(t) = N_0e^{-rt.}$

Using the first equation:

$A/A_0 = 0.5^{t/t_{1/2}}$ plug in the given numbers $.9379 = 0.5^{t/5730}$ and solve for t.

$ln.9379 = (t/5730)(ln0.5)$ (using the rule of logs)

$-.0641 = (t/5730)(-.693)$

$-367.36 = -.693t$

$t = 530.1 years$

Using $N(t) = N_0e^{-rt}$ this problem is solved by the following:

$1/2 = e^{-5730r}$

$r = 0.000121$

Now that we know what r is, we can use this value in our original formula and solve for t, the amount of years that have passed.

This time, we use 93.78, the percent of the carbon-14 remaining as N(t) and 100 as the original, N_0.

$93.78 = 100e^{-0.000121t}$

$t = 530.7$ years

Another way of doing this is by using these two equations:

$\lambda = \frac{0.693}{t_{1/2}}$ and $\frac{n_t}{n_0} = -\lambda t$

n_t = concentration at time t (93.79)

n_0 = initial concentration (100)

First solve for lambda or the decay constant by plugging in the half life.

Then plug in lambda and the other numbers into the second equation, and solve for t- which should equal to 530.1 years as well.

If we want to find out what year King Richard III died, we take the current year, 2017, and subtract 530 years. Doing this, we find that King Richard III died in the year 1487.

Answer

King Richard III died in the year 1487

Q 4.50

Nitroglycerine is an extremely sensitive explosive. In a series of carefully controlled experiments, samples of the explosive were heated to 160 °C and their first-order decomposition studied. Determine the average rate constants for each experiment using the following data:

Initial [$C_3H_5N_3O_9$] (*M*)	4.88	3.52	2.29	1.81	5.33	4.05	2.95	1.72
***t* (s)**	300	300	300	300	180	180	180	180
% Decomposed	52.0	52.9	53.2	53.9	34.6	35.9	36.0	35.4

Solution

First we need to understand what the question is asking for: the average rate constant. The average rate constant is the variable "k" when discussing kinetics and it can be defined as the proportionality constant in the equation that expresses the relationship

between the rate of a chemical reaction and the concentrations of the reacting substances. Knowing that we need to find K in this first order reaction, we can look to formulas that include "k," initial and final concentrations $[A]_o and [A]_t$, and half life time "t." Since this is a first order reaction, we can look to the first order equations, and doing that we find one that includes the variables given in the question:

$$\ln[A]_t = -kt + \ln[A]_o$$

For the first reaction, we have an initial concentration of 4.88 M, and a percentage decomposed. To find the final concentration, we must multiply the initial concentration by the percentage decomposed to know how much decomposed, and subtract that from the original to find out how much is left: 4.88M x 0.52= 2.54 M and 4.88M-2.54M=2.34M

Now, we have the variables we need, and we plug it into the equation above:

$\ln[A]_t = -kt + \ln[A]_o$

$\ln[2.34M] = -k(300s) + \ln[4.88M]$

k= $\frac{-(\ln[2.34M] - \ln[4.88M])}{300}$

$k = 2.45x10^{-3}$

Since it asks for the rate constant of each experiment, we now must do the same procedure for each data set to find the rate constant:

Second experiment

$\ln[A]_t = -kt + \ln[A]_o$

$\ln[1.66M] = -k(300s) + \ln[3.52M]$

k= $\frac{-(\ln[1.66M] - \ln[3.52M])}{300}$

$k = 2.51x10^{-3}$

Third experiment

$\ln[A]_t = -kt + \ln[A]_o$

$\ln[1.07M] = -k(300s) + \ln[2.29M]$

k= $\frac{-(\ln[1.07M] - \ln[2.29M])}{300}$

$k = 2.54x10^{-3}$

Fourth experiment

$\ln[A]_t = -kt + \ln[A]_o$

$\ln[0.834M] = -k(300s) + \ln[1.81M]$

k= $\frac{-(\ln[0.834M] - \ln[1.81M])}{300}$

$k = 2.58x10^{-3}$

Fifth Experiment

$\ln[A]_t = -kt + \ln[A]_o$

$\ln[3.49M] = -k(180s) + \ln[5.33M]$

k= $\frac{-(\ln[3.49M] - \ln[5.33M])}{180}$

$k = 2.35x10^{-3}$

Sixth Experiment

$\ln[A]_t = -kt + \ln[A]_o$

$\ln[2.60M] = -k(180s) + \ln[4.05M]$

$k=\frac{-(\ln[2.60M]-\ln[4.05M])}{180}$

$k=2.46x10^{-3}$

Seventh Experiment

$\ln[A]_t=-kt+\ln[A]_o$

$\ln[1.89M]=-k(180s)+\ln[2.95M]$

$k=\frac{-(\ln[1.89M]-\ln[2.95M])}{180}$

$k=2.47x10^{-3}$

Eighth experiment

$\ln[A]_t=-kt+\ln[A]_o$

$\ln[1.11M]=-k(180s)+\ln[1.72M]$

$k=\frac{-(\ln[1.11M]-\ln[1.72M])}{180}$

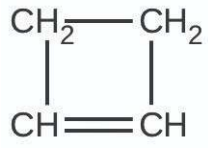
$k=2.43x10^{-3}$

Answer

$[A]_0$ (M)	$k \times 10^3$ (s^{-1})
4.88	2.45
3.52	2.51
2.29	2.54
1.81	2.58
5.33	2.35
4.05	2.44
2.95	2.47
1.72	2.43

Q 4.51

For the past 10 years, the unsaturated hydrocarbon 1,3-butadiene ($CH_2=CH-CH=CH_2$) has ranked 38th among the top 50 industrial chemicals. It is used primarily for the manufacture of synthetic rubber. An isomer exists also as cyclobutene:



The isomerization of cyclobutene to butadiene is first-order and the rate constant has been measured as 2.0×10^{-4} s^{-1} at 150 °C in a 0.53-L flask. Determine the partial pressure of cyclobutene and its concentration after 30.0 minutes if an isomerization reaction is carried out at 150 °C with an initial pressure of 55 torr.

Solution

Since this is a first order reaction, the integrated rate law is: $[A_t]=[A_0]e^{-kt}$

Partial Pressure: Use the integrated rate law to find the partial pressure at 30 minutes:

Use A_0 = 55 torr, t = 30 min, and k = $2.0*10^{-4}s^{-1}$ to solve the integrated rate law equation:

$[A_{30}]=(55torr)*e^{-(2.0x10^{-4}\frac{1}{sec})(30min\cdot\frac{60sec}{1min})}$

Solve this equation to get:

$[A_{30}] = (55torr) * e^{-0.36}$

$A_{30}]$ = 38.37 torr.

Initial Concentration: Find the initial concentration using the ideal gas law.

The ideal gas law is given by $PV = nRT \rightarrow n = \frac{PV}{RT}$. Use this form of the gas law to solve for the initial concentration n.

Use V = 0.53L, R = 0.08206 $\frac{L*atm}{mol*L}$, T = 423.15 K, and P = $\frac{1atm}{760}$ = 0.07237 atm .

Solve the ideal gas equation using these values:

$n = \frac{(55torr)(0.53L)}{(0.08206\frac{L*atm}{mol*K})(423.15K)} = 0.00110$ moles cyclobutene.

Now find the initial concentration of cyclobutene A_0 using the equation $[A_0] = \frac{n}{V}$:

$A_0 = \frac{n}{V} = \frac{0.00110moles}{0.53L} = 0.00208M$

Concentration at 30 minutes: Find the concentration of cyclobutene at 30 minutes by using the integrated rate law given above, using time t = 30 minutes, or 1800 seconds.

$[A_{30}] = (0.00208M)e^{-0.36} = 0.00145M$

So at 30 minutes, the cyclobutene concentration is 0.00145 M, and the partial pressure is 38.37 torr.

Answer

Partial Pressure: 38.37 torr.

Concentration: 0.00145 M

4.6: Collision Theory

Q 4.52

Chemical reactions occur when reactants collide. What are two factors that may prevent a collision from producing a chemical reaction?

Solution

The two factors that may prevent a collision from producing a chemical reaction are:

1. **Kinetic energy of the molecule**

In order for chemical reactions to occur, molecules require enough velocity to overcome the minimum activation energy needed to break the old bonds and form new bonds with other molecules. At higher temperatures, the molecules possess the minimum amount of kinetic energy needed which ensures the collisions will be energetic enough to lead to a reaction.

2. **The orientation of molecules during the collision**

Two molecules have to collide in the right orientation in order for the reaction to occur. Molecules have to orient properly for another molecule to collide at the right activation state.

Q 4.53

When every collision between reactants leads to a reaction, what determines the rate at which the reaction occurs?

Solution

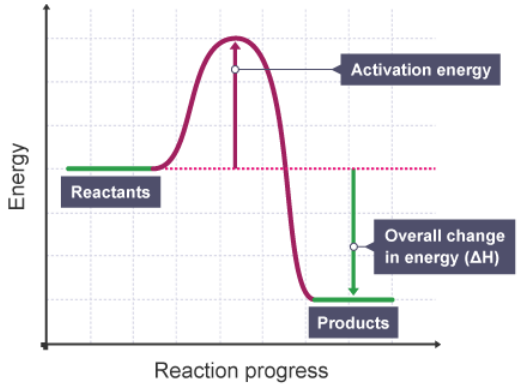
There has to be contact between reactants for a reaction to occur. The more the reactants collide, the more often reactions can occur. Factors that determine reaction rates include concentration of reactants, temperature, physical states of reactants, surface area, and the use of a catalyst. The reaction rate usually increases as the concentration of a reactant increases. Increasing the temperature increases the average kinetic energy of molecules, causing them to collide more frequently, which increases the reaction rate. When two reactants are in the same fluid phase, their particles collide more frequently, which increases the reaction rate. If the surface area of a reactant is increased, more particles are exposed to the other reactant therefore more

collisions occur and the rate of reaction increases. A catalyst participates in a chemical reaction and increases the reaction rate without changing itself.

Q 4.54

What is the activation energy of a reaction, and how is this energy related to the activated complex of the reaction?

Solution



Activation energy is the energy barrier that must be overcome in order for a reaction to occur. To get the molecules into a state that allows them to break and form bonds, the molecules must be contorted (deformed, or bent) into an unstable state called the transition state. The transition state is a high-energy state, and some amount of energy – the activation energy – must be added in order for the molecule reach it. Because the transition state is unstable, reactant molecules don't stay there long, but quickly proceed to the next step of the chemical reaction.The activated complex is the highest energy of the transition state of the reaction.

Q 4.55

Describe how graphical methods can be used to determine the activation energy of a reaction from a series of data that includes the rate of reaction at varying temperatures.

Solution

This method is based on the **Arrhenius equation** which can be used to show the effect of a change of temperature on the **rate constant**, and therefore on the rate of reaction.

The rate constant is different from reaction rat in that the reaction rate is the measure of how fast or slow a chemical reaction takes place while a rate constant is a constant that shows the relationship between the reaction rate and the concentrations of the reactants or products.

For example, for the reaction $A + B \rightarrow C$, the rate law would be:

$$rate = k[A]^a[B]^b$$

k = rate constant

[A] = concentration of reactant A

a = order of reaction with respect to A

[B] = concentration of reactant B

b = order of reaction with respect to B

However, the rate constant remains constant only if you are changing the concentration of the reactants. If you change the temperature or the catalyst of the reaction, the rate constant will change and this is demonstrated by the Arrhenius equation:

$$k = Ae^{\frac{-E_a}{RT}}$$

$$ln\left(\frac{k_1}{k_2}\right) = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

k = rate constant

A = frequency factor

E_a = activation energy

e = exponential function, e^x

R = gas constant

T = temperature (K)

In other words, the activation energy of a reaction, E_a, from a series of data that includes the rate of reaction, k, at varying temperatures can be determined by graphing it on a plot of $\ln k$ versus $\frac{1}{T}$. You can then use the slope of the graph you have plotted to solve for E_a by setting the slope equal to $\frac{-E_a}{R}$.

Q 4.56

How does an increase in temperature affect rate of reaction? Explain this effect in terms of the collision theory of the reaction rate.

Q 4.57

Collision theory states that the rates of chemical reactions depend on the fraction of molecules with the correct orientation, fraction of collisions with required energy, and the collision frequency. Because the fraction of collisions with required energy is a function of temperature, as temperature increases, the fraction of collisions with required energy also increases. The kinetic energy of reactants also increases with temperature which means molecules will collide more often increasing collisions frequency. With increased fraction of collisions with required energy and collisions frequency, the rate of chemical reaction increases. We see mathematically, from the Arrhenius equation, that temperature and the rate constant are related.

$$k = Ae^{\frac{E_a}{RT}} \tag{4.E.14}$$

where k is the rate constant, A is a specific constant, R is 8.3145 J/K, Ea is the reaction-specific activation energy in J, and T is temperature in K. We see from the equation that k is very sensitive to changes in the temperature.

Q 4.58

The rate of a certain reaction doubles for every 10 °C rise in temperature.

a. How much faster does the reaction proceed at 45 °C than at 25 °C?
b. How much faster does the reaction proceed at 95 °C than at 25 °C?

Solution

By finding the difference in temperature, 45 °C - 25 °C, we get 20 °C. Since the rate of the reaction doubles every 10 °C increase in temperature and the rate of the reaction experienced a 20 °C increase in temperature, we see that the reaction rate doubled twice ($2^2 = 4$). As a result, the **reaction proceeds four times faster**.

Following the same process as in part a, we get the difference in temperature to be 70 °C. Since the rate of the reaction doubles every 10 °C increase in temperature and the system experienced a 70 °C change, we see that the reaction doubled seven times ($2^7 = 128$). We can see the **reaction proceeds 128 times faster**.

(a) 4-times faster (b) 128-times faster

Q 4.59

In an experiment, a sample of $NaClO_3$ was 90% decomposed in 48 min. Approximately how long would this decomposition have taken if the sample had been heated 20 °C higher?

S 4.59

First off, it is important to recognize that this decomposition reaction is a **first-order reaction**, which can be written as follows: $2NaClO_3 \rightarrow 2NaCl + 3O_2$

Understanding this, it is important to be able to then be able to recognize which equation would be most useful given the initial conditions presented by the question. Since we are dealing with time, percentage of material left, and temperature, the only viable equation that could relate all of this would be the Arrhenius Equation, which is written as follows: $\ln(\frac{k_2}{k_1}) = \frac{Ea}{R}(\frac{1}{t_1} - \frac{1}{t_2})$

However, this problem does not give us enough information such as what the activation energy is or the initial temperature in order to mathematically solve this problem. Additionally, the problem tells us to approximate how long the decomposition would take, which means we are asked to answer this question conceptually based on our knowledge of thermodynamics and reaction rates. As a general rule of thumb, we know that for every 10˚C rise in temperature the rate of reaction doubles. Since the question tells us that there is a 20˚C rise in temperature we can deduce that the reaction rate doubles twice, as per the general rule mentioned before. This means **the overall reaction rate for this decomposition would quadruple**, or would be 4 times faster than the reaction rate at the initial temperature.

We can gut check this answer by recalling how an increase in the average kinetic energy (temperature) decreases the time it takes for the reaction to take place and increase the reaction rate. Thus, if we increase the temperature we should have a faster reaction rate.

Q 4.60

The rate constant at 325 °C for the decomposition reaction $\mathrm{C_4H_8} \longrightarrow 2\,\mathrm{C_2H_4}$ is 6.1 × 10^{-8} s^{-1}, and the activation energy is 261 kJ per mole of C_4H_8. Determine the frequency factor for the reaction.

Solution

S 4.60

Using the Arrhenius equation allows me to find the frequency factor, A.

$k=Ae^{-Ea/RT}$

k, Ea, R, and T are all known values. k, Ea, and T are given in the problem as $6.1x10^{-8}$, 261 kJ, and 598 K, respectively.

So, plugging them into the equation gives:

$6.1x10^{-8}\ s^{-1}=Ae^{(-261000\ J)/(8.3145\ J/mol)(598\ K)}$

Take $e^{(-261000\ J)/(8.3145\ J/mol)(598)}$ and get 1.59×10^{-23}. Divide k, 6.1×10^{-8}, by 1.59×10^{-23} and get $A=3.9 \times 10^{15} s^{-1}$

A 4.60

$3.9 \times 10^{15}\ s^{-1}$

Q 4.61

The rate constant for the decomposition of acetaldehyde (CH_3CHO), to methane (CH_4), and carbon monoxide (CO), in the gas phase is 1.1 × 10^{-2} L/mol/s at 703 K and 4.95 L/mol/s at 865 K. Determine the activation energy for this decomposition.

S4.61

The equation for relating the rate constant and activation energy of a reaction is the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}} \tag{4.E.15}$$

When given two rate constants at two different temperatures but for the same reaction, the Arrhenius equation can be rewritten as:

$$ln(\frac{k_2}{k_1}) = \frac{E_a}{R}(\frac{1}{T_1} - \frac{1}{T_2}) \tag{4.E.16}$$

In this problem, all the variables are given except for the E_a (activation energy).

k_1 = 1.1 × 10^{-2} L/mol/s

T_1 = 703 K

k_2 = 4.95 L/mol/s

T_2 = 865 K

R = 8.314 J/(mol K) (Ideal Gas Constant)

Now plug in all these values into the equation, and solve for E_a.

$$ln(\frac{4.95\frac{L}{mol\times s}}{1.1\times10^{-2}\frac{L}{mol\times s}}) = \frac{E_a}{8.314\times10^{-3}\frac{kJ}{mol\times K}}(\frac{1}{703}-\frac{1}{865}) \quad (4.E.17)$$

E_a = 190 kJ (2 sig figs)

Q 4.62

An elevated level of the enzyme alkaline phosphatase (ALP) in the serum is an indication of possible liver or bone disorder. The level of serum ALP is so low that it is very difficult to measure directly. However, ALP catalyzes a number of reactions, and its relative concentration can be determined by measuring the rate of one of these reactions under controlled conditions. One such reaction is the conversion of p-nitrophenyl phosphate (PNPP) to p-nitrophenoxide ion (PNP) and phosphate ion. Control of temperature during the test is very important; the rate of the reaction increases 1.47 times if the temperature changes from 30 °C to 37 °C. What is the activation energy for the ALP–catalyzed conversion of PNPP to PNP and phosphate?

Solution

43.0 kJ/mol

Q 4.63

In terms of collision theory, to which of the following is the rate of a chemical reaction proportional?

a. the change in free energy per second
b. the change in temperature per second
c. the number of collisions per second
d. the number of product molecules

Q 4.64

Hydrogen iodide, HI, decomposes in the gas phase to produce hydrogen, H_2, and iodine, I_2. The value of the rate constant, *k*, for the reaction was measured at several different temperatures and the data are shown here:

Temperature (K)	k (M^{-1} s^{-1})
555	6.23×10^{-7}
575	2.42×10^{-6}
645	1.44×10^{-4}
700	2.01×10^{-3}

What is the value of the activation energy (in kJ/mol) for this reaction?

Solution

177 kJ/mol

Q 4.65

The element Co exists in two oxidation states, Co(II) and Co(III), and the ions form many complexes. The rate at which one of the complexes of Co(III) was reduced by Fe(II) in water was measured. Determine the activation energy of the reaction from the following data:

T (K)	k (s^{-1})

T (K)	k (s^{-1})
293	0.054
298	0.100

Q 4.66

The hydrolysis of the sugar sucrose to the sugars glucose and fructose,

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

follows a first-order rate equation for the disappearance of sucrose: Rate = $k[C_{12}H_{22}O_{11}]$ (The products of the reaction, glucose and fructose, have the same molecular formulas but differ in the arrangement of the atoms in their molecules.)

a. In neutral solution, $k = 2.1 \times 10^{-11}$ s^{-1} at 27 °C and 8.5×10^{-11} s^{-1} at 37 °C. Determine the activation energy, the frequency factor, and the rate constant for this equation at 47 °C (assuming the kinetics remain consistent with the Arrhenius equation at this temperature).
b. When a solution of sucrose with an initial concentration of 0.150 *M* reaches equilibrium, the concentration of sucrose is 1.65×10^{-7} *M*. How long will it take the solution to reach equilibrium at 27 °C in the absence of a catalyst? Because the concentration of sucrose at equilibrium is so low, assume that the reaction is irreversible.
c. Why does assuming that the reaction is irreversible simplify the calculation in part (b)?

Solution

E_a = 108 kJ

$A = 2.0 \times 10^8$ s^{-1}

$k = 3.2 \times 10^{-10}$ s^{-1}

(b) 1.81×10^8 h or 7.6×10^6 day. (c) Assuming that the reaction is irreversible simplifies the calculation because we do not have to account for any reactant that, having been converted to product, returns to the original state.

Q 4.67

Use the PhET Reactions & Rates interactive simulation to simulate a system. On the “Single collision” tab of the simulation applet, enable the “Energy view” by clicking the “+” icon. Select the first $A + BC \longrightarrow AB + C$ reaction (A is yellow, B is purple, and C is navy blue). Using the “straight shot” default option, try launching the *A* atom with varying amounts of energy. What changes when the Total Energy line at launch is below the transition state of the Potential Energy line? Why? What happens when it is above the transition state? Why?

Q4.68

Use the PhET Reactions & Rates interactive simulation to simulate a system. On the “Single collision” tab of the simulation applet, enable the “Energy view” by clicking the “+” icon. Select the first $A + BC \longrightarrow AB + C$ reaction (A is yellow, B is purple, and C is navy blue). Using the “angled shot” option, try launching the *A* atom with varying angles, but with more Total energy than the transition state. What happens when the *A* atom hits the *BC* molecule from different directions? Why?

Solution

The *A* atom has enough energy to react with *BC*; however, the different angles at which it bounces off of *BC* without reacting indicate that the orientation of the molecule is an important part of the reaction kinetics and determines whether a reaction will occur.

4.7 Reaction Mechanisms

Q4.69

Why are elementary reactions involving three or more reactants very uncommon?

Q4.70

In general, can we predict the effect of doubling the concentration of *A* on the rate of the overall reaction $A + B \longrightarrow C$? Can we predict the effect if the reaction is known to be an elementary reaction?

Solution

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No. In general, for the overall reaction, we cannot predict the effect of changing the concentration without knowing the rate equation. Yes. If the reaction is an elementary reaction, then doubling the concentration of *A* doubles the rate.

Q4.71

Phosgene, $COCl_2$, one of the poison gases used during World War I, is formed from chlorine and carbon monoxide. The mechanism is thought to proceed by:

step 1:	Cl + CO → COCl
step 2:	$COCl + Cl_2 \rightarrow COCl_2 + Cl$

a. Write the overall reaction equation.
b. Identify any reaction intermediates.
c. Identify any intermediates.

Q4.72

Define these terms:

a. unimolecular reaction
b. bimolecular reaction
c. elementary reaction
d. overall reaction

Q4.73

What is the rate equation for the elementary termolecular reaction $A + 2B \longrightarrow \text{products}$? For $3A \longrightarrow \text{products}$?

Solution

We are given that both of these reactions are elementary termolecular. The molecularity of a reaction refers to the number of reactant particles that react together with the proper and energy and orientation. Termolecular reactions have three atoms to collide simultaneously. As it is termolecular, and there are no additional reactants aside from the three given in each reaction, there are no intermediate reactions. The rate law for elementary reactions is determined by the stoichiometry of the reaction without needed experimental data.

The basic rate form for the elementary step is what follows:

$rate = k \cdot reactant\ 1^{i} \cdot reactant\ 2^{ii} \cdot \ldots$ Where i and ii are the stochiometric coefficient from reactant 1 and 2 respectively.

For: $3A \rightarrow products$

$k \cdot A^3 = rate$

For: $A + 2B \rightarrow products$

$k \cdot [A] \cdot [B]^2 = rate$

Note that the order of these reactions are both three.

Answer

Rate = $k[A][B]^2$; Rate = $k[A]^3$

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Q4.74

Given the following reactions and the corresponding rate laws, in which of the reactions might the elementary reaction and the overall reaction be the same?

(a) $\mathrm{Cl_2 + CO \longrightarrow Cl_2CO}$

$\text{rate} = k[\mathrm{Cl_2}]^{\frac{3}{2}}[\mathrm{CO}]$

(b) $\mathrm{PCl_3 + Cl_2 \longrightarrow PCl_5}$

$\text{rate} = k[\mathrm{PCl_3}][\mathrm{Cl_2}]$

(c) $\mathrm{2\,NO + H_2 \longrightarrow N_2 + H_2O}$

$\text{rate} = k[\mathrm{NO}][\mathrm{H_2}]$

(d) $\mathrm{2\,NO + O_2 \longrightarrow 2\,NO_2}$

$\text{rate} = k[\mathrm{NO}]^2[\mathrm{O_2}]$

(e) $\mathrm{NO + O_3 \longrightarrow NO_2 + O_2}$

$\text{rate} = k[\mathrm{NO}][\mathrm{O_3}]$

Solution

An elementary reaction is a chemical reaction in which the reactants directly form products in a single step. In another words, the rate law for the overall reaction is same as experimentally found rate law. Out of 5 options, option (b),(d), and (e) are such reactions

Q4.75

Write the rate equation for each of the following elementary reactions:

a. $\mathrm{O_3 \xrightarrow{sunlight} O_2 + O}$
b. $\mathrm{O_3 + Cl \longrightarrow O_2 + ClO}$
c. $\mathrm{ClO + O \longrightarrow Cl + O_2}$
d. $\mathrm{O_3 + NO \longrightarrow NO_2 + O_2}$
e. $\mathrm{NO_2 + O \longrightarrow NO + O_2}$

Solution

Rate equations are **dependent on the reactants and not the products.**

The rate law of a reaction can be found using a rate constant (which is found experimentally), and the initial concentrations of reactants.

A general solution for the equation

$aA + bB \rightarrow cC + dD$

is $rate = k[A]^m[B]^n$ where m and n are reaction orders.

However, reaction orders are found experimentally, and since we do not have experimental data for these reactions, we can disregard that part of the equation.

To find the rate laws, all we have to do is plug the reactants into the rate formula. This is only due to the case that these are elementary reactions. Further reading on elementary reactions can be found on Libre Texts.

a. $\mathrm{O_3 \longrightarrow O_2 + O}$

To write this reaction's rate equation, only focus on the reactant(s) and its/their concentration and multiplying that by a rate constant, "k".

$$\text{Rate} = k[\mathrm{O_3}]$$

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b. $O_3 + Cl \longrightarrow O_2 + ClO$

To write this reaction's rate equation, only focus on the reactant(s) and its/their concentration and multiplying that by a rate constant, "k".

$$\text{Rate} = k[O_3][Cl]$$

c. $ClO + O \longrightarrow Cl + O_2$

To write this reaction's rate equation, only focus on the reactant(s) and its/their concentration and multiplying that by a rate constant, "k".

$$\text{Rate} = k[ClO][O]$$

d. $O_3 + NO \longrightarrow NO_2 + O_2$

To write this reaction's rate equation, only focus on the reactant(s) and its/their concentration and multiplying that by a rate constant, "k".

$$\text{Rate} = k[O_3][NO]$$

e. $NO_2 + O \longrightarrow NO + O_2$

To write this reaction's rate equation, only focus on the reactant(s) and its/their concentration and multiplying that by a rate constant, "k".

$$\text{Rate} = k[NO_2][O]$$

Answer

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(a) $\text{Rate}_1 = k[O_3]$; (b) $\text{Rate}_2 = k[O_3][Cl]$; (c) $\text{Rate}_3 = k[ClO][O]$; (d) $\text{Rate}_2 = k[O_3][NO]$; (e) $\text{Rate}_3 = k[NO_2][O]$

Q4.76

Nitrogen(II) oxide, NO, reacts with hydrogen, H_2, according to the following equation:

$$2\,NO + 2\,H_2 \longrightarrow N_2 + 2\,H_2O$$

What would the rate law be if the mechanism for this reaction were:

$$2\,NO + H_2 \longrightarrow N_2 + H_2O_2\ (\text{slow})$$

$$H_2O_2 + H_2 \longrightarrow 2\,H_2O\ (\text{fast})$$

The rate law of the mechanism is determined by the slow step of the reaction. Since the slow step is an elementary step, the rate law can be drawn from the coefficients of the chemical equation. So therefore, the rate law is as follows: rate=k$[NO]^2[H_2]$. Since both NO and H_2 are reactants in the overall reaction (therefore are not intermediates in the reaction), no further steps have to be done to determine the rate law.

Q4.77

Consider the reaction

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ (occurs under light)

The mechanism is a chain reaction involving Cl atoms and CH_3 radicals. Which of the following steps does not terminate this chain reaction?

a. $CH_3 + Cl \rightarrow CH_3CI$
b. $CH_3 + HCl \rightarrow CH_4 + Cl$
c. $CH_3 + CH_3 \rightarrow C_2H_2$
d. $Cl + Cl \rightarrow Cl_2$

Solution

Chain reactions involve reactions that create products necessary for more reactions to occur. In this case, a reaction step will continue the chain reaction if a radical is generated. Radicals are highly reactive particles, so more reactions in the chain will take place as long as they are present. The chlorine is considered a free radical as it has an unpaired electron; for this reason it is very reactive and propagates a chain reaction. It does so by taking an electron from a stable molecule and making that molecule reactive, and that molecule goes on to react with stable species, and in that manner a long series of "chain" reactions are initiated. A chlorine radical will continue the chain by completing the following reaction:

$$Cl\cdot + CH_4 \rightarrow CH_3\cdot + HCl$$

The CH_3 generated by this reaction can then react with other species, continuing to propagate the chain reaction.

Option 1 is incorrect because the only species it produces is CH_3Cl, a product in the overall reaction that is unreactive. This terminates the chain reaction because it fails to produce any Cl or CH_3 radicals that are necessary for further propagating the overall reaction.

Option 2 is the correct answer because it produces a Cl radical. This Cl radical can continue the chain by colliding with CH_4 molecules.

Option 3 is incorrect because it fails to produce a radical capable of continuing the chain.

Option 4 is incorrect because it produces Cl_2, a molecule that does not react unless additional light is supplied. Therefore, this step breaks the chain.

Answer

Answer: Option 2: $CH_3 + HCl \rightarrow CH_4 + Cl$

Q4.78

Experiments were conducted to study the rate of the reaction represented by this equation.

$$2\,\mathrm{NO}(g) + 2\,\mathrm{H_2}(g) \longrightarrow \mathrm{N_2}(g) + 2\,\mathrm{H_2O}(g)$$

Initial concentrations and rates of reaction are given here.

Experiment	Initial Concentration [NO] (mol/L)	Initial Concentration, [H_2] (mol/L)	Initial Rate of Formation of N_2 (mol/L min)
1	0.0060	0.0010	1.8×10^{-4}
2	0.0060	0.0020	3.6×10^{-4}
3	0.0010	0.0060	0.30×10^{-4}
4	0.0020	0.0060	1.2×10^{-4}

Consider the following questions:

a. Determine the order for each of the reactants, NO and H_2, from the data given and show your reasoning.
b. Write the overall rate law for the reaction.
c. Calculate the value of the rate constant, *k*, for the reaction. Include units.
d. For experiment 2, calculate the concentration of NO remaining when exactly one-half of the original amount of H_2 had been consumed.
e. The following sequence of elementary steps is a proposed mechanism for the reaction.

Step 1: $\mathrm{NO} + \mathrm{NO} \rightleftharpoons \mathrm{N_2O_2}$

Step 2: $\mathrm{N_2O_2} + \mathrm{H_2} \rightleftharpoons \mathrm{H_2O} + \mathrm{N_2O}$

Step 3: $\mathrm{N_2O} + \mathrm{H_2} \rightleftharpoons \mathrm{N_2} + \mathrm{H_2O}$

Based on the data presented, which of these is the rate determining step? Show that the mechanism is consistent with the observed rate law for the reaction and the overall stoichiometry of the reaction.

S12.6.10

1. i) Find the order for [NO] by using experiment 3 and 4 where [H_2] is constant

Notice that [NO] doubles from experiment 3 to 4 and the rate quadruples. So the order for [NO] is **2**

ii) Find the order for [H_2] by using experiment 1 and 2 where [NO] is constant

Notice that [H_2] doubles from experiment 1 to 2 and the rate doubles as well. So the order for [H_2] is **1**

2. Put in the order for each product as the exponents for the corresponding reactant.

$$rate = k[NO]^2[H_2]$$

3. Put in the concentrations and the rate from one of the experiments into the rate law and solve for k. (Here, experiement 1 is used but any of them will work)

$$rate = k[NO]^2[H_2]\ \ .00018 = k[.006]^2[.001] k = 5000 M^{-2} s^{-1}$$

4. Plug in values for experiment 2 into the rate law equation and solve for the concentration of NO

$$.00036 = 5000[NO]^2[.001] [NO]^2 = 7.2x10^{-5}\ \ [NO] = .0085M$$

5. Write the rate laws for each step and then see which matches the rate law we found in question 2. The rate determining step (the slow step) is the one that gives the rate for the overall reaction. Because of this, only those concentrations will influence the overall reaction, contrary to what we would believe if we just looked at the overall reaction.

Step 1: $NO + NO \rightleftharpoons N_2O_2$

$rate = k_1[NO]^2$ This rate law is not the same as the one we calculate in question 2 so this **can not** be the rate determining step

Step 2: $N_2O_2 + H_2 \rightleftharpoons N_2O + N_2O$

$rate = k_2[N_2O_2][H_2]$

Since N_2O_2 is an intermediate you must replace it in the rate law equation. Intermediates can not be in the rate law because they do not appear in the overall reaction. Here you can take the reverse of equation 1 (k_{-1}) and substitute the other side (the reactants of equation 1) for the intermediate in the rate law equation.

$$rate_1 = rate_{-1}$$

$$k_1[NO]^2 = k_{-1}[N_2O_2]$$

$$[N_2O_2] = \frac{k_1[NO]^2}{k_{-1}}$$

$rate = \frac{k_2 k_1 [NO]^2 [H_2]}{k_{-1}}$

Overall: $rate = k[NO]^2[H_2]$ This **is the same** so it is the rate determining step.

So $N_2O_2 + H_2 \rightleftharpoons N_2O + N_2O$ is the rate determining step step.

Answer

(a) NO: 2

H_2 : 1

(b) Rate = k $[NO]^2[H_2]$;

(c) k = 5.0 × 10^3 mol^{-2} L^{-2} min^{-1};

(d) 0.0050 mol/L;

(e) Step II is the rate-determining step.

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Q4.79

The reaction of CO with Cl_2 gives phosgene ($COCl_2$), a nerve gas that was used in World War I. Use the mechanism shown here to complete the following exercises:

- $Cl_2(g) \rightleftharpoons 2\,Cl(g)$ (fast, k_1 represents the forward rate constant, k_{-1} the reverse rate constant)
- $CO(g) + Cl(g) \longrightarrow COCl(g)$ (slow, k_2 the rate constant)
- $COCl(g) + Cl(g) \longrightarrow COCl_2(g)$ (fast, k_3 the rate constant)

a. Write the overall reaction.
b. Identify all intermediates.
c. Write the rate law for each elementary reaction.
d. Write the overall rate law expression.

Solution

1. To write the overall reaction you have to identify the intermediates and leave them out. The easiest way to do this is to write out all the products and reactants and cross out anything that is on both sides.

$$Cl_2(g) + CO(g) + \cancel{2Cl(g)} + \cancel{COCl(g)} \Rightarrow \cancel{2Cl(g)} + \cancel{COCl(g)} + COCl_2(g)$$

In this you will cross out the 2Cl(g) molecules and the COCl(g). What is left after that is the overall reaction.

$Cl_2(g) + CO(g) \Rightarrow + COCl_2(g)$

2. For part two you will just list the intermediates that you crossed out.

Cl and COCl are intermediates

3. Each rate law will be the rate equal to the rate constant times the concentrations of the reactants

reaction 1

(forward) rate=$k_1[Cl_2]$ (reverse) rate=$k_{-1}[Cl]$

reaction 2

rate=$k_2[CO][Cl]$

Reaction 3

rate=$k_3[COCl][Cl]$

4. The overall rate law is based off the slowest step (step #2), since it is the rate determining step, but Cl is present in that rate law so we have to replace it with an equivalent that does not contain an intermediate. To do this you use the equilibrium since the rates are the same you can set up the rate laws of the forward and reverse equal to each other.

$k_1[Cl_2] = k_{-1}[Cl]$

$[Cl] = k_1[Cl_2]/k_{-1}$

rate=$k_2[CO]k_1[Cl_2]/k_{-1}$

rate=$k^{\circ}[CO][Cl_2]$

Steps to replacing and intermediate

1. Set the forward and reverse reaction equal to each other using separate constants
2. Solve for the intermediate using algebra
3. Plug into the rate determining formula
4. All the k's will be condensed into a K prime constant

4.8 Catalysis

Q4.80

Account for the increase in reaction rate brought about by a catalyst.

Q4.81

Compare the functions of homogeneous and heterogeneous catalysts.

Q4.82

Consider this scenario and answer the following questions: Chlorine atoms resulting from decomposition of chlorofluoromethanes, such as CCl_2F_2, catalyze the decomposition of ozone in the atmosphere. One simplified mechanism for the decomposition is:

$$\begin{aligned} O_3 &\xrightarrow{\text{sunlight}} O_2 + O \\ O_3 + Cl &\longrightarrow O_2 + ClO \\ ClO + O &\longrightarrow Cl + O_2 \end{aligned}$$

a. Explain why chlorine atoms are catalysts in the gas-phase transformation:

$$2\,O_3 \longrightarrow 3\,O_2$$

b. Nitric oxide is also involved in the decomposition of ozone by the mechanism:

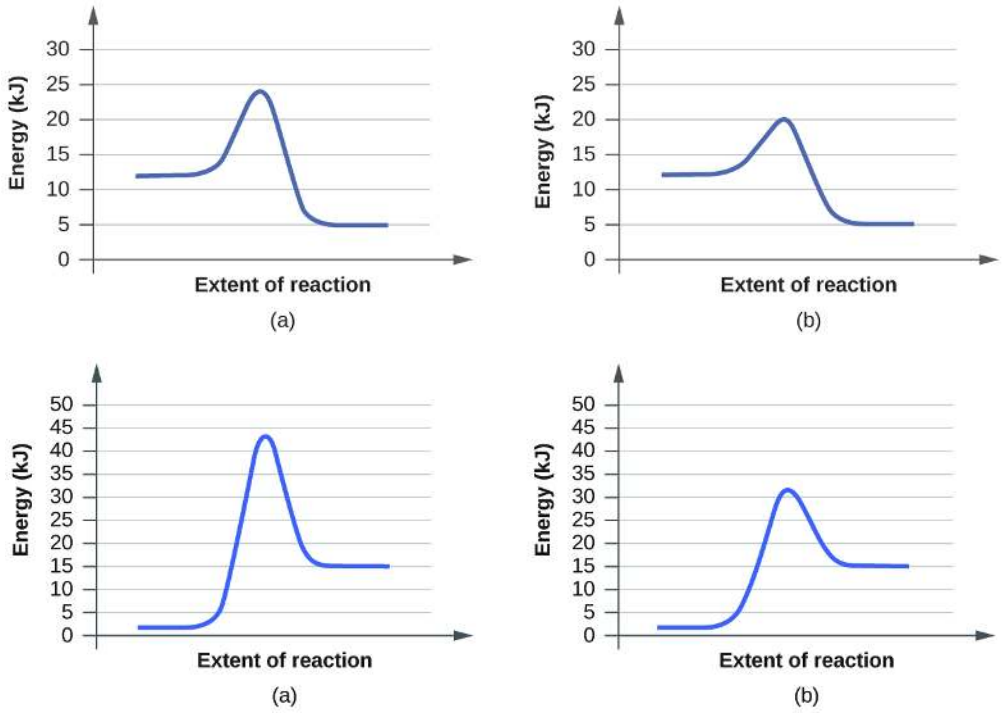
$$\begin{aligned} O_3 &\xrightarrow{\text{sunlight}} O_2 + O \\ O_3 + NO &\longrightarrow NO_2 + O_2 \\ NO_2 + O &\longrightarrow NO + O_2 \end{aligned}$$

Is NO a catalyst for the decomposition? Explain your answer.

Q4.83

For each of the following pairs of reaction diagrams, identify which of the pair is catalyzed:

(a)

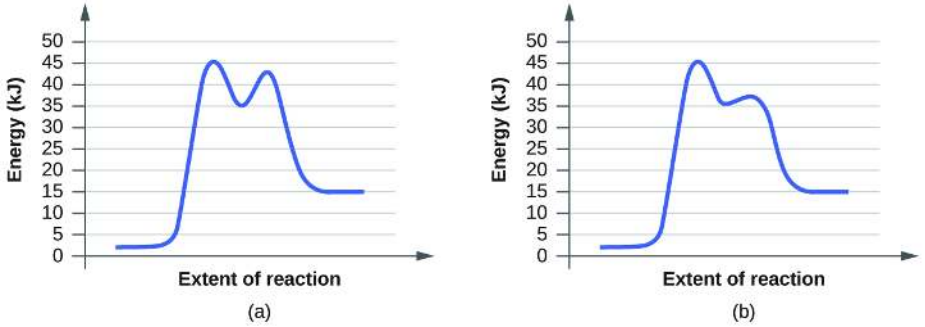


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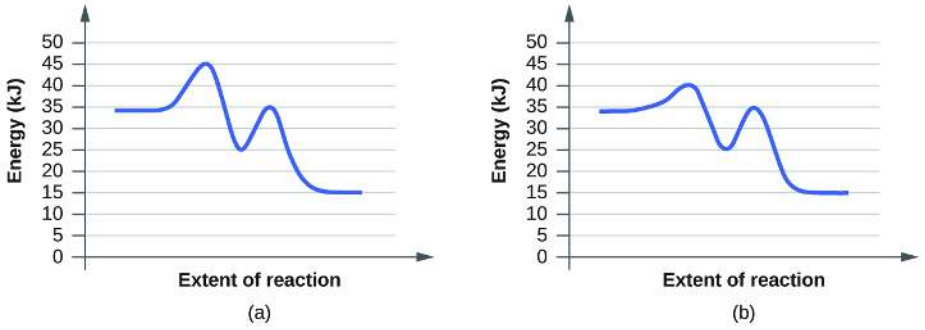
Q4.84

For each of the following pairs of reaction diagrams, identify which of the pairs is catalyzed:

(a)



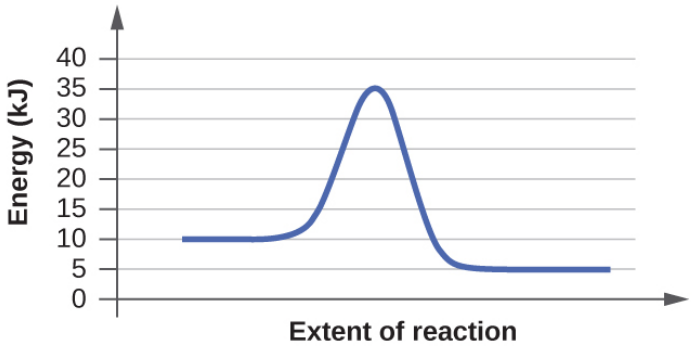
(b)



Q4.85

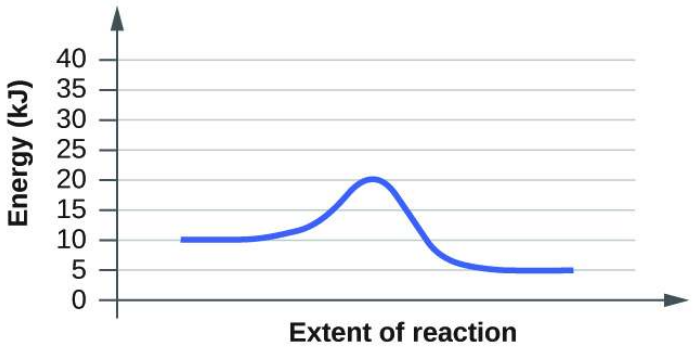
For each of the following reaction diagrams, estimate the activation energy (E_a) of the reaction:

(a)



(b)

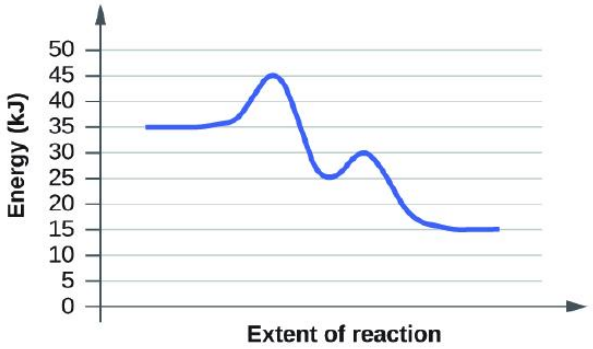
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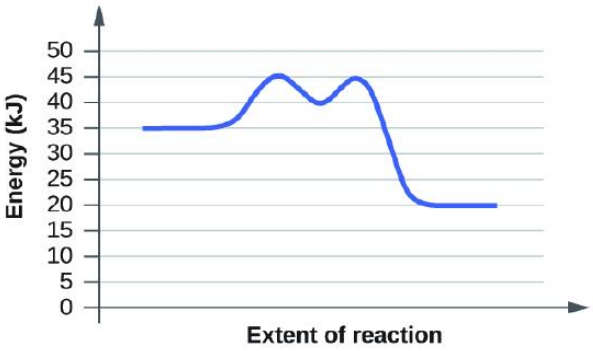
Q4.86

For each of the following reaction diagrams, estimate the activation energy (E_a) of the reaction:

(a)



(b)



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4.S: Kinetics (Study Guide)

4.1: Prelude to Kinetics

chemical kinetics – area of chemistry dealing with speeds/rates of reactions

4.2: Reaction Rates

- **reaction rate** – speed of a chemical reaction

$$average\ rate = \frac{change\ \#moles\ B}{change\ in\ time} = \frac{\Delta moles\ B}{\Delta t}\ if\ A \rightarrow B$$

$$\Delta moles\ B = moles\ B\ at\ final\ time - moles\ B\ at\ initial\ time$$

$$average\ rate = -\frac{\Delta moles\ A}{\Delta t}\ if\ A \rightarrow B$$

- rate calculated in units of M/s
- brackets around a substance indicate the concentration
- **instantaneous rate** – rate at a particular time
- instantaneous rate obtained from the straight line tangent that touches the curve at a specific point
- slopes give instantaneous rates
- instantaneous rate also referred to as the rate

- for the irreversible reaction $aA + bB \rightarrow cC + dD$

$$rate = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

4.3: Factors that Affect Reaction Rates

- rates of reactions affected by four factors
  1. concentrations of reactants
  2. temperature at which reaction occurs
  3. presence of a catalyst
  4. surface area of solid or liquid reactants and/or catalysts

4.4: Rate Laws

- **Rate law** – expression that shows that rate depends on concentrations of reactants
- k = rate constant

- Rate = k[reactant 1]^m[reactant 2]^n
- m, n are called reaction orders
- m+n, overall reaction order
- reaction orders do not have to correspond with coefficients in balanced equation
- values of reaction order determined experimentally
- reaction order can be fractional or negative

4.4.1 Reaction Order and Rate Constant Units

- units of rate constant depend on overall reaction order of rate law
- for reaction of second order overall
- units of rate = (units of rate constant)(units of concentration)^2
- units of rate constant = $M^{-1}s^{-1}$

- **zero order** – no change in rate when concentration changed
- **first order** – change in concentration gives proportional changes in rate
- **second order** – change in concentration changes rate by the square of the concentration change, such as 2^2 or 3^2, etc…
- rate constant does not depend on concentration

4.5: Integrated Rate Laws

- rate laws can be converted into equations that give concentrations of reactants or products

4.5.1 First-Order Reactions

$$rate = -\frac{\Delta[A]}{\Delta t} = k[A]$$

and in integral form:

$$\ln[A]_t - \ln[A]_0 = -kt$$

or

$$\ln\frac{[A]_t}{[A]_0} = -kt$$

$$\ln[A]_t = -kt + \ln[A]_0$$

- corresponds to a straight line with $y = mx + b$
- equations used to determine:
  1. concentration of reactant remaining at any time
  2. time required for given fraction of sample to react
  3. time required for reactant concentration to reach a certain level

4.5.2 Second-Order Reactions

- rate depends on reactant concentration raised to second power or concentrations of two different reactants each raised to first power

$$\text{Rate} = k[A]^2$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$half\ life = t_{\frac{1}{2}} = \frac{1}{k[A]_0}$$

- half life dependent on initial concentration of reactant

4.5.2 Zero-Order Reactions

- A zero-order reaction thus exhibits a constant reaction rate, regardless of the concentration of its reactants.

4.5.4 Half-Life

- half-life of first order reaction

$$t_{\frac{1}{2}} = -\frac{\ln\frac{1}{2}}{k} = \frac{0.693}{k}$$

- **half-life** – time required for concentration of reactant to drop to one-half of initial value
- $t_{1/2}$ of first order independent of initial concentrations
- half-life same at any given time of reaction
- in first order reaction – concentrations of reactant decreases by ½ in each series of regularly spaced time intervals

4.6: Collision Theory

- **collision model** – molecules must collide to react
- greater frequency of collisions the greater the reaction rate
- for most reactions only a small fraction of collisions leads to a reaction
- rate constant must increase with increasing temperature, thus increasing the rate of reaction

4.6.1 Activation Energy

- Svante August Arrhenius
- Molecules must have a minimum amount of energy to react
- Energy comes from kinetic energy of collisions
- Kinetic energy used to break bonds
- Activation energy, E_a – minimum energy required to initiate a chemical reaction
- Activated complex or transition state – atoms at the top of the energy barrier
- Rate depends on temperature and E_a
- Lower E_a means faster reaction
- Reactions occur when collisions between molecules occur with enough energy and proper orientation

4.6.1 The Arrhenius Equation

- reaction rate data:
- theArrhenius Equation:

$$k = Ae^{\frac{-E_a}{RT}}$$

- k = rate constant, E_a = activation energy, R = gas constant (8.314 J/(mol K)), T = absolute temperature, A = frequency factor
- A relates to frequency of collisions, favorable orientations

$$\ln k = -\frac{E_a}{RT} + \ln A$$

- the $\ln k$ vs. $1/t$ graph (also known as an Arrhenius plot) has a slope – E_a/R and the y-intercept $\ln A$
- for two temperatures:

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

- used to calculate rate constant, k_1 and T_1

4.7: Reaction Mechanisms

- **reaction mechanism** – process by which a reaction occurs

- **elementary steps** – each step in a reaction
- **molecularity** – if only one molecule involved in step
- **unimolecular** – if only one molecule involved in step
- **bimolecular** – elementary step involving collision of two reactant molecules
- **termolecular** – elementary step involving simultaneous collision of three molecules
- elementary steps in multi-step mechanism must always add to give chemical equation of overall process
- **intermediate** – product formed in one step and consumed in a later step

- if reaction is known to be an elementary step then the rate law is known
- rate of unimolecular step is first order (Rate = k[A])
- rate of bimolecular steps is second order (Rate = k[A][B])
- first order in [A] and [B]
- if double [A] than number of collisions of A and B will double

- **rate-determining step** – slowest elementary step
- determines rate law of overall reaction

- intermediates are usually unstable, in low concentration, and difficult to isolate
- when a fast step precedes a slow one, solve for concentration of intermediate by assuming that equilibrium is established in fast step

4.8: Catalysis

- **catalyst** – substance that changes speed of chemical reaction without undergoing a permanent chemical change

- **homogeneous catalyst** – catalyst that is present in same phase as reacting molecule
- catalysts alter E_a or A
- generally catalysts lowers overall E_a for chemical reaction
- catalysts provides a different mechanism for reaction

- Heterogeneous catalyst exists in different phase from reactants
  - initial step in heterogeneous catalyst is adsorption
  - **adsorption** – binding of molecules to surface
  - adsorption occurs because ions/atoms at surface of solid extremely reactive

- Enzymes are biological catalysts
  - large protein molecules with molecular weights 10,000 – 1 million amu
  - **catalase** – enzyme in blood and liver that decomposes hydrogen peroxide into water and oxygen
  - **substrates** – substances that undergo reaction at the active site
  - **lock-and-key model** – substrate molecules bind specifically to the active site
  - **enzyme-substrate complex** – combination of enzyme and substrate
  - binding between enzyme and substrate involves intermolecular forces (dipole-dipole, hydrogen bonding, and London dispersion forces)
  - product from reaction leaves enzyme allowing for another substrate to enter enzyme
  - **enzyme inhibitors** – molecules that bind strongly to enzymes
  - **turnover number** – number of catalyzed reactions occurring at a particular active site
  - large turnover numbers = low activation energies

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CHAPTER OVERVIEW

5: Chemical Equilibrium

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General Chemistry

In this chapter, you will learn how to predict the position of the balance and the yield of a product of a reaction under specific conditions, how to change a reaction's conditions to increase or reduce yield, and how to evaluate an equilibrium system's reaction to disturbances.

5.1: Prelude to Equilibrium
5.2: Chemical Equilibria
5.3: Equilibrium Constants
5.4: Equilibrium Calculations
5.5: Shifting Equilibria - Le Chatelier’s Principle
5.E: Fundamental Equilibrium Concepts (Exercises)
5.S: Fundamental Equilibrium Concepts (Study Guide)

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5.1: Prelude to Equilibrium

Imagine a beach populated with sunbathers and swimmers. As those basking in the sun get too hot and want to cool off, they head into the surf to swim. As the swimmers tire, they head to the beach to rest. If these two rates of transfer (sunbathers entering the water, swimmers leaving the water) are equal, the number of sunbathers and swimmers would be constant, or at equilibrium, although the identities of the people are constantly changing from sunbather to swimmer and back. An analogous situation occurs in chemical reactions. Reactions can occur in both directions simultaneously (reactants to products and products to reactants) and eventually reach a state of balance.

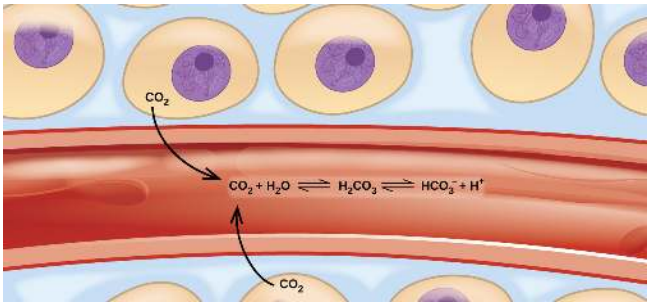


Figure 5.1.1: Movement of carbon dioxide through tissues and blood cells involves several equilibrium reactions.

An image depicts three tan squares, lying side-by-side along the upper left corner. Two of the same squares also lie side-by-side in the lower right corner. Each square has a black dot in the center. One of the squares is labeled, “C O subscript 2,” and has a double-headed arrow pointing from it to a red tube-like structure that runs between the squares across the image from the upper right to the lower left. This arrow is labeled, “C O subscript 2 dissolved in plasma.” The red tube has two round red shapes in it, and the upper one is labeled, “C O subscript 2 carried in red blood cells.” The gaps between the squares and the red tube are colored light blue. One of the squares along the top of the image is labeled, “C O subscript 2,” and is connected by a double-headed arrow to an equation in the red tube that is labeled, “C O subscript 2, a plus sign, H subscript 2 O, right-facing arrow, H subscript 2 C O subscript 3, right-facing arrow, H C O subscript 3 superscript negative sign, plus sign, H superscript positive sign.” The compound “H C O subscript 3 superscript negative sign” is then connected by a double-headed arrow to the space in the red tube and is labeled, “H C O subscript 3 superscript negative sign dissolved in plasma as carbonic acid.”

These balanced two-way reactions occur all around and even in us. For example, they occur in our blood, where the reaction between carbon dioxide and water forms carbonic acid (HCO_3^-) (Figure 5.1.1). Human physiology is adapted to the amount of ionized products produced by this reaction (HCO_3^- and H^+). In this chapter, you will learn how to predict the position of the balance and the yield of a product of a reaction under specific conditions, how to change a reaction's conditions to increase or reduce yield, and how to evaluate an equilibrium system's reaction to disturbances.

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5.2: Chemical Equilibria

Learning Objectives

- Describe the nature of equilibrium systems
- Explain the dynamic nature of a chemical equilibrium

A chemical reaction is usually written in a way that suggests it proceeds in one direction, the direction in which we read, but all chemical reactions are reversible, and both the forward and reverse reaction occur to one degree or another depending on conditions. In a chemical equilibrium, the forward and reverse reactions occur at equal rates, and the concentrations of products and reactants remain constant. If we run a reaction in a closed system so that the products cannot escape, we often find the reaction does not give a 100% yield of products. Instead, some reactants remain after the concentrations stop changing. At this point, when there is no further change in concentrations of reactants and products, we say the reaction is at equilibrium. A mixture of reactants and products is found at equilibrium.

For example, when we place a sample of dinitrogen tetroxide (N_2O_4, a colorless gas) in a glass tube, it forms nitrogen dioxide (NO_2, a brown gas) by the reaction

$$\mathrm{N_2O_4(g) \rightleftharpoons 2\,NO_2(g)} \tag{5.2.1}$$

The color becomes darker as $\mathrm{N_2O_4}$ is converted to $\mathrm{NO_2}$. When the system reaches equilibrium, both $\mathrm{N_2O_4}$ and $\mathrm{NO_2}$ are present (Figure 5.2.1).

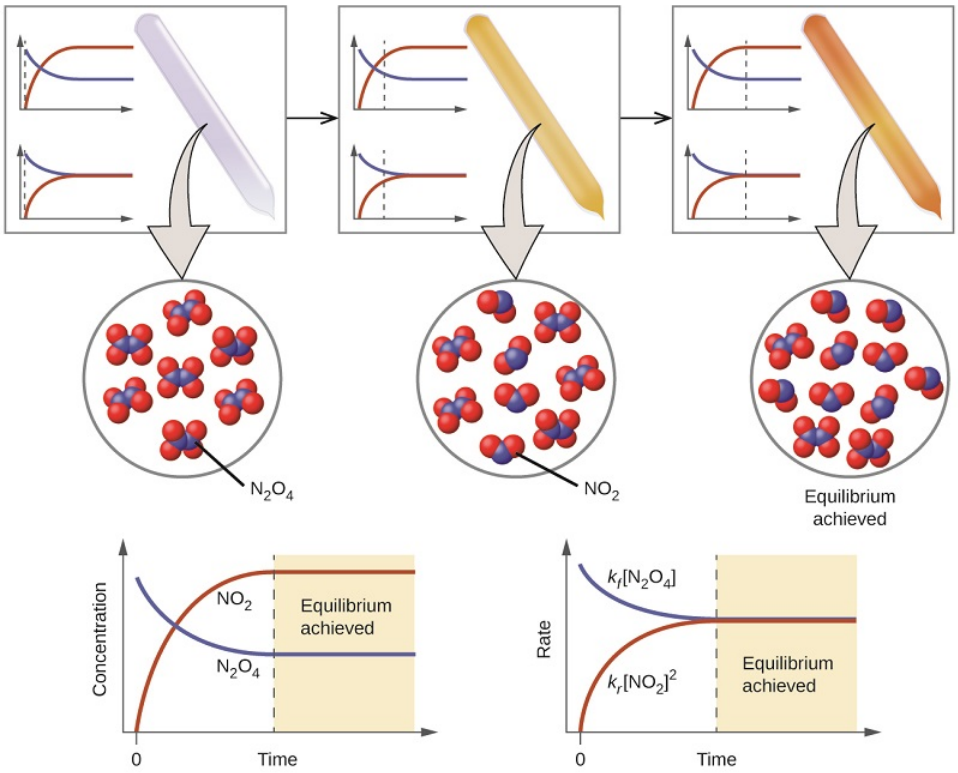


Figure 5.2.1: A mixture of $\mathrm{NO_2}$ and $\mathrm{N_2O_4}$ moves toward equilibrium. Colorless $\mathrm{N_2O_4}$ reacts to form brown $\mathrm{NO_2}$. As the reaction proceeds toward equilibrium, the color of the mixture darkens due to the increasing concentration of $\mathrm{NO_2}$.

The formation of $\mathrm{NO_2}$ from $\mathrm{N_2O_4}$ is a reversible reaction, which is identified by the equilibrium arrow ($\rightleftharpoons$). All reactions are reversible, but many reactions, for all practical purposes, proceed in one direction until the reactants are exhausted and will reverse only under certain conditions. Such reactions are often depicted with a one-way arrow from reactants to products. Many other reactions, such as the formation of $\mathrm{NO_2}$ from $\mathrm{N_2O_4}$, are reversible under more easily obtainable conditions and, therefore, are named as such. In a reversible reaction, the reactants can combine to form products and the products can react to form the reactants. Thus, not only can $\mathrm{N_2O_4}$ decompose to form $\mathrm{NO_2}$, but the $\mathrm{NO_2}$ produced can react to form $\mathrm{N_2O_4}$. As soon as the forward

reaction produces any NO_2, the reverse reaction begins and NO_2 starts to react to form N_2O_4. At equilibrium, the concentrations of N_2O_4 and NO_2 no longer change because the rate of formation of NO_2 is exactly equal to the rate of consumption of NO_2, and the rate of formation of N_2O_4 is exactly equal to the rate of consumption of N_2O_4. *Chemical equilibrium is a dynamic process*: As with the swimmers and the sunbathers, the numbers of each remain constant, yet there is a flux back and forth between them (Figure 5.2.2).



Figure 5.2.2: These jugglers provide an illustration of dynamic equilibrium. Each throws clubs to the other at the same rate at which he receives clubs from that person. Because clubs are thrown continuously in both directions, the number of clubs moving in each direction is constant, and the number of clubs each juggler has at a given time remains (roughly) constant.

In a chemical equilibrium, the forward and reverse reactions do not stop, rather they continue to occur at the same rate, leading to constant concentrations of the reactants and the products. Plots showing how the reaction rates and concentrations change with respect to time are shown in Figure 5.2.1.

We can detect a state of equilibrium because the concentrations of reactants and products do not appear to change. However, it is important that we verify that the absence of change is due to equilibrium and not to a reaction rate that is so slow that changes in concentration are difficult to detect.

We use a double arrow when writing an equation for a reversible reaction. Such a reaction may or may not be at equilibrium. For example, Figure 5.2.1 shows the reaction:

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \tag{5.2.2}$$

When we wish to speak about one particular component of a reversible reaction, we use a single arrow. For example, in the equilibrium shown in Figure 5.2.1, the rate of the forward reaction

$$2\,NO_2(g) \rightarrow N_2O_4(g) \tag{5.2.3}$$

is equal to the rate of the backward reaction

$$N_2O_4(g) \rightarrow 2\,NO_2(g) \tag{5.2.4}$$

Equilibrium and Soft Drinks

The connection between chemistry and carbonated soft drinks goes back to 1767, when Joseph Priestley (1733–1804; mostly known today for his role in the discovery and identification of oxygen) discovered a method of infusing water with carbon dioxide to make carbonated water. In 1772, Priestly published a paper entitled “Impregnating Water with Fixed Air.” The paper describes dripping oil of vitriol (today we call this sulfuric acid, but what a great way to describe sulfuric acid: “oil of vitriol” literally means “liquid nastiness”) onto chalk (calcium carbonate). The resulting CO_2 falls into the container of water beneath the vessel in which the initial reaction takes place; agitation helps the gaseous CO_2 mix into the liquid water.

$$H_2SO_4(l) + CaCO_3(s) \rightarrow CO_2(g) + H_2O(l) + CaSO_4(aq)$$

Carbon dioxide is slightly soluble in water. There is an equilibrium reaction that occurs as the carbon dioxide reacts with the water to form carbonic acid (H_2CO_3). Since carbonic acid is a weak acid, it can dissociate into protons (H^+) and hydrogen carbonate ions (HCO_3^-).

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$$

Today, CO_2 can be pressurized into soft drinks, establishing the equilibrium shown above. Once you open the beverage container, however, a cascade of equilibrium shifts occurs. First, the CO_2 gas in the air space on top of the bottle escapes, causing the equilibrium between gas-phase CO_2 and dissolved or aqueous CO_2 to shift, lowering the concentration of CO_2 in the soft drink. Less CO_2 dissolved in the liquid leads to carbonic acid decomposing to dissolved CO_2 and H_2O. The lowered carbonic acid concentration causes a shift of the final equilibrium. As long as the soft drink is in an open container, the CO_2 bubbles up out of the beverage, releasing the gas into the air (Figure 5.2.3). With the lid off the bottle, the CO_2 reactions are no longer at equilibrium and will continue until no more of the reactants remain. This results in a soft drink with a much lowered CO_2 concentration, often referred to as "flat."



Figure 5.2.3: When a soft drink is opened, several equilibrium shifts occur. (credit: modification of work by "D Coetzee"/Flickr)

A bottle of soda sitting on the ground is shown with a large amount of fizz-filled liquid spewing out of the top.

Sublimation of Bromine

Let us consider the evaporation of bromine as a second example of a system at equilibrium.

$$Br_2(l) \rightleftharpoons Br_2(g)$$

An equilibrium can be established for a physical change—like this liquid to gas transition—as well as for a chemical reaction. Figure 5.2.4 shows a sample of liquid bromine at equilibrium with bromine vapor in a closed container. When we pour liquid bromine into an empty bottle in which there is no bromine vapor, some liquid evaporates, the amount of liquid decreases, and the amount of vapor increases. If we cap the bottle so no vapor escapes, the amount of liquid and vapor will eventually stop changing and an equilibrium between the liquid and the vapor will be established. If the bottle were not capped, the bromine vapor would escape and no equilibrium would be reached.



Figure 5.2.4: An equilibrium is pictured between liquid bromine, $Br_2(l)$, the dark liquid, and bromine vapor, $Br_2(g)$, the orange gas. Because the container is sealed, bromine vapor cannot escape and equilibrium is maintained. (credit: Bromine [images-of-elements.com]).

A glass container is shown that is filled with an orange-brown gas and a small amount of dark orange liquid.

Summary

A reaction is at equilibrium when the amounts of reactants or products no longer change. Chemical equilibrium is a dynamic process, meaning the rate of formation of products by the forward reaction is equal to the rate at which the products re-form reactants by the reverse reaction.

Glossary

equilibrium

in chemical reactions, the state in which the conversion of reactants into products and the conversion of products back into reactants occur simultaneously at the same rate; state of balance

reversible reaction

chemical reaction that can proceed in both the forward and reverse directions under given conditions

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5.3: Equilibrium Constants

Learning Objectives

- Derive reaction quotients from chemical equations representing homogeneous and heterogeneous reactions
- Calculate values of reaction quotients and equilibrium constants, using concentrations and pressures
- Relate the magnitude of an equilibrium constant to properties of the chemical system

Now that we have a symbol ($\rightleftharpoons$) to designate reversible reactions, we will need a way to express mathematically how the amounts of reactants and products affect the equilibrium of the system. A general equation for a reversible reaction may be written as follows:

$$m\mathrm{A} + n\mathrm{B} + \rightleftharpoons x\mathrm{C} + y\mathrm{D} \tag{5.3.1}$$

We can write the reaction quotient (Q) for this equation. When evaluated using concentrations, it is called Q_c. We use brackets to indicate molar concentrations of reactants and products.

$$Q_c = \frac{[\mathrm{C}]^x[\mathrm{D}]^y}{[\mathrm{A}]^m[\mathrm{B}]^n} \tag{5.3.2}$$

The reaction quotient is equal to the molar concentrations of the products of the chemical equation (multiplied together) over the reactants (also multiplied together), with each concentration raised to the power of the coefficient of that substance in the balanced chemical equation. For example, the reaction quotient for the reversible reaction

$$2\,\mathrm{NO}_{2(g)} \rightleftharpoons \mathrm{N_2O}_{4(g)} \tag{5.3.3}$$

is given by this expression:

$$Q_c = \frac{[\mathrm{N_2O_4}]}{[\mathrm{NO_2}]^2} \tag{5.3.4}$$

Example 5.3.1: Writing Reaction Quotient Expressions

Write the expression for the reaction quotient for each of the following reactions:

a. $3\,\mathrm{O}_{2(g)} \rightleftharpoons 2\,\mathrm{O}_{3(g)}$
b. $\mathrm{N}_{2(g)} + 3\,\mathrm{H}_{2(g)} \rightleftharpoons 2\,\mathrm{NH}_{3(g)}$
c. $4\,\mathrm{NH}_{3(g)} + 7\,\mathrm{O}_{2(g)} \rightleftharpoons 4\,\mathrm{NO}_{2(g)} + 6\,\mathrm{H_2O}_{(g)}$

Solution

a. $Q_c = \dfrac{[\mathrm{O_3}]^2}{[\mathrm{O_2}]^3}$
b. $Q_c = \dfrac{[\mathrm{NH_3}]^2}{[\mathrm{N_2}][\mathrm{H_2}]^3}$
c. $Q_c = \dfrac{[\mathrm{NO_2}]^4[\mathrm{H_2O}]^6}{[\mathrm{NH_3}]^4[\mathrm{O_2}]^7}$

Exercise 5.3.1

Write the expression for the reaction quotient for each of the following reactions:

a. $2\,\mathrm{SO}_2(g) + \mathrm{O}_2(g) \rightleftharpoons 2\,\mathrm{SO}_3(g)$
b. $\mathrm{C_4H_8}(g) \rightleftharpoons 2\,\mathrm{C_2H_4}(g)$
c. $2\,\mathrm{C_4H_{10}}(g) + 13\,\mathrm{O}_2(g) \rightleftharpoons 8\,\mathrm{CO}_2(g) + 10\,\mathrm{H_2O}(g)$

Answer a

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

Answer b

$$Q_c = \frac{[C_2H_4]^2}{[C_4H_8]}$$

Answer c

$$Q_c = \frac{[CO_2]^8[H_2O]^{10}}{[C_4H_{10}]^2[O_2]^{13}}$$

The numeric value of Q_c for a given reaction varies; it depends on the concentrations of products and reactants present at the time when Q_c is determined. When pure reactants are mixed, Q_c is initially zero because there are no products present at that point. As the reaction proceeds, the value of Q_c increases as the concentrations of the products increase and the concentrations of the reactants simultaneously decrease (Figure 5.3.1). When the reaction reaches equilibrium, the value of the reaction quotient no longer changes because the concentrations no longer change.

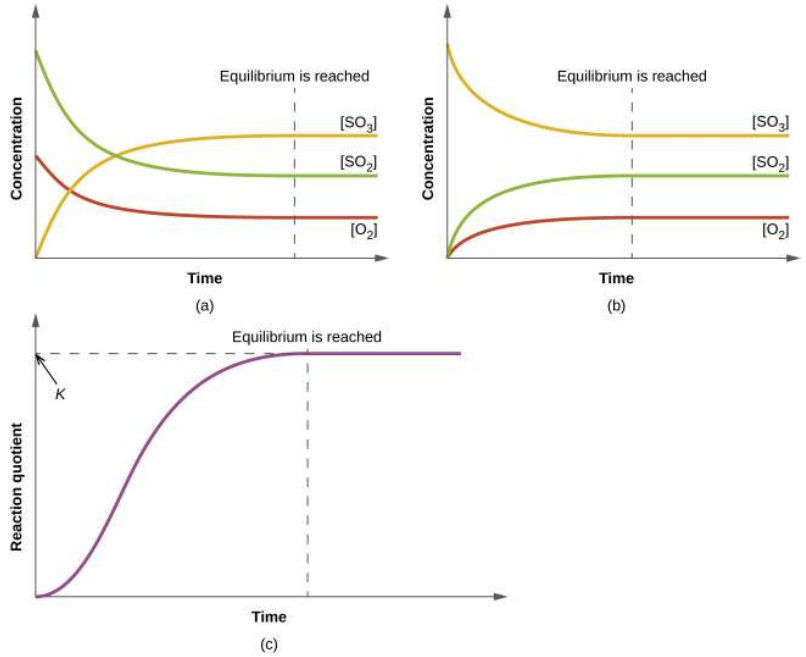


Figure 5.3.1: (a) The change in the concentrations of reactants and products is depicted as the $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$ reaction approaches equilibrium. (b) The change in concentrations of reactants and products is depicted as the reaction $2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g)$ approaches equilibrium. (c) The graph shows the change in the value of the reaction quotient as the reaction approaches equilibrium.

When a mixture of reactants and products of a reaction reaches equilibrium at a given temperature, its reaction quotient always has the same value. This value is called the equilibrium constant (K) of the reaction at that temperature. As for the reaction quotient, when evaluated in terms of concentrations, it is noted as K_c.

That a reaction quotient always assumes the same value at equilibrium can be expressed as:

$$Q_c \text{ at equilibrium} = K_c = \frac{[C]^x[D]^y\ldots}{[A]^m[B]^n\ldots} \tag{5.3.5}$$

This equation is a mathematical statement of the law of mass action: When a reaction has attained equilibrium at a given temperature, the reaction quotient for the reaction always has the same value.

Example 5.3.2: Evaluating a Reaction Quotient

Gaseous nitrogen dioxide forms dinitrogen tetroxide according to this equation:

$$2\,NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$$

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

a. Before any product is formed, $[NO_2] = \dfrac{0.10\text{ mol}}{1.0\text{ L}} = 0.10\ M$, and [$N_2O_4$] = 0 *M*. Thus,

$$Q_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0}{0.10^2} = 0$$

b. At equilibrium, the value of the equilibrium constant is equal to the value of the reaction quotient. At equilibrium,

$$K_c = Q_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0.042}{0.016^2} = 1.6 \times 10^2.$$

The equilibrium constant is 1.6 × 10^2.

Note that dimensional analysis would suggest the unit for this K_c value should be M^{-1}. However, it is common practice to omit units for K_c values computed as described here, since it is the magnitude of an equilibrium constant that relays useful information. As will be discussed later in this module, the rigorous approach to computing equilibrium constants uses dimensionless quantities derived from activities instead of molar concentrations, and so K_c values are truly unitless.

Exercise 5.3.2

For the reaction

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$$

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?

Answer

K_c = 4.3

The magnitude of an equilibrium constant is a measure of the yield of a reaction when it reaches equilibrium. A large value for K_c indicates that equilibrium is attained only after the reactants have been largely converted into products. A small value of K_c—much less than 1—indicates that equilibrium is attained when only a small proportion of the reactants have been converted into products.

Once a value of K_c is known for a reaction, it can be used to predict directional shifts when compared to the value of Q_c. A system that is not at equilibrium will proceed in the direction that establishes equilibrium. The data in Figure 5.3.2 illustrate this. When heated to a consistent temperature, 800 °C, different starting mixtures of CO, H_2O, CO_2, and H_2 react to reach compositions adhering to the same equilibrium (the value of Q_c changes until it equals the value of K_c). This value is 0.640, the equilibrium constant for the reaction under these conditions.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \quad K_c = 0.640 \quad T = 800^\circ C \tag{5.3.6}$$

It is important to recognize that an equilibrium can be established starting either from reactants or from products, or from a mixture of both. For example, equilibrium was established from Mixture 2 in Figure 5.3.2 when the products of the reaction were heated in a closed container. In fact, one technique used to determine whether a reaction is truly at equilibrium is to approach equilibrium

starting with reactants in one experiment and starting with products in another. If the same value of the reaction quotient is observed when the concentrations stop changing in both experiments, then we may be certain that the system has reached equilibrium.

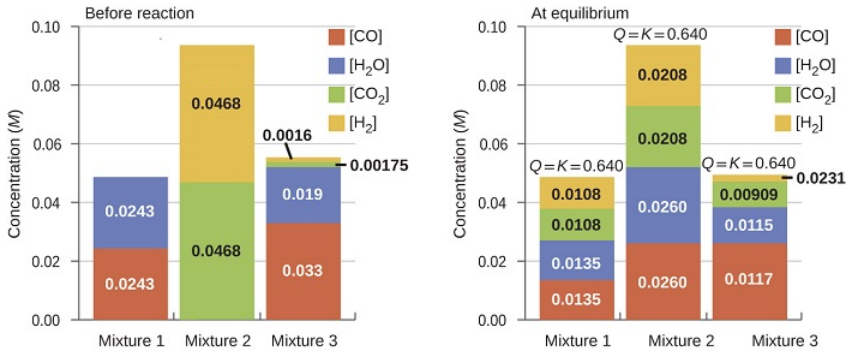


Figure 5.3.2: Concentrations of three mixtures are shown before and after reaching equilibrium at 800 °C for the so-called water gas shift reaction (Equation 5.3.6).

Example 5.3.3: Predicting the Direction of Reaction

Given here are the starting concentrations of reactants and products for three experiments involving this reaction:

$$\mathrm{CO}(g) + \mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO_2}(g) + \mathrm{H_2}(g)$$

with $K_c = 0.64$. Determine in which direction the reaction proceeds as it goes to equilibrium in each of the three experiments shown.

Reactant/Products for Three Experiments

Reactants/Products	Experiment 1	Experiment 2	Experiment 3
$[\mathrm{CO}]_i$	0.0203 M	0.011 M	0.0094 M
$[\mathrm{H_2O}]_i$	0.0203 M	0.0011 M	0.0025 M
$[\mathrm{CO_2}]_i$	0.0040 M	0.037 M	0.0015 M
$[\mathrm{H_2}]_i$	0.0040 M	0.046 M	0.0076 M

Solution

Experiment 1:

$$Q_c = \frac{[\mathrm{CO_2}][\mathrm{H_2}]}{[\mathrm{CO}][\mathrm{H_2O}]} = \frac{(0.0040)(0.0040)}{(0.0203)(0.0203)} = 0.039.$$

$Q_c < K_c$ (0.039 < 0.64)

The reaction will shift to the right.

Experiment 2:

$$Q_c = \frac{[\mathrm{CO_2}][\mathrm{H_2}]}{[\mathrm{CO}][\mathrm{H_2O}]} = \frac{(0.037)(0.046)}{(0.011)(0.0011)} = 1.4 \times 10^2$$

$Q_c > K_c$ (140 > 0.64)

The reaction will shift to the left.

Experiment 3:

$$Q_c = \frac{[\mathrm{CO_2}][\mathrm{H_2}]}{[\mathrm{CO}][\mathrm{H_2O}]} = \frac{(0.0015)(0.0076)}{(0.0094)(0.0025)} = 0.48$$

$Q_c < K_c$ (0.48 < 0.64)

The reaction will shift to the right.

? Exercise 5.3.3

Calculate the reaction quotient and determine the direction in which each of the following reactions will proceed to reach equilibrium.

(a) 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:

$$2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g) \quad K_c = 4.6 \times 10^4$$

(b) A 5.0-L flask containing 17 g of NH_3, 14 g of N_2, and 12 g of H_2:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \quad K_c = 0.060$$

(c) A 2.00-L flask containing 230 g of SO_3(g):

$$2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g) \quad K_c = 0.230$$

Answer a

Q_c = 6.45 × 10^3, shifts right.

Answer b

Q_c = 0.12, shifts left.

Answer c

Q_c = 0, shifts right

In Example 5.3.2, it was mentioned that the common practice is to omit units when evaluating reaction quotients and equilibrium constants. It should be pointed out that using concentrations in these computations is a convenient but simplified approach that sometimes leads to results that seemingly conflict with the law of mass action. For example, equilibria involving aqueous ions often exhibit equilibrium constants that vary quite significantly (are *not* constant) at high solution concentrations. This may be avoided by computing K_c values using the *activities* of the reactants and products in the equilibrium system instead of their concentrations. The activity of a substance is a measure of its effective concentration under specified conditions. While a detailed discussion of this important quantity is beyond the scope of an introductory text, it is necessary to be aware of a few important aspects:

- Activities are dimensionless (**unitless**) quantities and are in essence “adjusted” concentrations.
- For relatively dilute solutions, a solute's activity and its molar concentration are roughly equal.
- Activities for pure condensed phases (solids and liquids) are equal to 1.
- Activities for solvents in dilute solutions are equal to 1.

As a consequence of this last two aspects, Q_c and K_c expressions do not contain terms for solids or liquids or solvents in dilute solutions (being numerically equal to 1, these terms have no effect on the expression's value). Several examples of equilibria yielding such expressions will be encountered in this section.

5.3.1: Homogeneous Equilibria

A homogeneous equilibrium is one in which all of the reactants and products are present in a single solution (by definition, a homogeneous mixture). In this chapter, we will concentrate on the two most common types of homogeneous equilibria: those occurring in liquid-phase solutions and those involving exclusively gaseous species. Reactions between solutes in liquid solutions belong to one type of homogeneous equilibria. The chemical species involved can be molecules, ions, or a mixture of both. Several examples are provided here:

Example 1

$$C_2H_2(aq) + 2\,Br_2(aq) \rightleftharpoons C_2H_2Br_4(aq) \tag{5.3.7}$$

with associated equilibrium constant

$$K_c = \frac{[C_2H_2Br_4]}{[C_2H_2][Br_2]^2} \tag{5.3.8}$$

Example 2

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \tag{5.3.9}$$

with associated equilibrium constant

$$K_c = \frac{[I_3^-]}{[I_2][I^-]} \tag{5.3.10}$$

Example 3

$$Hg_2^{2+}(aq) + NO_3^-(aq) + 3\,H_3O^+(aq) \rightleftharpoons 2\,Hg^{2+}(aq) + HNO_2(aq) + 4\,H_2O(l) \tag{5.3.11}$$

with associated equilibrium constant

$$K_c = \frac{[Hg^{2+}]^2[HNO_2]}{[Hg_2^{2+}][NO_3^-][H_3O^+]^3} \tag{5.3.12}$$

Example 4

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq) \tag{5.3.13}$$

with associated equilibrium constant

$$K_c = \frac{[H_3O^+][F^-]}{[HF]} \tag{5.3.14}$$

Example 5

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \tag{5.3.15}$$

with associated equilibrium constant

$$K_c = \frac{[NH_4^+][OH^-]}{[NH_3]} \tag{5.3.16}$$

In each of these examples, the equilibrium system is an aqueous solution, as denoted by the *aq* annotations on the solute formulas. Since $H_2O(l)$ is the solvent for these solutions, it is assigned an activity of 1, and thus **does not** appear explicitly as a term in the K_c expression, as discussed earlier, even though it may also appear as a reactant or product in the chemical equation.

Reactions in which all reactants and products are gases represent a second class of homogeneous equilibria. We use molar concentrations in the following examples, but we will see shortly that partial pressures of the gases may be used as well:

Example 1

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g) \tag{5.3.17}$$

with associated equilibrium constant

$$K_c = \frac{[C_2H_4][H_2]}{[C_2H_6]} \tag{5.3.18}$$

Example 2

$$3\,O_2(g) \rightleftharpoons 2\,O_3(g) \tag{5.3.19}$$

with associated equilibrium constant

$$K_c = \frac{[O_3]^2}{[O_2]^3} \tag{5.3.20}$$

Example 3

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{NH_3}(g) \tag{5.3.21}$$

with associated equilibrium constant

$$K_c = \frac{[\mathrm{NH_3}]^2}{[\mathrm{N_2}][\mathrm{H_2}]^3} \tag{5.3.22}$$

Example 4

$$\mathrm{C_3H_8}(g) + 5\,\mathrm{O_2}(g) \rightleftharpoons 3\,\mathrm{CO_2}(g) + 4\,\mathrm{H_2O}(g) \tag{5.3.23}$$

with associated equilibrium constant

$$K_c = \frac{[\mathrm{CO_2}]^3[\mathrm{H_2O}]^4}{[\mathrm{C_3H_8}][\mathrm{O_2}]^5} \tag{5.3.24}$$

Note that the concentration of $\mathrm{H_2O}_{(g)}$ has been included in the last example because water is not the solvent in this gas-phase reaction and its concentration (and activity) changes.

Whenever gases are involved in a reaction, the partial pressure of each gas can be used instead of its concentration in the equation for the reaction quotient because the partial pressure of a gas is directly proportional to its concentration at constant temperature. This relationship can be derived from the ideal gas equation, where *M* is the molar concentration of gas, $\frac{n}{V}$.

$$PV = nRT \tag{5.3.25}$$

$$P = \left(\frac{n}{V}\right) RT \tag{5.3.26}$$

$$= MRT \tag{5.3.27}$$

Thus, at constant temperature, the pressure of a gas is **directly proportional** to its concentration. Using the partial pressures of the gases, we can write the reaction quotient for the system

$$\mathrm{C_2H_6}(g) \rightleftharpoons \mathrm{C_2H_4}(g) + \mathrm{H_2}(g) \tag{5.3.28}$$

by following the same guidelines for deriving concentration-based expressions:

$$Q_P = \frac{P_{\mathrm{C_2H_4}} P_{\mathrm{H_2}}}{P_{\mathrm{C_2H_6}}} \tag{5.3.29}$$

In this equation we use Q_P to indicate a reaction quotient written with partial pressures: $P_{\mathrm{C_2H_6}}$ is the partial pressure of $\mathrm{C_2H_6}$; $P_{\mathrm{H_2}}$, the partial pressure of $\mathrm{H_2}$; and $P_{\mathrm{C_2H_6}}$, the partial pressure of $\mathrm{C_2H_4}$. At equilibrium:

$$K_P = Q_P = \frac{P_{\mathrm{C_2H_4}} P_{\mathrm{H_2}}}{P_{\mathrm{C_2H_6}}} \tag{5.3.30}$$

The subscript P in the symbol K_P designates an equilibrium constant derived using partial pressures instead of concentrations. The equilibrium constant, K_P, is still a constant, but its numeric value may differ from the equilibrium constant found for the same reaction by using concentrations.

Conversion between a value for K_c, an equilibrium constant expressed in terms of concentrations, and a value for K_P, an equilibrium constant expressed in terms of pressures, is straightforward (a K or Q without a subscript could be either concentration or pressure).

The equation relating K_c and K_P is derived as follows. For the gas-phase reaction:

$$m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D} \tag{5.3.31}$$

with

$$K_P = \frac{(P_C)^x (P_D)^y}{(P_A)^m (P_B)^n} \tag{5.3.32}$$

$$= \frac{([\mathrm{C}] \times RT)^x ([\mathrm{D}] \times RT)^y}{([\mathrm{A}] \times RT)^m ([\mathrm{B}] \times RT)^n} \tag{5.3.33}$$

$$= \frac{[\mathrm{C}]^x [\mathrm{D}]^y}{[\mathrm{A}]^m [\mathrm{B}]^n} \times \frac{(RT)^{x+y}}{(RT)^{m+n}} \tag{5.3.34}$$

$$= K_c (RT)^{(x+y)-(m+n)} \tag{5.3.35}$$

$$= K_c (RT)^{\Delta n} \tag{5.3.36}$$

The relationship between K_c and K_P is

$$K_P = K_c (RT)^{\Delta n} \tag{5.3.37}$$

In this equation, Δn is the difference between the sum of the coefficients of the *gaseous* products and the sum of the coefficients of the *gaseous* reactants in the reaction (the change in moles of gas between the reactants and the products). For the gas-phase reaction $m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$, we have

$$\Delta n = (x + y) - (m + n) \tag{5.3.38}$$

Example 5.3.4: Calculation of K_P

Write the equations for the conversion of K_c to K_P for each of the following reactions:

a. $\mathrm{C_2H_6}(g) \rightleftharpoons \mathrm{C_2H_4}(g) + \mathrm{H_2}(g)$
b. $\mathrm{CO}(g) + \mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO_2}(g) + \mathrm{H_2}(g)$
c. $\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{NH_3}(g)$
d. K_c is equal to 0.28 for the following reaction at 900 °C:

$$\mathrm{CS_2}(g) + 4\,\mathrm{H_2}(g) \rightleftharpoons \mathrm{CH_4}(g) + 2\,\mathrm{H_2S}(g)$$

What is K_P at this temperature?

Solution

(a) $\Delta n = (2) - (1) = 1$

$$K_P = K_c\,(RT)^{\Delta n} = K_c\,(RT)^1 = K_c\,(RT)$$

(b) $\Delta n = (2) - (2) = 0$

$$K_P = K_c\,(RT)^{\Delta n} = K_c\,(RT)^0 = K_c$$

(c) $\Delta n = (2) - (1 + 3) = -2$

$$K_P = K_c\,(RT)^{\Delta n} = K_c\,(RT)^{-2} = \frac{K_c}{(RT)^2}$$

d) $K_P = K_c\,(\mathrm{RT})^{\Delta n} = (0.28)[(0.0821)(1173)]^{-2} = 3.0 \times 10^{-5}$

Exercise 5.3.4

Write the equations for the conversion of K_c to K_P for each of the following reactions, which occur in the gas phase:

a. $2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{SO_3}(g)$
b. $\mathrm{N_2O_4}(g) \rightleftharpoons 2\,\mathrm{NO_2}(g)$
c. $\mathrm{C_3H_8}(g) + 5\,\mathrm{O_2}(g) \rightleftharpoons 3\,\mathrm{CO_2}(g) + 4\,\mathrm{H_2O}(g)$
d. At 227 °C, the following reaction has K_c = 0.0952:

$$\mathrm{CH_3OH}(g) \rightleftharpoons \mathrm{CO}(g) + 2\,\mathrm{H_2}(g)$$

What would be the value of K_P at this temperature?

Answer a

$K_P = K_c\,(RT)^{-1}$

Answer b

$K_P = K_c\,(RT)$

Answer c

$K_P = K_c\,(RT)$;

Answer d

160 or 1.6×10^2

5.3.2: Heterogeneous Equilibria

A heterogeneous equilibrium is a system in which reactants and products are found in two or more phases. The phases may be any combination of solid, liquid, or gas phases, and solutions. When dealing with these equilibria, remember that solids and pure liquids do not appear in equilibrium constant expressions (the activities of pure solids, pure liquids, and solvents are 1).

Some heterogeneous equilibria involve chemical changes:

Example 1

$$\mathrm{PbCl_2}(s) \rightleftharpoons \mathrm{Pb^{2+}}(aq) + 2\,\mathrm{Cl^-}(aq) \tag{5.3.39}$$

with associated equilibrium constant

$$K_c = [\mathrm{Pb^{2+}}][\mathrm{Cl^-}]^2 \tag{5.3.40}$$

Example 1

$$\mathrm{CaO}(s) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{CaCO_3}(s) \tag{5.3.41}$$

with associated equilibrium constant

$$K_c = \frac{1}{[\mathrm{CO_2}]} \tag{5.3.42}$$

Example 1

$$\mathrm{C}(s) + 2\,\mathrm{S}(g) \rightleftharpoons \mathrm{CS_2}(g) \tag{5.3.43}$$

with associated equilibrium constant

$$K_c = \frac{[\mathrm{CS_2}]}{[\mathrm{S}]^2} \tag{5.3.44}$$

Other heterogeneous equilibria involve phase changes, for example, the evaporation of liquid bromine, as shown in the following equation:

$$\mathrm{Br_2}(l) \rightleftharpoons \mathrm{Br_2}(g) \tag{5.3.45}$$

with associated equilibrium constant

$$K_c = [\mathrm{Br_2}] \tag{5.3.46}$$

We can write equations for reaction quotients of heterogeneous equilibria that involve gases, using **partial pressures** instead of concentrations. Two examples are:

$$\mathrm{CaO}(s) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{CaCO_3}(s) \tag{5.3.47}$$

with associated equilibrium constant

$$K_P = \frac{1}{P_{\mathrm{CO_2}}} \tag{5.3.48}$$

$$\mathrm{C}(s) + 2\,\mathrm{S}(g) \rightleftharpoons \mathrm{CS_2}(g) \tag{5.3.49}$$

with associated equilibrium constant

$$K_P = \frac{P_{\mathrm{CS_2}}}{(P_{\mathrm{S}})^2} \tag{5.3.50}$$

Summary

For any reaction that is at equilibrium, the reaction quotient *Q* is equal to the equilibrium constant *K* for the reaction. If a reactant or product is a pure solid, a pure liquid, or the solvent in a dilute solution, the concentration of this component does not appear in the expression for the equilibrium constant. At equilibrium, the values of the concentrations of the reactants and products are constant. Their particular values may vary depending on conditions, but the value of the reaction quotient will always equal *K* (K_c when using concentrations or K_P when using partial pressures).

A homogeneous equilibrium is an equilibrium in which all components are in the same phase. A heterogeneous equilibrium is an equilibrium in which components are in two or more phases. We can decide whether a reaction is at equilibrium by comparing the reaction quotient with the equilibrium constant for the reaction.

5.3.3: Key Equations

- $Q = \dfrac{[\mathrm{C}]^x[\mathrm{D}]^y}{[\mathrm{A}]^m[\mathrm{B}]^n}$ where $m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$
- $Q_P = \dfrac{(P_C)^x(P_D)^y}{(P_A)^m(P_B)^n}$ where $m\mathrm{A} + n\mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$
- $P = MRT$
- $K_P = K_c\,(RT)^{\Delta n}$

Glossary

equilibrium constant (*K*)
value of the reaction quotient for a system at equilibrium

heterogeneous equilibria
equilibria between reactants and products in different phases

homogeneous equilibria
equilibria within a single phase

***K*$_c$**
equilibrium constant for reactions based on concentrations of reactants and products

***K*$_P$**
equilibrium constant for gas-phase reactions based on partial pressures of reactants and products

law of mass action
when a reversible reaction has attained equilibrium at a given temperature, the reaction quotient remains constant

reaction quotient (*Q*)
ratio of the product of molar concentrations (or pressures) of the products to that of the reactants, each concentration (or pressure) being raised to the power equal to the coefficient in the equation

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5.4: Equilibrium Calculations

Learning Objectives

- Write equations representing changes in concentration and pressure for chemical species in equilibrium systems
- Use algebra to perform various types of equilibrium calculations

We know that at equilibrium, the value of the reaction quotient of any reaction is equal to its equilibrium constant. Thus, we can use the mathematical expression for *Q* to determine a number of quantities associated with a reaction at equilibrium or approaching equilibrium. While we have learned to identify in which direction a reaction will shift to reach equilibrium, we want to extend that understanding to quantitative calculations. We do so by evaluating the ways that the concentrations of products and reactants change as a reaction approaches equilibrium, keeping in mind the stoichiometric ratios of the reaction. This algebraic approach to equilibrium calculations will be explored in this section.

Changes in concentrations or pressures of reactants and products occur as a reaction system approaches equilibrium. In this section we will see that we can relate these changes to each other using the coefficients in the balanced chemical equation describing the system. We use the decomposition of ammonia as an example.

On heating, ammonia reversibly decomposes into nitrogen and hydrogen according to this equation:

$$2\,\mathrm{NH_3}(g) \rightleftharpoons \mathrm{N_2}(g) + 3\,\mathrm{H_2}(g)$$

If a sample of ammonia decomposes in a closed system and the concentration of $\mathrm{N_2}$ increases by 0.11 *M*, the change in the $\mathrm{N_2}$ concentration, $\Delta[\mathrm{N_2}]$, the final concentration minus the initial concentration, is 0.11 *M*. The change is positive because the concentration of $\mathrm{N_2}$ increases.

The change in the $\mathrm{H_2}$ concentration, $\Delta[\mathrm{H_2}]$, is also positive—the concentration of $\mathrm{H_2}$ increases as ammonia decomposes. The chemical equation tells us that the change in the concentration of $\mathrm{H_2}$ is three times the change in the concentration of $\mathrm{N_2}$ because for each mole of $\mathrm{N_2}$ produced, 3 moles of $\mathrm{H_2}$ are produced.

$$\begin{aligned}\Delta[\mathrm{H_2}] &= 3 \times \Delta[\mathrm{N_2}] \\ &= 3 \times (0.11\ M) \\ &= 0.33\ M\end{aligned}$$

The change in concentration of $\mathrm{NH_3}$, $\Delta[\mathrm{NH_3}]$, is twice that of $\Delta[\mathrm{N_2}]$; the equation indicates that 2 moles of $\mathrm{NH_3}$ must decompose for each mole of $\mathrm{N_2}$ formed. However, the change in the $\mathrm{NH_3}$ concentration is negative because the concentration of ammonia *decreases* as it decomposes.

$$\begin{aligned}\Delta[\mathrm{NH_3}] &= -2 \times \Delta[\mathrm{N_2}] \\ &= -2 \times (0.11\ M) \\ &= -0.22\ M\end{aligned}$$

We can relate these relationships directly to the coefficients in the equation

$$\begin{array}{ccccc} 2\,\mathrm{NH_3}(g) & \rightleftharpoons & \mathrm{N_2}(g) & + & 3\,\mathrm{H_2}(g) \\ \Delta[\mathrm{NH_3}] = -2 \times \Delta[\mathrm{N_2}] & & \Delta[\mathrm{N_2}] = 0.11\ M & & \Delta[\mathrm{H_2}] = 3 \times \Delta[\mathrm{N_2}] \end{array} \quad (5.4.1)\ (5.4.2)$$

Note that all the changes on one side of the arrows are of the same sign and that all the changes on the other side of the arrows are of the opposite sign.

If we did not know the magnitude of the change in the concentration of $\mathrm{N_2}$, we could represent it by the symbol *x*.

$$\Delta[\mathrm{N_2}] = x$$

The changes in the other concentrations would then be represented as:

$$\Delta[\mathrm{H_2}] = 3 \times \Delta[\mathrm{N_2}] = 3x$$
$$\Delta[\mathrm{NH_3}] = -2 \times \Delta[\mathrm{N_2}] = -2x$$

The coefficients in the Δ terms are identical to those in the balanced equation for the reaction.

$$2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g) \tag{5.4.3}$$
$$-2x \qquad x \qquad 3x \tag{5.4.4}$$

The simplest way for us to find the coefficients for the concentration changes in any reaction is to use the coefficients in the balanced chemical equation. The sign of the coefficient is positive when the concentration increases; it is negative when the concentration decreases.

Example 5.4.1: Determining Relative Changes in Concentration

Complete the changes in concentrations for each of the following reactions.

(a)

$$C_2H_2(g) + 2\,Br_2(g) \rightleftharpoons C_2H_2Br_4(g) \tag{5.4.5}$$
$$x \qquad ____ \qquad ____ \tag{5.4.6}$$

(b)

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \tag{5.4.7}$$
$$____ \qquad ____ \qquad x \tag{5.4.8}$$

(c)

$$C_3H_8(g) + 5\,O_2(g) \rightleftharpoons 3\,CO_2(g) + 4\,H_2O(g) \tag{5.4.9}$$
$$x \qquad ____ \qquad ____ \qquad ____ \tag{5.4.10}$$

Solution

(a)

$$C_2H_2(g) + 2\,Br_2(g) \rightleftharpoons C_2H_2Br_4(g) \tag{5.4.11}$$
$$x \qquad 2x \qquad -x \tag{5.4.12}$$

(b)

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \tag{5.4.13}$$
$$-x \qquad -x \qquad x \tag{5.4.14}$$

(c)

$$C_3H_8(g) + 5\,O_2(g) \rightleftharpoons 3\,CO_2(g) + 4\,H_2O(g) \tag{5.4.15}$$
$$x \qquad 5x \qquad -3x \qquad -4x \tag{5.4.16}$$

Exercise 5.4.1

Complete the changes in concentrations for each of the following reactions:

(a)

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g) \tag{5.4.17}$$
$$____ \qquad x \qquad ____ \tag{5.4.18}$$

(b)

$$C_4H_8(g) \rightleftharpoons 2\,C_2H_4(g) \tag{5.4.19}$$
$$____ \qquad -2x \tag{5.4.20}$$

(c)

$$4\,NH_3(g) + 7\,H_2O(g) \rightleftharpoons 4\,NO_2(g) + 6\,H_2O(g) \tag{5.4.21}$$
$$____ \qquad ____ \qquad ____ \qquad ____ \tag{5.4.22}$$

Answer a

$2x$, x, $-2x$

Answer b

x, $-2x$

Answer c

$4x$, $7x$, $-4x$, $-6x$ or $-4x$, $-7x$, $4x$, $6x$

5.4.0.1: Calculations Involving Equilibrium Concentrations

Because the value of the reaction quotient of any reaction at equilibrium is equal to its equilibrium constant, we can use the mathematical expression for Q_c (i.e., *the law of mass action*) to determine a number of quantities associated with a reaction at equilibrium. It may help if we keep in mind that $Q_c = K_c$ (at equilibrium) in all of these situations and that there are only three basic types of calculations:

1. **Calculation of an equilibrium constant**. If concentrations of reactants and products at equilibrium are known, the value of the equilibrium constant for the reaction can be calculated.
2. **Calculation of missing equilibrium concentrations**. If the value of the equilibrium constant and all of the equilibrium concentrations, except one, are known, the remaining concentration can be calculated.
3. **Calculation of equilibrium concentrations from initial concentrations**. If the value of the equilibrium constant and a set of concentrations of reactants and products that are not at equilibrium are known, the concentrations at equilibrium can be calculated.

A similar list could be generated using Q_P, K_P, and partial pressure. We will look at solving each of these cases in sequence.

5.4.1: Calculation of an Equilibrium Constant

Since the law of mass action is the only equation we have to describe the relationship between K_c and the concentrations of reactants and products, any problem that requires us to solve for K_c must provide enough information to determine the reactant and product concentrations at equilibrium. Armed with the concentrations, we can solve the equation for K_c, as it will be the only unknown.

Example 5.4.1 showed us how to determine the equilibrium constant of a reaction if we know the concentrations of reactants and products at equilibrium. The following example shows how to use the stoichiometry of the reaction and a combination of initial concentrations and equilibrium concentrations to determine an equilibrium constant. This technique, commonly called an ICE table —for **I**nitial, **C**hange, and **E**quilibrium–will be helpful in solving many equilibrium problems. A chart is generated beginning with the equilibrium reaction in question. Underneath the reaction the initial concentrations of the reactants and products are listed—these conditions are usually provided in the problem and we consider no shift toward equilibrium to have happened. The next row of data is the change that occurs as the system shifts toward equilibrium—do not forget to consider the reaction stoichiometry as described in a previous section of this chapter. The last row contains the concentrations once equilibrium has been reached.

Example 5.4.2: Calculation of an Equilibrium Constant

Iodine molecules react reversibly with iodide ions to produce triiodide ions.

$$\mathrm{I_2}(aq) + \mathrm{I^-}(aq) \rightleftharpoons \mathrm{I_3^-}(aq)$$

If a solution with the concentrations of $\mathrm{I_2}$ and $\mathrm{I^-}$ both equal to 1.000×10^{-3} M before reaction gives an equilibrium concentration of $\mathrm{I_2}$ of 6.61×10^{-4} M, what is the equilibrium constant for the reaction?

Solution

We will begin this problem by calculating the changes in concentration as the system goes to equilibrium. Then we determine the equilibrium concentrations and, finally, the equilibrium constant. First, we set up a table with the initial concentrations, the changes in concentrations, and the equilibrium concentrations using $-x$ as the change in concentration of $\mathrm{I_2}$.

	$\mathrm{I_2}$ + $\mathrm{I^-}$ $\rightleftharpoons$ $\mathrm{I_3^-}$		
Initial concentration (*M*)	1.000×10^{-3}	1.000×10^{-3}	0
Change (*M*)	$-x$	$-x$	$+x$
Equilibrium concentration (*M*)	$1.000 \times 10^{-3} - x$	$1.000 \times 10^{-3} - x$	x

Since the equilibrium concentration of I_2 is given, we can solve for x. At equilibrium the concentration of I_2 is $6.61 \times 10^{-4}\ M$ so that

$$1.000 \times 10^{-3} - x = 6.61 \times 10^{-4}$$
$$x = 1.000 \times 10^{-3} - 6.61 \times 10^{-4}$$
$$= 3.39 \times 10^{-4}\ M$$

Now we can fill in the table with the concentrations at equilibrium.

	I_2 + I^- ⇌ I_3^-		
Initial concentration (*M*)	1.000×10^{-3}	1.000×10^{-3}	0
Change (*M*)	$-x = -3.39 \times 10^{-4}$	$-x$	$+x$
Equilibrium concentration (*M*)	6.61×10^{-4}	6.61×10^{-4}	3.39×10^{-4}

We now calculate the value of the equilibrium constant.

$$K_c = Q_c = \frac{[I_3^-]}{[I_2][I^-]}$$
$$= \frac{3.39 \times 10^{-4}\ M}{(6.61 \times 10^{-4}\ M)(6.61 \times 10^{-4}\ M)} = 776$$

Exercise 5.4.2

Ethanol and acetic acid react and form water and ethyl acetate, the solvent responsible for the odor of some nail polish removers.

$$C_2H_5OH + CH_3CO_2H \rightleftharpoons CH_3CO_2C_2H_5 + H_2O$$

When 1 mol each of C_2H_5OH and CH_3CO_2H are allowed to react in 1 L of the solvent dioxane, equilibrium is established when $\frac{1}{3}$ mol of each of the reactants remains. Calculate the equilibrium constant for the reaction. (Note: Water is not a solvent in this reaction.)

Answer

$K_c = 4$

5.4.1.1: Calculation of a Missing Equilibrium Concentration

If we know the equilibrium constant for a reaction and know the concentrations at equilibrium of all reactants and products except one, we can calculate the missing concentration.

Example 5.4.3: Calculation of a Missing Equilibrium Concentration

Nitrogen oxides are air pollutants produced by the reaction of nitrogen and oxygen at high temperatures. At 2000 °C, the value of the equilibrium constant for the reaction, $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$, is 4.1×10^{-4}. Find the concentration of NO(g) in an equilibrium mixture with air at 1 atm pressure at this temperature. In air, [N_2] = 0.036 mol/L and [O_2] 0.0089 mol/L.

Solution

We are given all of the equilibrium concentrations except that of NO. Thus, we can solve for the missing equilibrium concentration by rearranging the equation for the equilibrium constant.

$$K_c = Q_c = \frac{[NO]^2}{[N_2][O_2]}$$

$$[NO]^2 = K_c[N_2][O_2]$$

$$[NO] = \sqrt{K_c[N_2][O_2]}$$

$$= \sqrt{(4.1 \times 10^{-4})(0.036)(0.0089)}$$

$$= \sqrt{1.31 \times 10^{-7}}$$

$$= 3.6 \times 10^{-4}$$

Thus [NO] is 3.6×10^{-4} mol/L at equilibrium under these conditions.

We can check our answer by substituting all equilibrium concentrations into the expression for the reaction quotient to see whether it is equal to the equilibrium constant.

$$Q_c = \frac{[NO]^2}{[N_2][O_2]}$$

$$= \frac{(3.6 \times 10^{-4})^2}{(0.036)(0.0089)}$$

$$= 4.0 \times 10^{-4} = K_c$$

The answer checks; our calculated value gives the equilibrium constant within the error associated with the significant figures in the problem.

? Exercise 5.4.3

The equilibrium constant 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.

Answer

1.53 mol/L

5.4.1.2: Calculation of Changes in Concentration

If we know the equilibrium constant for a reaction and a set of concentrations of reactants and products that are *not at equilibrium*, we can calculate the changes in concentrations as the system comes to equilibrium, as well as the new concentrations at equilibrium. The typical procedure can be summarized in four steps.

1. Determine the direction the reaction proceeds to come to equilibrium.
   - Write a balanced chemical equation for the reaction.
   - If the direction in which the reaction must proceed to reach equilibrium is not obvious, calculate Q_c from the initial concentrations and compare to K_c to determine the direction of change.
2. Determine the relative changes needed to reach equilibrium, then write the equilibrium concentrations in terms of these changes.
   - Define the changes in the initial concentrations that are needed for the reaction to reach equilibrium. Generally, we represent the smallest change with the symbol *x* and express the other changes in terms of the smallest change.
   - Define missing equilibrium concentrations in terms of the initial concentrations and the changes in concentration determined in (a).
3. Solve for the change and the equilibrium concentrations.
   - Substitute the equilibrium concentrations into the expression for the equilibrium constant, solve for *x*, and check any assumptions used to find *x*.
   - Calculate the equilibrium concentrations.
4. Check the arithmetic.

- Check the calculated equilibrium concentrations by substituting them into the equilibrium expression and determining whether they give the equilibrium constant.

Sometimes a particular step may differ from problem to problem—it may be more complex in some problems and less complex in others. However, every calculation of equilibrium concentrations from a set of initial concentrations will involve these steps.

In solving equilibrium problems that involve changes in concentration, sometimes it is convenient to set up an ICE table, as described in the previous section.

Example 5.4.4: Calculation of Concentration as a Reaction Equilibrates

Under certain conditions, the equilibrium constant for the decomposition of $PCl_5(g)$ into $PCl_3(g)$ and $Cl_2(g)$ is 0.0211. What are the equilibrium concentrations of PCl_5, PCl_3, and Cl_2 if the initial concentration of PCl_5 was 1.00 *M*?

Solution

Use the stepwise process described earlier.

1. The balanced equation for the decomposition of PCl_5 is

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Because we have no products initially, $Q_c = 0$ and the reaction will proceed to the right.

- Let us represent the increase in concentration of PCl_3 by the symbol *x*. The other changes may be written in terms of *x* by considering the coefficients in the chemical equation.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \tag{5.4.23}$$
$$-x \qquad x \qquad x \tag{5.4.24}$$

- The changes in concentration and the expressions for the equilibrium concentrations are:

	$PCl_5 \rightleftharpoons PCl_3 + Cl_2$		
Initial concentration (*M*)	1.00	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$1.00 - x$	$0 + x = x$	$0 + x = x$

- Substituting the equilibrium concentrations into the equilibrium constant equation gives

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = 0.0211$$
$$= \frac{(x)(x)}{(1.00 - x)}$$

This equation contains only one variable, *x*, the change in concentration. We can write the equation as a quadratic equation and solve for *x* using the quadratic formula.

$$0.0211 = \frac{(x)(x)}{(1.00 - x)}$$
$$0.0211(1.00 - x) = x^2$$
$$x^2 + 0.0211x - 0.0211 = 0$$

An equation of the form $ax^2 + bx + c = 0$ can be rearranged to solve for *x*:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

In this case, $a = 1$, $b = 0.0211$, and $c = -0.0211$. Substituting the appropriate values for *a*, *b*, and *c* yields:

$$x = \frac{-0.0211 \pm \sqrt{(0.0211)^2 - 4(1)(-0.0211)}}{2(1)}$$

$$= \frac{-0.0211 \pm \sqrt{(4.45 \times 10^{-4}) + (8.44 \times 10^{-2})}}{2}$$
$$= \frac{-0.0211 \pm 0.291}{2}$$

Hence

$$x = \frac{-0.0211 + 0.291}{2} = 0.135$$

or

$$x = \frac{-0.0211 - 0.291}{2} = -0.156$$

Quadratic equations often have two different solutions, one that is physically possible and one that is physically impossible (an extraneous root). In this case, the second solution (−0.156) is physically impossible because we know the change must be a positive number (otherwise we would end up with negative values for concentrations of the products). Thus, x = 0.135 M.

The equilibrium concentrations are

$[PCl_5] = 1.00 - 0.135 = 0.87\ M$
$[PCl_3] = x = 0.135\ M$
$[Cl_2] = x = 0.135\ M$

- Substitution into the expression for K_c (to check the calculation) gives

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(0.135)(0.135)}{0.87} = 0.021$$

The equilibrium constant calculated from the equilibrium concentrations is equal to the value of K_c given in the problem (when rounded to the proper number of significant figures). Thus, the calculated equilibrium concentrations check.

Exercise 5.4.4A

Acetic acid, CH_3CO_2H, reacts with ethanol, C_2H_5OH, to form water and ethyl acetate, $CH_3CO_2C_2H_5$.

$$CH_3CO_2H + C_2H_5OH \rightleftharpoons CH_3CO_2C_2H_5 + H_2O$$

The equilibrium constant for this reaction with dioxane as a solvent is 4.0. What are the equilibrium concentrations when a mixture that is 0.15 M in CH_3CO_2H, 0.15 M in C_2H_5OH, 0.40 M in $CH_3CO_2C_2H_5$, and 0.40 M in H_2O are mixed in enough dioxane to make 1.0 L of solution?

Answer

$[CH_3CO_2H]$ = 0.36 M, $[C_2H_5OH]$ = 0.36 M, $[CH_3CO_2C_2H_5]$ = 0.17 M, $[H_2O]$ = 0.17 M

Exercise 5.4.4B

A 1.00-L flask is filled with 1.00 moles 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?

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

Answer

$[H_2]$ = 0.06 M, $[I_2]$ = 1.06 M, [HI] = 1.88 M

Sometimes it is possible to use **chemical insight** to find solutions to equilibrium problems without actually solving a quadratic (or more complicated) equation. First, however, it is useful to verify that equilibrium can be obtained starting from two extremes: all (or mostly) reactants and all (or mostly) products.

Consider the ionization of 0.150 M HA, a weak acid.

$$\mathrm{HA}(aq) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{A^-}(aq) \qquad K_c = 6.80 \times 10^{-4}$$

The most obvious way to determine the equilibrium concentrations would be to start with only reactants. This could be called the "all reactant" starting point. Using *x* for the amount of acid ionized at equilibrium, this is the ICE table and solution.

	HA(*aq*) ⇌	H^+(*aq*)	+ A^-(*aq*)
Initial concentration (*M*)	0.150	0	0
Change (*M*)	−*x*	*x*	*x*
Equilibrium concentration (*M*)	0.150 − *x*	*x*	*x*

Setting up and solving the quadratic equation gives

$$K_c = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]} = \frac{(x)(x)}{(0.150 - x)} = 6.80 \times 10^{-4}$$

$$x^2 + 6.80 \times 10^{-4} x - 1.02 \times 10^{-4} = 0$$

$$x = -6.80 \times 10^{-4} \pm \sqrt{(6.80 \times 10^{-4})^2 - (4)(1)(-1.02 \times 10^{-4})}\ (2)(1)$$

$$x = 0.00977\ M \text{ or } -0.0104\ M$$

Using the positive (physical) root, the equilibrium concentrations are

$$[\mathrm{HA}] = 0.150 - x = 0.140\ M$$
$$[\mathrm{H^+}] = [\mathrm{A^-}] = x = 0.00977\ M$$

A less obvious way to solve the problem would be to assume all the HA ionizes first, then the system comes to equilibrium. This could be called the "all product" starting point. Assuming all of the HA ionizes gives

$$[\mathrm{HA}] = 0.150 - 0.150 = 0\ M$$
$$[\mathrm{H^+}] = 0 + 0.150 = 0.150\ M$$
$$[\mathrm{A^-}] = 0 + 0.150 = 0.150\ M$$

Using these as initial concentrations and "*y*" to represent the concentration of HA at equilibrium, this is the ICE table for this starting point.

	HA(*aq*) ⇌	H^+(*aq*)	+ A^-(*aq*)
Initial concentration (*M*)	0	0.150	0.150
Change (*M*)	+*y*	−*y*	−*y*
Equilibrium concentration (*M*)	*y*	0.150 − *y*	0.150 − *y*

Setting up and solving the quadratic equation gives

$$K_c = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]} = \frac{(0.150 - y)(0.150 - y)}{(y)} = 6.80 \times 10^{-4}$$

$$6.80 \times 10^{-4} y = 0.0225 - 0.300y + y^2$$

Retain a few extra significant figures to minimize rounding problems.

$$y^2 - 0.30068y + 0.022500 = 0$$

$$y = \frac{0.30068 \pm \sqrt{(0.30068)^2 - (4)(1)(0.022500)}}{(2)(1)}$$

$$y = \frac{0.30068 \pm 0.020210}{2}$$

Rounding each solution to three significant figures gives

$$y = 0.160\ M \text{ or } y = 0.140\ M$$

Using the physically significant root (0.140 M) gives the equilibrium concentrations as

$$[\mathrm{HA}] = y = 0.140\ M$$
$$[\mathrm{H^+}] = 0.150 - y = 0.010\ M$$
$$[\mathrm{A^-}] = 0.150 - y = 0.010\ M$$

Thus, the two approaches give the same results (to three *decimal places*), and show that *both* starting points lead to the same equilibrium conditions. The "**all reactant**" starting point resulted in a relatively small change (x) because the system was close to equilibrium, while the "**all product**" starting point had a relatively large change (y) that was nearly the size of the initial concentrations. It can be said that a system that starts "close" to equilibrium will require only a "small" change in conditions (x) to reach equilibrium.

Recall that a **small K_c** means that very little of the reactants form products and a **large K_c** means that most of the reactants form products. If the system can be arranged so it starts "close" to equilibrium, then if the change (x) is small compared to any initial concentrations, it can be neglected. Small is usually defined as resulting in an error of less than 5%. The following two examples demonstrate this.

Example 5.4.5: Approximate Solution Starting Close to Equilibrium

What are the concentrations at equilibrium of a 0.15 *M* solution of HCN?

$$\mathrm{HCN}(aq) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{CN^-}(aq) \quad K_c = 4.9 \times 10^{-10}$$

Solution

Using "*x*" to represent the concentration of each product at equilibrium gives this ICE table.

	HCN(*aq*) ⇌	H$^+$(*aq*)	+ CN$^-$(*aq*)
Initial concentration (*M*)	0.15	0	0
Change (*M*)	−*x*	*x*	*x*
Equilibrium concentration (*M*)	0.15 − *x*	*x*	*x*

The exact solution may be obtained using the quadratic formula with

$$K_c = \frac{(x)(x)}{0.15 - x}$$

solving

$$x^2 + 4.9 \times 10^{-10} - 7.35 \times 10^{-11} = 0$$

$$x = 8.56 \times 10^{-6}\ M\ (3 \text{ sig. figs.}) = 8.6 \times 10^{-6}\ M\ (2 \text{ sig. figs.})$$

Thus [H$^+$] = [CN$^-$] = *x* = 8.6 × 10^{-6} *M* and [HCN] = 0.15 – *x* = 0.15 *M*.

In this case, chemical intuition can provide a simpler solution. From the equilibrium constant and the initial conditions, *x* must be small compared to 0.15 *M*. More formally, if $x \ll 0.15$, then 0.15 – *x* ≈ 0.15. If this assumption is true, then it simplifies obtaining *x*

$$K_c = \frac{(x)(x)}{0.15 - x} \approx \frac{x^2}{0.15}$$

$$4.9 \times 10^{-10} = \frac{x^2}{0.15}$$

$$x^2 = (0.15)(4.9 \times 10^{-10}) = 7.4 \times 10^{-11}$$

$$x = \sqrt{7.4 \times 10^{-11}} = 8.6 \times 10^{-6}\ M$$

In this example, solving the exact (quadratic) equation and using approximations gave the same result to two significant figures. While most of the time the approximation is a bit different from the exact solution, as long as the error is less than 5%, the approximate solution is considered valid. In this problem, the 5% applies to IF (0.15 – *x*) ≈ 0.15 *M*, so if

$$\frac{x}{0.15} \times 100\% = \frac{8.6 \times 10^{-6}}{0.15} \times 100\% = 0.006\%$$

is less than 5%, as it is in this case, the assumption is valid. The approximate solution is thus a valid solution.

Exercise 5.4.5

What are the equilibrium concentrations in a 0.25 *M* NH_3 solution?

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_c = 1.8 \times 10^{-5}$$

Assume that *x* is much less than 0.25 M and calculate the error in your assumption.

Answer

$[OH^-] = [NH_4^+] = 0.0021\ M$; $[NH_3]$ = 0.25 *M*, error = 0.84%

The second example requires that the original information be processed a bit, but it still can be solved using a small *x* approximation.

Example 5.4.6: Approximate Solution After Shifting Starting Concentration

Copper(II) ions form a complex ion in the presence of ammonia

$$Cu^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq) \qquad K_c = 5.0 \times 10^{13} = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}(aq)][NH_3]^4}$$

If 0.010 mol Cu^{2+} is added to 1.00 L of a solution that is 1.00 *M* NH_3 what are the concentrations when the system comes to equilibrium?

Solution The initial concentration of copper(II) is 0.010 *M*. The equilibrium constant is very large so it would be better to start with as much product as possible because “all products” is much closer to equilibrium than “all reactants.” Note that Cu^{2+} is the limiting reactant; if all 0.010 *M* of it reacts to form product the concentrations would be

$$[Cu^{2+}] = 0.010 - 0.010 = 0\ M$$

$$[Cu(NH_3)_4^{2+}] = 0.010\ M$$

$$[NH_3] = 1.00 - 4 \times 0.010 = 0.96\ M$$

Using these “shifted” values as initial concentrations with *x* as the free copper(II) ion concentration at equilibrium gives this ICE table.

	$Cu^{2+}(aq)$ +	$4NH_3(aq) \rightleftharpoons$	$Cu(NH_3)_4^{2+}(aq)$
Initial concentration (*M*)	0	0.96	0.010
Change (*M*)	+*x*	+4*x*	−*x*
Equilibrium concentration (*M*)	*x*	0.96 + 4*x*	0.010 − *x*

Since we are starting close to equilibrium, *x* should be small so that

$$0.96 + 4x \approx 0.96\ M$$

$$0.010 - x \approx 0.010\ M$$

$$K_c = \frac{(0.010 - x)}{x(0.96 - 4x)^4} \approx \frac{(0.010)}{x(0.96)^4} = 5.0 \times 10^{13}$$

$$x = \frac{(0.010)}{K_c(0.96)^4} = 2.4 \times 10^{-16}\ M$$

Select the smallest concentration for the 5% rule.

$$\frac{2.4 \times 10^{-16}}{0.010} \times 100\% = 2 \times 10^{-12}\%$$

This is much less than 5%, so the assumptions are valid. The concentrations at equilibrium are

$$[\mathrm{Cu}^{2+}] = x = 2.4 \times 10^{-16}\ M$$
$$[\mathrm{NH_3}] = 0.96 - 4x = 0.96\ M$$
$$[\mathrm{Cu(NH_3)_4^{2+}}] = 0.010 - x = 0.010\ M$$

By starting with the maximum amount of product, this system was near equilibrium and the change (*x*) was very small. With only a small change required to get to equilibrium, the equation for *x* was greatly simplified and gave a valid result well within the 5% error maximum.

? Exercise 5.4.6

What are the equilibrium concentrations when 0.25 mol Ni^{2+} is added to 1.00 L of 2.00 *M* $\mathrm{NH_3}$ solution?

$$\mathrm{Ni}^{2+}(aq) + 6\,\mathrm{NH_3}(aq) \rightleftharpoons \mathrm{Ni(NH_3)_6^{2+}}(aq)$$

with $K_c = 5.5 \times 10^8$.

With such a large equilibrium constant, first form as much product as possible, then assume that only a small amount (*x*) of the product shifts left. Calculate the error in your assumption.

Answer

$[\mathrm{Ni(NH_3)_6^{2+}}] = 0.25\ M$, [$\mathrm{NH_3}$] = 0.50 *M*, [$\mathrm{Ni}^{2+}$] = 2.9 × 10^{-8} *M*, error = 1.2 × 10^{-5}%

Summary

The ratios of the rate of change in concentrations of a reaction are equal to the ratios of the coefficients in the balanced chemical equation. The sign of the coefficient of X is positive when the concentration increases and negative when it decreases. We learned to approach three basic types of equilibrium problems. When given the concentrations of the reactants and products at equilibrium, we can solve for the equilibrium constant; when given the equilibrium constant and some of the concentrations involved, we can solve for the missing concentrations; and when given the equilibrium constant and the initial concentrations, we can solve for the concentrations at equilibrium. Chemical insight can be used to make assumptions that lead to simpler soltuons for equilibrium problems.

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5.5: Shifting Equilibria - Le Chatelier's Principle

Learning Objectives

- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Chatelier's principle

As we saw in the previous section, reactions proceed in both directions (reactants go to products and products go to reactants). We can tell a reaction is at equilibrium if the reaction quotient (Q) is equal to the equilibrium constant (K). We next address what happens when a system at equilibrium is disturbed so that Q is no longer equal to K. If a system at equilibrium is subjected to a perturbance or stress (such as a change in concentration) the position of equilibrium changes. Since this stress affects the concentrations of the reactants and the products, the value of Q will no longer equal the value of K. To re-establish equilibrium, the system will either shift toward the products (if $Q < K$) or the reactants (if $Q > K$) until Q returns to the same value as K.

This process is described by Le Chatelier's principle: When a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance. As described in the previous paragraph, the disturbance causes a change in Q; the reaction will shift to re-establish $Q = K$.

5.5.1: Predicting the Direction of a Reversible Reaction

Le Chatelier's principle can be used to predict changes in equilibrium concentrations when a system that is at equilibrium is subjected to a stress. However, if we have a mixture of reactants and products that have not yet reached equilibrium, the changes necessary to reach equilibrium may not be so obvious. In such a case, we can compare the values of *Q* and *K* for the system to predict the changes.

A chemical system at equilibrium can be **temporarily** shifted out of equilibrium by adding or removing one or more of the reactants or products. The concentrations of both reactants and products then undergo additional changes to return the system to equilibrium.

The stress on the system in Figure 5.5.1 is the reduction of the equilibrium concentration of SCN^- (lowering the concentration of one of the reactants would cause *Q* to be larger than *K*). As a consequence, Le Chatelier's principle leads us to predict that the concentration of $Fe(SCN)^{2+}$ should decrease, increasing the concentration of SCN^- part way back to its original concentration, and increasing the concentration of Fe^{3+} above its initial equilibrium concentration.



Figure 5.5.1: (a) The test tube contains 0.1 M Fe^{3+}. (b) Thiocyanate ion has been added to solution in (a), forming the red $Fe(SCN)^{2+}$ ion. $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$. *(c) Silver nitrate has been added to the solution in (b), precipitating some of the SCN− as the white solid AgSCN.* $Ag^+(aq) + SCN^-(aq) \rightleftharpoons AgSCN(s)$ *The decrease in the SCN− concentration shifts the first equilibrium in the solution to the left, decreasing the concentration (and lightening color) of the* $Fe(SCN)^{2+}$*. (credit: modification of work by Mark Ott).*

The effect of a change in concentration on a system at equilibrium is illustrated further by the equilibrium of this chemical reaction:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2\,HI_{(g)} \tag{5.5.1}$$

$$K_c = 50.0 \text{ at } 400^\circ C \tag{5.5.2}$$

The numeric values for this example have been determined experimentally. A mixture of gases at 400 °C with $[H_2] = [I_2] = 0.221\ M$ and $[HI] = 1.563\ M$ is at equilibrium; for this mixture, $Q_c = K_c = 50.0$. If H_2 is introduced into the

system so quickly that its concentration doubles before it begins to react (new $[\mathrm{H_2}] = 0.442\ M$), the reaction will shift so that a new equilibrium is reached, at which

- $[\mathrm{H_2}] = 0.374\ M$,
- $[\mathrm{I_2}] = 0.153\ M$, and
- $[\mathrm{HI}] = 1.692\ M$.

This gives:

$$Q_c = \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}][\mathrm{I_2}]} = \frac{(1.692)^2}{(0.374)(0.153)} = 50.0 = K_c \tag{5.5.3}$$

We have stressed this system by introducing additional $\mathrm{H_2}$. The stress is relieved when the reaction shifts to the right, using up some (but not all) of the excess $\mathrm{H_2}$, reducing the amount of uncombined $\mathrm{I_2}$, and forming additional HI.

5.5.2: Effect of Change in Pressure on Equilibrium

Sometimes we can change the position of equilibrium by changing the pressure of a system. However, changes in pressure have a measurable effect only in systems in which gases are involved, and then only when the chemical reaction produces a change in the total number of gas molecules in the system. An easy way to recognize such a system is to look for different numbers of moles of gas on the reactant and product sides of the equilibrium. While evaluating pressure (as well as related factors like volume), it is important to remember that equilibrium constants are defined with regard to concentration (for K_c) or partial pressure (for K_P). Some changes to total pressure, like adding an inert gas that is not part of the equilibrium, will change the total pressure but not the partial pressures of the gases in the equilibrium constant expression. Thus, addition of a gas not involved in the equilibrium will not perturb the equilibrium.

As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of one of the components of the equilibrium mixture, we introduce a stress by increasing the partial pressures of one or more of the components. In accordance with Le Chatelier's principle, a shift in the equilibrium that reduces the total number of molecules per unit of volume will be favored because this relieves the stress. The reverse reaction would be favored by a decrease in pressure.

Consider what happens when we increase the pressure on a system in which NO, $\mathrm{O_2}$, and $\mathrm{NO_2}$ are at equilibrium:

$$2\,\mathrm{NO(g)} + \mathrm{O_2(g)} \rightleftharpoons 2\,\mathrm{NO_2(g)} \tag{5.5.4}$$

The formation of additional amounts of $\mathrm{NO_2}$ decreases the total number of molecules in the system because each time two molecules of $\mathrm{NO_2}$ form, a total of three molecules of NO and $\mathrm{O_2}$ are consumed. This reduces the total pressure exerted by the system and reduces, but does not completely relieve, the stress of the increased pressure. On the other hand, a decrease in the pressure on the system favors decomposition of $\mathrm{NO_2}$ into NO and $\mathrm{O_2}$, which tends to restore the pressure.

Now consider this reaction:

$$\mathrm{N_2(g)} + \mathrm{O_2(g)} \rightleftharpoons 2\,\mathrm{NO(g)} \tag{5.5.5}$$

Because there is no change in the total number of molecules in the system during reaction, a change in pressure does not favor either formation or decomposition of gaseous nitrogen monoxide.

5.5.3: Effect of Change in Temperature on Equilibrium

Changing concentration or pressure perturbs an equilibrium because the reaction quotient is shifted away from the equilibrium value. Changing the temperature of a system at equilibrium has a different effect: A change in temperature actually changes the value of the equilibrium constant. However, we can qualitatively predict the effect of the temperature change by treating it as a stress on the system and applying Le Chatelier's principle.

When hydrogen reacts with gaseous iodine, heat is evolved.

$$\mathrm{H_2(g)} + \mathrm{I_2(g)} \rightleftharpoons 2\,\mathrm{HI(g)} \quad \Delta H = -9.4\ \mathrm{kJ\ (exothermic)} \tag{5.5.6}$$

Because this reaction is exothermic, we can write it with heat as a product.

$$\mathrm{H_2(g)} + \mathrm{I_2(g)} \rightleftharpoons 2\,\mathrm{HI(g)} + \mathrm{heat} \tag{5.5.7}$$

Increasing the temperature of the reaction increases the internal energy of the system. Thus, increasing the temperature has the effect of increasing the amount of one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of H_2 and I_2 and a reduction in the concentration of HI. Lowering the temperature of this system reduces the amount of energy present, favors the production of heat, and favors the formation of hydrogen iodide.

When we change the temperature of a system at equilibrium, the equilibrium constant for the reaction changes. Lowering the temperature in the HI system increases the equilibrium constant: At the new equilibrium the concentration of HI has increased and the concentrations of H_2 and I_2 decreased. Raising the temperature decreases the value of the equilibrium constant, from 67.5 at 357 °C to 50.0 at 400 °C.

Temperature affects the equilibrium between NO_2 and N_2O_4 in this reaction

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \quad \Delta H = 57.20 \text{ kJ} \tag{5.5.8}$$

The positive ΔH value tells us that the reaction is endothermic and could be written

$$\text{heat} + N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \tag{5.5.9}$$

At higher temperatures, the gas mixture has a deep brown color, indicative of a significant amount of brown NO_2 molecules. If, however, we put a stress on the system by cooling the mixture (withdrawing energy), the equilibrium shifts to the left to supply some of the energy lost by cooling. The concentration of colorless N_2O_4 increases, and the concentration of brown NO_2 decreases, causing the brown color to fade.

5.5.4: Catalysts Do Not Affect Equilibrium

As we learned during our study of kinetics, a catalyst can speed up the rate of a reaction. Though this increase in reaction rate may cause a system to reach equilibrium more quickly (by speeding up the forward and reverse reactions), a catalyst has no effect on the value of an equilibrium constant nor on equilibrium concentrations.

The interplay of changes in concentration or pressure, temperature, and the lack of an influence of a catalyst on a chemical equilibrium is illustrated in the industrial synthesis of ammonia from nitrogen and hydrogen according to the equation

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \tag{5.5.10}$$

A large quantity of ammonia is manufactured by this reaction. Each year, ammonia is among the top 10 chemicals, by mass, manufactured in the world. About 2 billion pounds are manufactured in the United States each year. Ammonia plays a vital role in our global economy. It is used in the production of fertilizers and is, itself, an important fertilizer for the growth of corn, cotton, and other crops. Large quantities of ammonia are converted to nitric acid, which plays an important role in the production of fertilizers, explosives, plastics, dyes, and fibers, and is also used in the steel industry.

Fritz Haber

Haber was born in Breslau, Prussia (presently Wroclaw, Poland) in December 1868. He went on to study chemistry and, while at the University of Karlsruhe, he developed what would later be known as the Haber process: the catalytic formation of ammonia from hydrogen and atmospheric nitrogen under high temperatures and pressures.



The work of Nobel Prize recipient Fritz Haber revolutionized agricultural practices in the early 20th century. His work also affected wartime strategies, adding chemical weapons to the artillery.

For this work, Haber was awarded the 1918 Nobel Prize in Chemistry for synthesis of ammonia from its elements. The Haber process was a boon to agriculture, as it allowed the production of fertilizers to no longer be dependent on mined feed stocks such as sodium nitrate.

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

Currently, the annual production of synthetic nitrogen fertilizers exceeds 100 million tons and synthetic fertilizer production has increased the number of humans that arable land can support from 1.9 persons per hectare in 1908 to 4.3 in 2008. The availability of nitrogen is a strong limiting factor to the growth of plants. Despite accounting for 78% of air, diatomic nitrogen (N_2) is nutritionally unavailable due the tremendous stability of the nitrogen-nitrogen triple bond. For plants to use atmospheric nitrogen, the nitrogen must be converted to a more bioavailable form (this conversion is called nitrogen fixation).

In addition to his work in ammonia production, Haber is also remembered by history as one of the fathers of chemical warfare. During World War I, he played a major role in the development of poisonous gases used for trench warfare. Regarding his role in these developments, Haber said, “During peace time a scientist belongs to the World, but during war time he belongs to his country.”[1] Haber defended the use of gas warfare against accusations that it was inhumane, saying that death was death, by whatever means it was inflicted. He stands as an example of the ethical dilemmas that face scientists in times of war and the double-edged nature of the sword of science.

Like Haber, the products made from ammonia can be multifaceted. In addition to their value for agriculture, nitrogen compounds can also be used to achieve destructive ends. Ammonium nitrate has also been used in explosives, including improvised explosive devices. Ammonium nitrate was one of the components of the bomb used in the attack on the Alfred P. Murrah Federal Building in downtown Oklahoma City on April 19, 1995.

It has long been known that nitrogen and hydrogen react to form ammonia. However, it became possible to manufacture ammonia in useful quantities by the reaction of nitrogen and hydrogen only in the early 20th century after the factors that influence its equilibrium were understood.

To be practical, an industrial process must give a large yield of product relatively quickly. One way to increase the yield of ammonia is to increase the pressure on the system in which N_2, H_2, and NH_3 are at equilibrium or are coming to equilibrium.

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \tag{5.5.11}$$

The formation of additional amounts of ammonia reduces the total pressure exerted by the system and somewhat reduces the stress of the increased pressure.

Although increasing the pressure of a mixture of N_2, H_2, and NH_3 will increase the yield of ammonia, at low temperatures, the rate of formation of ammonia is slow. At room temperature, for example, the reaction is so slow that if we prepared a mixture of N_2 and H_2, no detectable amount of ammonia would form during our lifetime. The formation of ammonia from hydrogen and nitrogen is an exothermic process:

$$N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g) \quad \Delta H = -92.2\ \text{kJ} \tag{5.5.12}$$

Thus, increasing the temperature to increase the rate lowers the yield. If we lower the temperature to shift the equilibrium to favor the formation of more ammonia, equilibrium is reached more slowly because of the large decrease of reaction rate with decreasing temperature.

Part of the rate of formation lost by operating at lower temperatures can be recovered by using a catalyst. The net effect of the catalyst on the reaction is to cause equilibrium to be reached more rapidly. In the commercial production of ammonia, conditions of about 500 °C, 150–900 atm, and the presence of a catalyst are used to give the best compromise among rate, yield, and the cost of the equipment necessary to produce and contain high-pressure gases at high temperatures (Figure 5.5.2).

Figure 5.5.2: Commercial production of ammonia requires heavy equipment to handle the high temperatures and pressures required. This schematic outlines the design of an ammonia plant.

Summary

Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure; volume and pressure changes will disturb equilibrium if the number of moles of gas is different on the reactant and product sides of the reaction. The system's response to these disturbances is described by Le Chatelier's principle: The system will respond in a way that counteracts the disturbance. Not all changes to the system result in a disturbance of the equilibrium. Adding a catalyst affects the rates of the reactions but does not alter the equilibrium, and changing pressure or volume will not significantly disturb systems with no gases or with equal numbers of moles of gas on the reactant and product side.

Table 5.5.1: Effects of Disturbances of Equilibrium and K

Disturbance	Observed Change as Equilibrium is Restored	Direction of Shift	Effect on K
reactant added	added reactant is partially consumed	toward products	none
product added	added product is partially consumed	toward reactants	none
decrease in volume/increase in gas pressure	pressure decreases	toward side with fewer moles of gas	none
increase in volume/decrease in gas pressure	pressure increases	toward side with more moles of gas	none
temperature increase	heat is absorbed	toward products for endothermic, toward reactants for exothermic	changes
temperature decrease	heat is given off	toward reactants for endothermic, toward products for exothermic	changes

Footnotes

1. Herrlich, P. “The Responsibility of the Scientist: What Can History Teach Us About How Scientists Should Handle Research That Has the Potential to Create Harm?” *EMBO Reports* 14 (2013): 759–764.

Glossary

Le Chatelier's principle

when a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

position of equilibrium

concentrations or partial pressures of components of a reaction at equilibrium (commonly used to describe conditions before a disturbance)

stress

change to a reaction's conditions that may cause a shift in the equilibrium

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5.E: Fundamental Equilibrium Concepts (Exercises)

5.2 Chemical Equilibria

Exercise 5.E.1

What does it mean to describe a reaction as “reversible”?

Answer

The reaction can proceed in both the forward and reverse directions.

Exercise 5.E.2

If a reaction is reversible, when can it be said to have reached equilibrium?

Answer

When a system has reached equilibrium, no further changes in the reactant and product concentrations occur; the reactions continue to occur, but at equivalent rates.

Exercise \PageIndex{3

If the concentrations of products and reactants are equal, is the system at equilibrium?

Answer

The concept of equilibrium does not imply equal concentrations, though it is possible.

5.3 Equilibrium Constants

Exercise 5.E.4

Explain why an equilibrium between $Br_2(l)$ and $Br_2(g)$ would not be established if the container were not a closed vessel shown below:



Answer

Equilibrium cannot be established between the liquid and the gas phase if the top is removed from the bottle because the system is not closed; one of the components of the equilibrium, the Br_2 vapor, would escape from the bottle until all liquid disappeared. Thus, more liquid would evaporate than can condense back from the gas phase to the liquid phase.

Exercise 5.E.5

(a) Write the expression for the equilibrium constant for the reaction represented by the equation $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

(b) Write the expression for the equilibrium constant for the reaction represented by the equation $Pb^{2+}(aq) + 2\,Cl^-(aq) \rightleftharpoons PbCl_2(s)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

Answer

(a) $K_c = [Ag^+][Cl^-] < 1$. AgCl is insoluble; thus, the concentrations of ions are much less than 1 *M*

(b) $K_c = \dfrac{1}{[Pb^{2+}][Cl^-]^2} > 1$ because $PbCl_2$ is insoluble and formation of the solid will reduce the concentration of ions to a low level (<1 *M*).

Exercise 5.E.6

Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene: $3\,C_2H_2(g) \longrightarrow C_6H_6(g)$. Which value of K_c would make this reaction most useful commercially? $K_c \approx 0.01$, $K_c \approx 1$, or $K_c \approx 10$. Explain your answer.

Answer

Since $K_c = \dfrac{[C_6H_6]}{[C_2H_2]^3}$, a value of $K_c \approx 10$ means that C_6H_6 predominates over C_2H_2. In such a case, the reaction would be commercially feasible if the rate to equilibrium is suitable.

Exercise \PageIndex7}

For a titration to be effective, the reaction must be rapid and the yield of the reaction must essentially be 100%. Is $K_c > 1$, < 1, or ≈ 1 for a titration reaction?

Answer

$K_c > 1$

Exercise 5.E.8

Write the mathematical expression for the reaction quotient, Q_c, for each of the following reactions:

a. $CH_4(g) + Cl_2(g) \rightleftharpoons CH_3Cl(g) + HCl(g)$
b. $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$
c. $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$
d. $BaSO_3(s) \rightleftharpoons BaO(s) + SO_2(g)$
e. $P_4(g) + 5\,O_2(g) \rightleftharpoons P_4O_{10}(s)$
f. $Br_2(g) \rightleftharpoons 2\,Br(g)$
g. $CH_4(g) + 2\,O_2(g) \rightleftharpoons CO_2(g) + 2\,H_2O(l)$
h. $CuSO_4 \cdot 5\,H_2O(s) \rightleftharpoons CuSO_4(s) + 5\,H_2O(g)$

Answer

(a) $Q_c = \dfrac{[CH_3Cl][HCl]}{[CH_4][Cl_2]}$; (b) $Q_c = \dfrac{[NO]^2}{[N_2][O_2]}$; (c) $Q_c = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$; (d) $Q_c = [SO_2]$; (e) $Q_c = \dfrac{1}{[P_4][O_2]^5}$; (f) $Q_c = \dfrac{[Br]^2}{[Br_2]}$; (g) $Q_c = \dfrac{[CO_2]}{[CH_4][O_2]^2}$; (h) $Q_c = [H_2O]^5$

Exercise 5.E.9

The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.

a. $2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g)$ $K_c = 17$; [NH_3] = 0.20 *M*, [N_2] = 1.00 *M*, [H_2] = 1.00 *M*
b. $2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g)$ $K_P = 6.8 \times 10^4$; initial pressures: NH_3 = 3.0 atm, N_2 = 2.0 atm, H_2 = 1.0 atm
c. $2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g)$ $K_c = 0.230$; [SO_3] = 0.00 *M*, [SO_2] = 1.00 *M*, [O_2] = 1.00 *M*
d. $2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g)$ $K_P = 16.5$; initial pressures: SO_3 = 1.00 atm, SO_2 = 1.00 atm, O_2 = 1.00 atm
e. $2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g)$ $K_c = 4.6 \times 10^4$; [NO] = 1.00 *M*, [Cl_2] = 1.00 *M*, [NOCl] = 0 *M*
f. $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$ $K_P = 0.050$; initial pressures: NO = 10.0 atm, N_2 = O_2 = 5 atm

Answer

(a) Q_c 25 proceeds left; (b) Q_P 0.22 proceeds right; (c) Q_c undefined proceeds left; (d) Q_P 1.00 proceeds right; (e) Q_P 0 proceeds right; (f) Q_c 4 proceeds left

Exercise 5.E.10

Write the reaction quotient expression for the ionization of NH_3 in water.

Answer

$$Q_c = \frac{[NH_4^+][OH^-]}{[HN_3]} \tag{5.E.1}$$

5.4 Equilibrium Calculations

Exercise 5.E.11

What is the value of the equilibrium constant at 500 °C for the formation of NH_3 according to the following equation?

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \tag{5.E.2}$$

An equilibrium mixture of $NH_3(g)$, $H_2(g)$, and $N_2(g)$ at 500 °C was found to contain 1.35 *M* H_2, 1.15 *M* N_2, and 4.12×10^{-1} *M* NH_3.

Answer

$K_c = 6.00 \times 10^{-2}$

Exercise 5.E.12

Hydrogen is prepared commercially by the reaction of methane and water vapor at elevated temperatures.

$$CH_4(g) + H_2O(g) \rightleftharpoons 3\,H_2(g) + CO(g) \tag{5.E.3}$$

What is the equilibrium constant for the reaction if a mixture at equilibrium contains gases with the following concentrations: CH_4, 0.126 *M*; H_2O, 0.242 *M*; CO, 0.126 *M*; H_2 1.15 *M*, at a temperature of 760 °C?

Answer

$K_c = 6.28$

Exercise 5.E.13

A 0.72-mol sample of PCl_5 is put into a 1.00-L vessel and heated. At equilibrium, the vessel contains 0.40 mol of $PCl_3(g)$ and 0.40 mol of $Cl_2(g)$. Calculate the value of the equilibrium constant for the decomposition of PCl_5 to PCl_3 and Cl_2 at this temperature.

Answer

$K_c = 0.50$

Exercise 5.E.14

Analysis of the gases in a sealed reaction vessel containing NH_3, N_2, and H_2 at equilibrium at 400 °C established the concentration of N_2 to be 1.2 *M* and the concentration of H_2 to be 0.24 *M*.

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightleftharpoons 2\,\mathrm{NH_3}(g) \quad K_c = 0.50 \text{ at } 400\ ^\circ\mathrm{C} \tag{5.E.4}$$

Calculate the equilibrium molar concentration of NH_3.

Answer

$[NH_3] = 9.1 \times 10^{-2}\ M$

Exercise 5.E.15

Cobalt metal can be prepared by reducing cobalt(II) oxide with carbon monoxide.

$$\mathrm{CoO}(s) + \mathrm{CO}(g) \rightleftharpoons \mathrm{Co}(s) + \mathrm{CO_2}(g) \quad K_c = 4.90 \times 10^2 \text{ at } 550\ ^\circ\mathrm{C}$$

What concentration of CO remains in an equilibrium mixture with $[CO_2] = 0.100\ M$?

Answer

$[CO] = 2.0 \times 10^{-4}\ M$

Exercise 5.E.16

A student solved the following problem and found the equilibrium concentrations to be $[SO_2] = 0.590\ M$, $[O_2] = 0.0450\ M$, and $[SO_3] = 0.260\ M$. How could this student check the work without reworking the problem? The problem was: For the following reaction at 600 °C:

$$2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{SO_3}(g) \quad K_c = 4.32$$

What are the equilibrium concentrations of all species in a mixture that was prepared with $[SO_3] = 0.500\ M$, $[SO_2] = 0\ M$, and $[O_2] = 0.350\ M$?

Answer

Calculate Q based on the calculated concentrations and see if it is equal to K_c. Because Q does equal 4.32, the system must be at equilibrium.

Exercise 5.E.17

What are the concentrations of H_2O, Cl_2O, and HOCl in an equilibrium mixture produced by the reaction below when 2.00 mol of H_2O (g) is added to 2.00 mol of Cl_2O (g) in a 2.00 L flask?

$$\mathrm{H_2O}(g) + \mathrm{Cl_2O}(g) \rightleftharpoons 2\,\mathrm{HOCl}(g) \quad K_c = 0.180 \tag{5.E.5}$$

Answer

$[H_2O]$ = 0.825 *M*; $[Cl_2O]$ = 0.825 *M*; [HOCl] = 0.350 *M*.

Exercise 5.E.18

Calculate the equilibrium concentrations of N_2O_4 and NO_2 in a 1.00 L vessel that was prepared staring from 0.129 mol of N_2O_4.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad K_c = 1.07 \times 10^{-5} \tag{5.E.6}$$

Answer

$[NO_2]$ = 1.17 x 10^{-3} *M*

$[N_2O_4]$ = 0.128 *M*

Exercise 5.E.19

Calculate the equilibrium concentrations of I_2, Br_2 and IBr in a 1.00 L vessel that was prepared staring from 0.129 mol of N_2O_4.

$$I_2(g) + Br_2(g) \rightleftharpoons 2IBr(g) \quad K_c = 280.0 \tag{5.E.7}$$

Answer

$[I_2]$ = 0.053 M

$[Br_2]$ = 0.053 M

[IBr] = 0.893 M

5.5 Shifting Equilibria - Le Chatelier's Principle

Exercise 5.E.20

The following equation represents a reversible decomposition:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Under what conditions will decomposition in a closed container proceed to completion so that no $CaCO_3$ remains?

Answer

The amount of $CaCO_3$ must be so small that P_{CO_2} is less than K_P when the $CaCO_3$ has completely decomposed. In other words, the starting amount of $CaCO_3$ cannot completely generate the full P_{CO_2} required for equilibrium.

Exercise 5.E.21

What property of a reaction can we use to predict the effect of a change in temperature on the value of an equilibrium constant?

Answer

The change in enthalpy may be used. If the reaction is exothermic, the heat produced can be thought of as a product. If the reaction is endothermic the heat added can be thought of as a reactant. Additional heat would shift an exothermic reaction back to the reactants but would shift an endothermic reaction to the products. Cooling an exothermic reaction causes the reaction to shift toward the product side; cooling an endothermic reaction would cause it to shift to the reactants' side.

Exercise 5.E.22

The following reaction occurs when a burner on a gas stove is lit:

$$\mathrm{CH_4}(g) + 2\,\mathrm{O_2}(g) \rightleftharpoons \mathrm{CO_2}(g) + \mathrm{C_2H_2O}(g)$$

Is an equilibrium among $\mathrm{CH_4}$, $\mathrm{O_2}$, $\mathrm{CO_2}$, and $\mathrm{H_2O}$ established under these conditions? Explain your answer.

Answer

No, it is not at equilibrium. Because the system is not confined, products continuously escape from the region of the flame; reactants are also added continuously from the burner and surrounding atmosphere.

Exercise 5.E.23

Suggest four ways in which the concentration of hydrazine, $\mathrm{N_2H_4}$, could be increased in an equilibrium described by the following equation:

$$\mathrm{N_2}(g) + 2\mathrm{H_2}(g) \rightleftharpoons \mathrm{N_2H_4}(g) \quad \Delta H = 95\ \mathrm{kJ} \tag{5.E.8}$$

Answer

Add $\mathrm{N_2}$; add $\mathrm{H_2}$; decrease the container volume; heat the mixture.

Exercise 5.E.24

How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?

a. $2\,\mathrm{NH_3}(g) \rightleftharpoons \mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \quad \Delta H = 92\ \mathrm{kJ}$
b. $\mathrm{N_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\,\mathrm{NO}(g) \quad \Delta H = 181\ \mathrm{kJ}$
c. $2\,\mathrm{O_3}(g) \rightleftharpoons 3\,\mathrm{O_2}(g) \quad \Delta H = -285\ \mathrm{kJ}$
d. $\mathrm{CaO}(s) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{CaCO_3}(s) \quad \Delta H = -176\ \mathrm{kJ}$

Answer

(a) ΔT increase = shift right, ΔP increase = shift left; (b) ΔT increase = shift right, ΔP increase = no effect; (c) ΔT increase = shift left, ΔP increase = shift left; (d) ΔT increase = shift left, ΔP increase = shift right.

Exercise 5.E.25

Water gas is a 1:1 mixture of carbon monoxide and hydrogen gas and is called water gas because it is formed from steam and hot carbon in the following reaction:

$$\mathrm{H_2O}(g) + \mathrm{C}(s) \rightleftharpoons \mathrm{H_2}(g) + \mathrm{CO}(g). \tag{5.E.9}$$

Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and hydrogen at high temperature and pressure in the presence of a suitable catalyst.

a. Write the expression for the equilibrium constant (K_c) for the reversible reaction

$$2\,\mathrm{H_2}(g) + \mathrm{CO}(g) \rightleftharpoons \mathrm{CH_3OH}(g) \quad \Delta H = -90.2\ \mathrm{kJ} \tag{5.E.10}$$

b. What will happen to the concentrations of $\mathrm{H_2}$, CO, and $\mathrm{CH_3OH}$ at equilibrium if more $\mathrm{H_2}$ is added?
c. What will happen to the concentrations of $\mathrm{HH_2}$, CO, and $\mathrm{CH_3OH}$ at equilibrium if CO is removed?
d. What will happen to the concentrations of $\mathrm{H_2}$, CO, and $\mathrm{CH_3OH}$ at equilibrium if $\mathrm{CH_3OH}$ is added?
e. What will happen to the concentrations of $\mathrm{HH_2}$, CO, and $\mathrm{CH_3OH}$ at equilibrium if the temperature of the system is increased?
f. What will happen to the concentrations of $\mathrm{H_2}$, CO, and $\mathrm{CH_3OH}$ at equilibrium if more catalyst is added?

Answer

$K_c = \dfrac{[CH_3OH]}{[H_2]^2[CO]}$; [$H_2$] increases, [CO] decreases, [CH_3OH] increases; [H_2] increases, [CO] decreases, [CH_3OH] decreases; [H_2] increases, [CO] increases, [CH_3OH] increases; [H_2] increases, [CO] increases, [CH_3OH] decreases; no changes.

Exercise 5.E.26

Ammonia is a weak base that reacts with water according to this equation:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4{}^+(aq) + OH^-(aq) \tag{5.E.11}$$

Will any of the following increase the percent of ammonia that is converted to the ammonium ion in water and why?

a. Addition of NaOH
b. Addition of HCl
c. Addition of NH_4Cl

Answer

Only (b)

Exercise 5.E.27

Suggest two ways in which the equilibrium concentration of Ag^+ can be reduced in a solution of Na^+, Cl^-, Ag^+, and NO_3^-, in contact with solid AgCl.

$$Na^+(aq) + Cl^- + Ag^+(aq) \rightleftharpoons AgCl(aq) + Na^+(aq) + NO_3{}^-(aq) \tag{5.E.12}$$

$$\Delta H = -65.9 \text{ kJ}$$

Answer

Add NaCl or some other salt that produces Cl^- to the solution. Cooling the solution forces the equilibrium to the right, precipitating more AgCl(s).

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5.S: Fundamental Equilibrium Concepts (Study Guide)

chemical equilibrium – condition where the concentration of products and reactants do not change with time

5.2: Chemical Equilibria

- **Chemical equilibrium** happens when the rates of forward and reverse reactions are equal, so the concentrations of products and reactants are constant
- **Equilibrium is a dynamic process:**

  the concentrations of reactants and products no longer change with time

  reactions do not stop

5.3 The Equilibrium Constant

- Relationship between concentrations of reactants and products at equilibrium

If $aA + bB \rightleftharpoons cC + dD$

then an equilibrium expression can be constructed

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- equilibrium expression depends only on stoichiometry of reaction and not mechanisms
- equilibrium constant:
- does not depend on initial concentrations
- does not matter if other substances present as long as they do not react with reactants or products
- varies with temperatures
- no units
- Can also be expressed in terms of pressure, K_p

$$K_p = \frac{(P_P)^p(P_Q)^q}{(P_A)^a(P_B)^b}$$

- Magnitude of Equilibrium Constants
  - $K \gg 1$; equilibrium lies to the right; products favored
  - $K \ll 1$; equilibrium lies to the left; reactants favored
- equilibrium expression written in one direction is the reciprocal of the one in the other direction
- homogeneous equilibria – substances in the same phase
- heterogeneous equilibria – substances in different phases
- a pure solid, a pure liquid, and a solvent in dilute solutions all appear in equilibrium laws, but they are all assigned activities that are equal to 1
- by convention the actvities of the pure solid, pure liquid, or solute are not explicitly written as part of the equilibrium law
- Predicting the Direction of Reaction
  - determine reaction quotient Q
  - at equilibrium Q=K
  - Q>K; reaction moves right to left
  - Q<K; reaction moves left to right

5.4 Calculating Equilibrium Constants

determining unknown equilibrium concentrations

- tabulate known initial and equilibrium concentrations
- calculate change in concentration that occurs as system reaches equilibrium
- use stoichiometry to determine change in concentration of unknown species

- from initial concentrations and changes in concentrations, calculate equilibrium concentrations
- Relating K_c and K_p

$$PV = nRT$$

\[P = (n/V)RT = MRT \nonumber \]

$$PA = [A](RT)$$

$$K_p = K_c(RT)D^n$$

- D n = change in moles from reactants to products

If system at equilibrium is disturbed by change in temperature, pressure or concentration then system will shift equilibrium position

5.5 Shifting Equilibria - Le Chatelier's Principle

- Change in Reactant or Product Concentration
  - addition of substance will result in consummation of part of added substance
  - if substance removed, reaction will move to produce more of the substance
- Effects of Volume and Pressure Changes
  - reducing volume, reaction shifts to reduce number of gas molecules
  - increase volume, reaction shifts to produce more gas molecules
  - increase pressure, decrease volume reduces total number of moles
  - pressure volume changes do not affect K as long as temperature is constant
  - changes concentrations of gaseous substances
- Effect on Temperature Change
  - endothermic: reactants + heat « products
  - exothermic: reactants « products + heat
  - increase temperature, equilibrium shifts in direction that absorbs heat
  - endothermic: increase T, increase K
  - exothermic: increase T, decrease K
  - cooling shifts equilibrium to produce heat
- The Effect of Catalysts
  - catalysts increase rate at which equilibrium is obtained
  - does not change composition of equilibrium mixture

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CHAPTER OVERVIEW

6: Acid-Base Equilibrium

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General Chemistry

This chapter will illustrate the chemistry of acid-base reactions and equilibria, and provide you with tools for quantifying the concentrations of acids and bases in solutions.

6.1: Brønsted-Lowry Acids and Bases
6.2: pH and pOH
6.3: Relative Strengths of Acids and Bases
6.4: Polyprotic Acids
6.5: Hydrolysis of Salt Solutions
6.6: Lewis Acids and Bases
6.E: Acid-Base Equilibrium (Exercises)
6.S: Acid–Base Equilibrium (Study Guide)

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6.1: Brønsted-Lowry Acids and Bases

Learning Objectives

- Identify acids, bases, and conjugate acid-base pairs according to the Brønsted-Lowry definition
- Write equations for acid and base ionization reactions
- Use the ion-product constant for water to calculate hydronium and hydroxide ion concentrations
- Describe the acid-base behavior of amphiprotic substances

Acids and bases have been known for a long time. When Robert Boyle characterized them in 1680, he noted that acids dissolve many substances, change the color of certain natural dyes (for example, they change litmus from blue to red), and lose these characteristic properties after coming into contact with alkalis (bases). In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO_2), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. 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.

In an earlier chapter on chemical reactions, we defined acids and bases as Arrhenius did: We identified an acid as a compound that dissolves in water to yield hydronium ions (H_3O^+) and a base as a compound that dissolves in water to yield hydroxide ions (OH^-). This definition is not wrong; it is simply limited.

Later, we extended the definition of an acid or a base using the more general definition proposed in 1923 by the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry. Their definition centers on the proton, H^+. A proton is what remains when a normal hydrogen atom, ${}^1_1H$, loses an electron. 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 the transfer of a proton from a proton donor (acid) to a proton acceptor (base). In a subsequent chapter of this text we will introduce the most general model of acid-base behavior introduced by the American chemist G. N. Lewis.

Acids may be compounds such as HCl or H_2SO_4, organic acids like acetic acid (CH_3COOH) or ascorbic acid (vitamin C), or H_2O. Anions (such as \(\ce{HSO_4^-}\), $H_2PO_4^-$, HS^-, and HCO_3^-) and cations (such as H_3O^+, NH_4^+, and $[Al(H_2O)_6]^{3+}$) may also act as acids. Bases fall into the same three categories. Bases may be neutral molecules (such as H_2O, NH_3, and CH_3NH_2), anions (such as OH^-, HS^-, HCO_3^-, CO_3^{2-}, F^-, and PO_4^{3-}), or cations (such as $[Al(H_2O)_5OH]^{2+}$). The most familiar bases are ionic compounds such as $NaOH$ and $Ca(OH)_2$, which contain the hydroxide ion, OH^-. The hydroxide ion in these compounds accepts a proton from acids to form water:

$$H^+ + OH^- \rightarrow H_2O \tag{6.1.1}$$

We call the product that remains after an acid donates a proton the conjugate base of the acid. This species is a base because it can accept a proton (to re-form the acid):

$$\text{acid} \rightleftharpoons \text{proton} + \text{conjugate base} \tag{6.1.2}$$

$$HF \rightleftharpoons H^+ + F^- \tag{6.1.3}$$

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \tag{6.1.4}$$

$$H_2O \rightleftharpoons H^+ + OH^- \tag{6.1.5}$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \tag{6.1.6}$$

$$NH_4^+ \rightleftharpoons H^+ + NH_3 \tag{6.1.7}$$

We call the product that results when a base accepts a proton the base's conjugate acid. This species is an acid because it can give up a proton (and thus re-form the base):

$$\text{base} + \text{proton} \rightleftharpoons \text{conjugate acid} \tag{6.1.8}$$

$$OH^- + H^+ \rightleftharpoons H_2O \tag{6.1.9}$$

$$H_2O + H^+ \rightleftharpoons H_3O^+ \tag{6.1.10}$$

$$NH_3 + H^+ \rightleftharpoons NH_4^+ \tag{6.1.11}$$

$$S^{2-} + H^+ \rightleftharpoons HS^- \tag{6.1.12}$$

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^- \tag{6.1.13}$$

$$F^- + H^+ \rightleftharpoons HF \tag{6.1.14}$$

In these two sets of equations, the behaviors of acids as proton donors and bases as proton acceptors are represented in isolation. In reality, all acid-base reactions involve the transfer of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water, OH^-, and the conjugate acid of ammonia, NH_4^+:

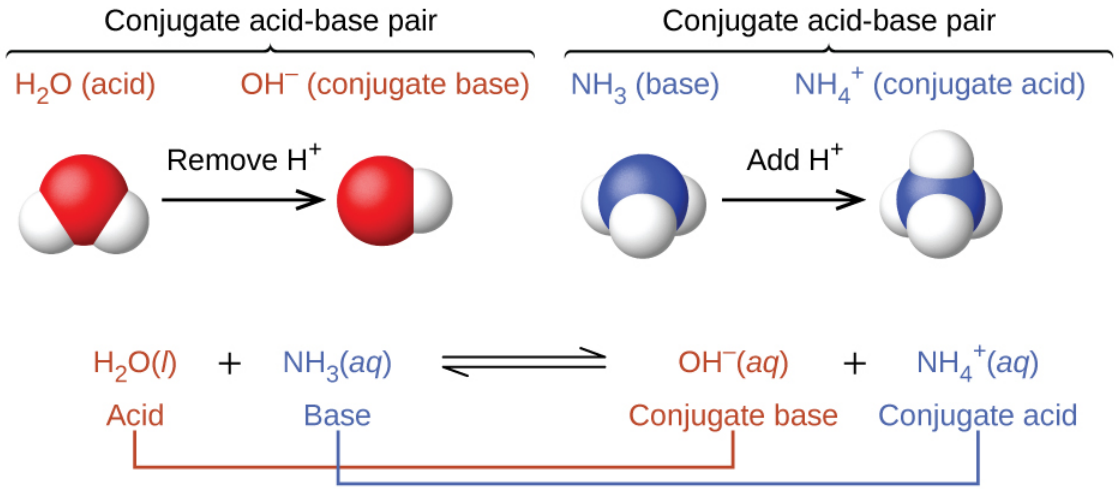


Figure 6.1.1: The acid-base reaction that takes place when ammonia dissolves in water has two conjugate acid-base pairs.

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:

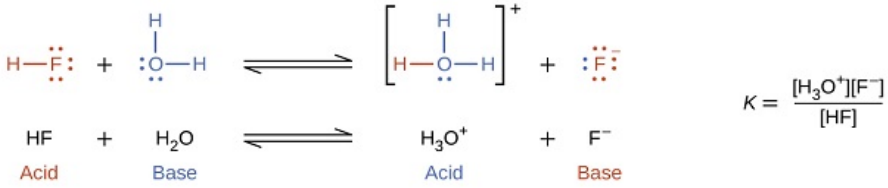


Figure 6.1.2: A Brønsted-Lowry acid-base reaction is a proton transfer reaction, as shown in this figure for the ionization of HF (aq).

When we add a base to water, a base ionization reaction occurs in which protons are transferred from water molecules to base molecules. For example, adding pyridine to water yields hydroxide ions and pyridinium ions:

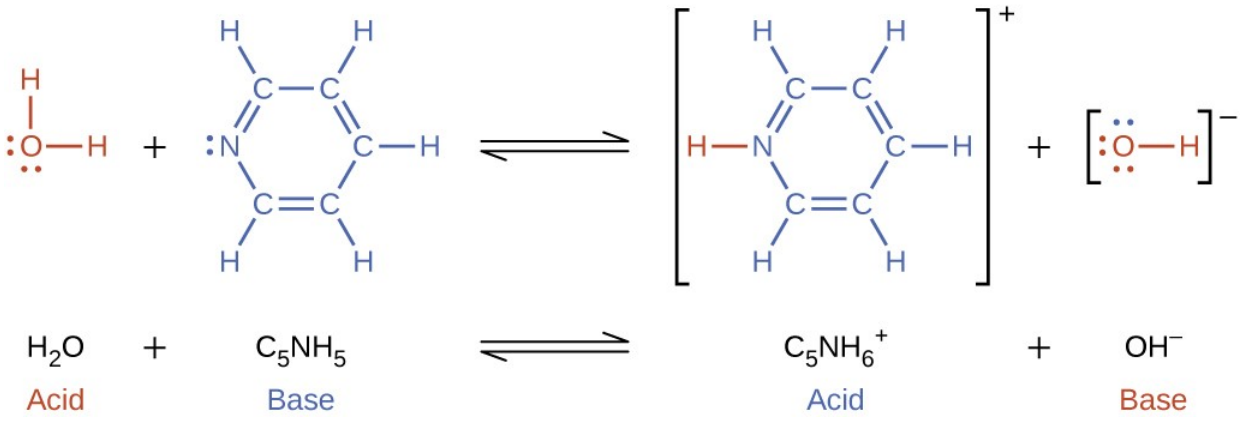


Figure 6.1.3: Water donates a proton to Pyridine.

Notice that both these ionization reactions are represented as equilibrium processes. The relative extent to which these acid and base ionization reactions proceed is an important topic treated in a later section of this chapter. In the preceding paragraphs we saw that water can function as either an acid or a base, depending on the nature of the solute dissolved in it. In fact, in pure water or in any aqueous solution, water acts both as an acid and a base. A very small fraction of water molecules donate protons to other water molecules to form hydronium ions and hydroxide ions:

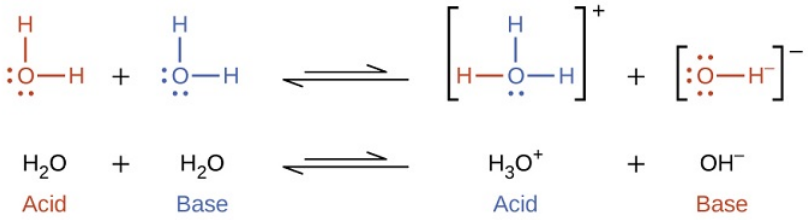


Figure 6.1.4: The autoionization of water reaction, where water is shown acting as both an acid and a base.

This type of reaction, in which a substance ionizes when one molecule of the substance reacts with another molecule of the same substance, is referred to as **autoionization**. Pure water undergoes autoionization to a very slight extent. Only about two out of every 10^9 molecules in a sample of pure water are ionized at 25 °C. The equilibrium constant for the ionization of water is called the ion-product constant for water (K_w):

$$\mathrm{H_2O_{(\mathit{l})} + H_2O_{(\mathit{l})} \rightleftharpoons H_3O^+_{(\mathit{aq})} + OH^-_{(\mathit{aq})}} \quad K_w = [\mathrm{H_3O^+}][\mathrm{OH^-}] \tag{6.1.15}$$

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, Kw 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 approximately 5.1×10^{-13}, roughly 50-times larger than the value at 25 °C.

Example 6.1.1: Ion Concentrations in Pure Water

What are the hydronium ion concentration and the hydroxide ion concentration in pure water at 25 °C?

Solution

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water, $[\mathrm{H_3O^+}] = [\mathrm{OH^-}]$. At 25 °C:

$$K_w = [\mathrm{H_3O^+}][\mathrm{OH^-}] = [\mathrm{H_3O^+}]^2 = [\mathrm{OH^-}]^2 = 1.0 \times 10^{-14}$$

So:

$$[\mathrm{H_3O^+}] = [\mathrm{OH^-}] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}\ M$$

The hydronium ion concentration and the hydroxide ion concentration are the same, and we find that both equal $1.0 \times 10^{-7}\ M$.

? Exercise 6.1.1

The ion product of water at 80 °C is 2.4×10^{-13}. What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

Answer

$$[H_3O^+] = [OH^-] = 4.9 \times 10^{-7}\ M$$

It is important to realize that the autoionization equilibrium for water is established in all aqueous solutions. Adding an acid or base to water will not change the position of the equilibrium. Example 14.12 demonstrates the quantitative aspects of this relation between hydronium and hydroxide ion concentrations.

✓ Example 6.1.2: The Inverse Proportionality of $[H_3O^+]$ and $[OH^-]$

The Inverse Proportionality of $[H_3O^+]$ and $[OH^-]$ A solution of carbon dioxide in water has a hydronium ion concentration of $2.0 \times 10^{-6}\ M$. What is the concentration of hydroxide ion at 25 °C?

Solution

We know the value of the ion-product constant for water at 25 °C:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

Thus, we can calculate the missing equilibrium concentration.

Rearrangement of the K_w expression yields that $[OH^-]$ is directly proportional to the inverse of $[H_3O^+]$:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9}$$

The hydroxide ion concentration in water is reduced to $5.0 \times 10^{-9}\ M$ as the hydrogen ion concentration increases to $2.0 \times 10^{-6}\ M$. This is expected from Le Chatelier's principle; the autoionization reaction shifts to the left to reduce the stress of the increased hydronium ion concentration and the $[OH^-]$ is reduced relative to that in pure water.

A check of these concentrations confirms that our arithmetic is correct:

$$\begin{aligned} K_w &= [H_3O^+][OH^-] \\ &= (2.0 \times 10^{-6})(5.0 \times 10^{-9}) \\ &= 1.0 \times 10^{-14} \end{aligned}$$

? Exercise 6.1.2

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 M at 25 °C?

Answer

$$[H_3O^+] = 1 \times 10^{-11} M$$

6.1.1: Amphiprotic Species

Like water, many molecules and ions may either gain or lose a proton under the appropriate conditions. Such species are said to be amphiprotic. Another term used to describe such species is amphoteric, which is a more general term for a species that may act

either as an acid or a base by any definition (not just the Brønsted-Lowry one). Consider for example the bicarbonate ion, which may either donate or accept a proton as shown here:

$$\mathrm{HCO_{3(aq)}^{-} + H_2O_{(l)} \rightleftharpoons CO_{3(aq)}^{2-} + H_3O_{(aq)}^{+}} \tag{6.1.16}$$

$$\mathrm{HCO_{3(aq)}^{-} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)} + OH_{(aq)}^{-}} \tag{6.1.17}$$

Example 6.1.3: The Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of $\mathrm{HSO_3^-}$

a. as an acid with $\mathrm{OH^-}$
b. as a base with HI

Solution

a. $\mathrm{HSO_3^-}(aq) + \mathrm{OH^-}(aq) \rightleftharpoons \mathrm{SO_3^{2-}}(aq) + \mathrm{H_2O}_{(l)}$
b. $\mathrm{HSO_3^-}(aq) + \mathrm{HI}(aq) \rightleftharpoons \mathrm{H_2SO_3}(aq) + \mathrm{I^-}(aq)$

Exercise 6.1.3

Write separate equations representing the reaction of $\mathrm{H_2PO_4^-}$

a. as a base with HBr
b. as an acid with $\mathrm{OH^-}$

Answer a

$\mathrm{H_2PO_4^-}(aq) + \mathrm{HBr}(aq) \rightleftharpoons \mathrm{H_3PO_4}(aq) + \mathrm{Br^-}(aq)$

Answer b

$\mathrm{H_2PO_4^-}(aq) + \mathrm{OH^-}(aq) \rightleftharpoons \mathrm{HPO_4^{2-}}(aq) + \mathrm{H_2O}_{(l)}$

Summary

A compound that can donate a proton (a hydrogen ion) to another compound is called a Brønsted-Lowry acid. The compound that accepts the proton is called a Brønsted-Lowry base. The species remaining after a Brønsted-Lowry acid has lost a proton is the conjugate base of the acid. The species formed when a Brønsted-Lowry base gains a proton is the conjugate acid of the base. Thus, an acid-base reaction occurs when a proton is transferred from an acid to a base, with formation of the conjugate base of the reactant acid and formation of the conjugate acid of the reactant base. Amphiprotic species can act as both proton donors and proton acceptors. Water is the most important amphiprotic species. It can form both the hydronium ion, H_3O^+, and the hydroxide ion, OH^- when it undergoes autoionization:

$$\mathrm{2\,H_2O_{(l)} \rightleftharpoons H_3O^+}(aq) + \mathrm{OH^-}(aq)$$

The ion product of water, K_w is the equilibrium constant for the autoionization reaction:

$$K_\mathrm{w} = [\mathrm{H_3O^+}][\mathrm{OH^-}] = 1.0 \times 10^{-14} \text{ at } 25\,^\circ\mathrm{C}$$

6.1.2: Key Equations

- $$K_\mathrm{w} = [\mathrm{H_3O^+}][\mathrm{OH^-}] = 1.0 \times 10^{-14} \text{ (at } 25\ ^\circ\mathrm{C})$$

Glossary

acid ionization
reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

amphiprotic
species that may either gain or lose a proton in a reaction

amphoteric
species that can act as either an acid or a base

autoionization
reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

base ionization
reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

Brønsted-Lowry acid
proton donor

Brønsted-Lowry base
proton acceptor

conjugate acid
substance formed when a base gains a proton

conjugate base
substance formed when an acid loses a proton

ion-product constant for water (K_w)
equilibrium constant for the autoionization of water

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6.2: pH and pOH

Learning Objectives

- Explain the characterization of aqueous solutions as acidic, basic, or neutral
- Express hydronium and hydroxide ion concentrations on the pH and pOH scales
- Perform calculations relating 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, the values of which 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:

$$\mathrm{pX} = -\log \mathrm{X} \tag{6.2.1}$$

The pH of a solution is therefore defined as shown here, where $[H_3O^+]$ is the molar concentration of hydronium ion in the solution:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] \tag{6.2.2}$$

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

$$[\mathrm{H_3O^+}] = 10^{-\mathrm{pH}} \tag{6.2.3}$$

Likewise, the hydroxide ion molarity may be expressed as a p-function, or pOH:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] \tag{6.2.4}$$

or

$$[\mathrm{OH^-}] = 10^{-\mathrm{pOH}} \tag{6.2.5}$$

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the K_w expression:

$$K_\mathrm{w} = [\mathrm{H_3O^+}][\mathrm{OH^-}] \tag{6.2.6}$$

$$-\log K_\mathrm{w} = -\log([\mathrm{H_3O^+}][\mathrm{OH^-}]) = -\log[\mathrm{H_3O^+}] + -\log[\mathrm{OH^-}] \tag{6.2.7}$$

$$\mathrm{p}K_\mathrm{w} = \mathrm{pH} + \mathrm{pOH} \tag{6.2.8}$$

At 25 °C, the value of K_w is 1.0×10^{-14}, and so:

$$14.00 = \mathrm{pH} + \mathrm{pOH} \tag{6.2.9}$$

The hydronium ion molarity in pure water (or any neutral solution) is $1.0 \times 10^{-7}\ M$ at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{6.2.10}$$

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{6.2.11}$$

And so, at this temperature, acidic solutions are those with hydronium ion molarities greater than $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities less than $1.0 \times 10^{-7}\ M$ (corresponding to pH values less than 7.00 and pOH values greater than 7.00). Basic solutions are those with hydronium ion molarities less than $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities greater than $1.0 \times 10^{-7}\ M$ (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

When $pH = 7$ Solutions are not Neutral

Since the autoionization constant K_w is temperature dependent, these correlations between pH values and the acidic/neutral/basic adjectives will be different at temperatures other than 25 °C. For example, the hydronium molarity of pure water at 80 °C is 4.9×10^{-7} *M*, which corresponds to pH and pOH values of:

$$\begin{aligned} pH &= -\log[\mathrm{H_3O^+}] \\ &= -\log(4.9 \times 10^{-7}) \\ &= 6.31 \\ pOH &= -\log[\mathrm{OH^-}] \\ &= -\log(4.9 \times 10^{-7}) \\ &= 6.31 \end{aligned}$$

At this temperature, then, neutral solutions exhibit pH = pOH = 6.31, acidic solutions exhibit pH less than 6.31 and pOH greater than 6.31, whereas basic solutions exhibit pH greater than 6.31 and pOH less than 6.31. This distinction can be important when studying certain processes that occur at nonstandard temperatures, such as enzyme reactions in warm-blooded organisms. Unless otherwise noted, references to pH values are presumed to be those at standard temperature (25 °C) (Table 6.2.1).

Table 6.2.1: 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 6.2.1 shows the relationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH, and gives values for these properties at standard temperatures for some common substances.

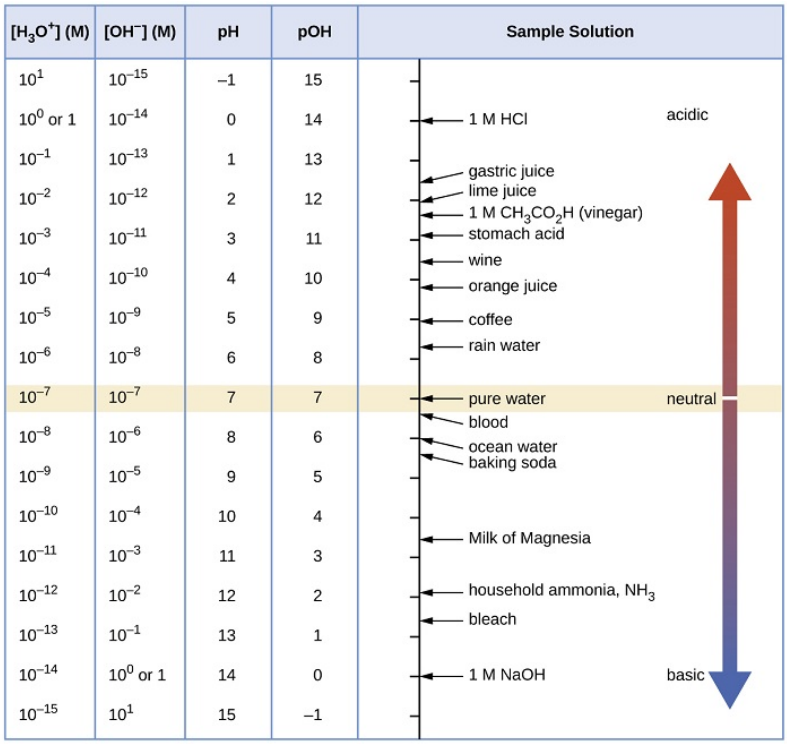


Figure 6.2.1: The pH and pOH scales represent concentrations of $[H_3O^+]$ and OH^-, respectively. The pH and pOH values of some common substances at standard temperature (25 °C) are shown in this chart.

Example 6.2.1: Calculation of pH from $[H_3O^+]$

What is the pH of stomach acid, a solution of HCl with a hydronium ion concentration of $1.2 \times 10^{-3}\ M$?

Solution

$$\begin{aligned} pH &= -\log[H_3O^+] \\ &= -\log(1.2 \times 10^{-3}) \\ &= -(-2.92) \\ &= 2.92 \end{aligned}$$

Exercise 6.2.1

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.

Answer

5.70

Example 6.2.2: Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3 (slightly alkaline).

Solution

$$pH = -\log[H_3O^+] = 7.3$$

$$\log[H_3O^+] = -7.3$$

$$[H_3O^+] = 10^{-7.3}$$

or

$$[H_3O^+] = \text{antilog of} - 7.3$$

$$[H_3O^+] = 5 \times 10^{-8}\ M$$

(On a calculator take the antilog, or the “inverse” log, of −7.3, or calculate $10^{-7.3}$.)

? Exercise 6.2.2

Calculate the hydronium ion concentration of a solution with a pH of −1.07.

Answer

12 M

6.2.1: Environmental Science

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved CO_2 which forms carbonic acid:

$$H_2O(l) + CO_2(g) \longrightarrow H_2CO_3(aq) \tag{6.2.12}$$

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \tag{6.2.13}$$

Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including CO_2, SO_2, SO_3, NO, and NO_2 being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

$$H_2O(l) + SO_3(g) \longrightarrow H_2SO_4(aq) \tag{6.2.14}$$

$$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq) \tag{6.2.15}$$

Carbon dioxide is naturally present in the atmosphere because we and most other organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems from burning fossil fuels, which have traces of sulfur, and from the process of “roasting” ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure 6.2.2). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.



(a)



(b)

Figure 6.2.2: (a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also is corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by "Eden, Janine and Jim"/Flickr)

Example 6.2.3: Calculation of pOH

What are the pOH and the pH of a 0.0125-M solution of potassium hydroxide, KOH?

Solution

Potassium hydroxide is a highly soluble ionic compound and completely dissociates when dissolved in dilute solution, yielding $[OH^-]$ = 0.0125 M:

$$\mathrm{pOH} = -\log[\mathrm{OH}^-] = -\log 0.0125$$

$$= -(-1.903) = 1.903$$

The pH can be found from the pOH:

$$\mathrm{pH} + \mathrm{pOH} = 14.00$$

$$\mathrm{pH} = 14.00 - \mathrm{pOH} = 14.00 - 1.903 = 12.10$$

Exercise 6.2.3

The hydronium ion concentration of vinegar is approximately $4 \times 10^{-3}\ M$. What are the corresponding values of pOH and pH?

Answer

pOH = 11.6,

pH = 14.00 - pOH = 2.4

The acidity of a solution is typically assessed experimentally by measurement of its pH. The pOH of a solution is not usually measured, as it is easily calculated from an experimentally determined pH value. The pH of a solution can be directly measured using a pH meter (Figure 6.2.3).



(a)



(b)

Figure 6.2.3: (a) A research-grade pH meter used in a laboratory can have a resolution of 0.001 pH units, an accuracy of ± 0.002 pH units, and may cost in excess of $1000. (b) A portable pH meter has lower resolution (0.01 pH units), lower accuracy (± 0.2 pH units), and a far lower price tag. (credit b: modification of work by Jacopo Werther)

The pH of a solution may also be visually estimated using colored indicators (Figure 6.2.3).



Figure 6.2.4: (a) A universal indicator assumes a different color in solutions of different pH values. Thus, it can be added to a solution to determine the pH of the solution. The eight vials each contain a universal indicator and 0.1-M solutions of progressively weaker acids: HCl (pH = l), CH_3CO_2H (pH = 3), and NH_4Cl (pH = 5), deionized water, a neutral substance (pH = 7); and 0.1-M solutions of the progressively stronger bases: KCl (pH = 7), aniline, $C_6H_5NH_2$ (pH = 9), NH_3 (pH = 11), and NaOH (pH = 13). (b) pH paper contains a mixture of indicators that give different colors in solutions of differing pH values. (credit: modification of work by Sahar Atwa).

Summary

The concentration of hydronium ion in a solution of an acid in water is greater than $1.0 \times 10^{-7}\ M$ at 25 °C. The concentration of hydroxide ion in a solution of a base in water is greater than $1.0 \times 10^{-7}\ M$ at 25 °C. The concentration of H_3O^+ in a solution can be expressed as the pH of the solution; $\text{pH} = -\log \text{H}_3\text{O}^+$. The concentration of OH^- can be expressed as the pOH of the solution: $\text{pOH} = -\log[\text{OH}^-]$. In pure water, pH = 7.00 and pOH = 7.00

6.2.2: Key Equations

- $\text{pH} = -\log[\text{H}_3\text{O}^+]$
- $\text{pOH} = -\log[\text{OH}^-]$
- $[H_3O^+] = 10^{-\text{pH}}$
- $[OH^-] = 10^{-\text{pOH}}$
- pH + pOH = pK_w = 14.00 at 25 °C

Glossary

acidic
describes a solution in which $[H_3O^+] > [OH^-]$

basic
describes a solution in which $[H_3O^+] < [OH^-]$

neutral
describes a solution in which $[H_3O^+] = [OH^-]$

pH
logarithmic measure of the concentration of hydronium ions in a solution

pOH
logarithmic measure of the concentration of hydroxide ions in a solution

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6.3: Relative Strengths of Acids and Bases

Learning Objectives

- Assess the relative strengths of acids and bases according to their ionization constants
- Rationalize trends in acid–base strength in relation to molecular structure
- Carry out equilibrium calculations for weak acid–base systems

We can rank the strengths of acids by the extent to which they ionize in aqueous solution. The reaction of an acid with water is given by the general expression:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq)$$

Water is the base that reacts with the acid HA, $\mathrm{A^-}$ is the conjugate base of the acid HA, and the hydronium ion is the conjugate acid of water. A strong acid yields 100% (or very nearly so) of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$ when the acid ionizes in water; Figure $6.3.1$ lists several strong acids. A weak acid gives small amounts of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$.

Figure $6.3.1$: Some of the common strong acids and bases are listed here.

Six Strong Acids		Six Strong Bases	
$\mathrm{HClO_4}$	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$\mathrm{Ca(OH)_2}$	calcium hydroxide
$\mathrm{HNO_3}$	nitric acid	$\mathrm{Sr(OH)_2}$	strontium hydroxide
$\mathrm{H_2SO_4}$	sulfuric acid	$\mathrm{Ba(OH)_2}$	barium hydroxide

The relative strengths of acids may be determined 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:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq)$$

we write the equation for the ionization constant as:

$$K_\mathrm{a} = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

where the concentrations are those at equilibrium. As noted in the section on equilibrium constants, although water is a reactant in the reaction, it is the solvent as well, so its activity has a value of 1, which does not change the value of K_a.

Note

It is a common error to claim that the molar concentration of the solvent is in some way involved in the equilibrium law. This error is a result of a misunderstanding of solution thermodynamics. For example, it is often claimed that $K_a = K_{eq}[H_2O]$ for aqueous solutions. This equation is incorrect because it is an erroneous interpretation of the correct equation $K_a = K_{eq}(a_{H_2O})$. Because $a_{H_2O} = 1$ for a dilute solution, $K_a = K_{eq}(1)$, or $K_a = K_{eq}$.

The following data on acid-ionization constants indicate the order of acid strength: $\mathrm{CH_3CO_2H} < \mathrm{HNO_2} < \mathrm{HSO_4^-}$

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq) \qquad K_\mathrm{a} = 1.8 \times 10^{-5}$$

$$\mathrm{HNO_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{NO_2^-}(aq) \qquad K_\mathrm{a} = 4.6 \times 10^{-4}$$

$$\mathrm{HSO_4^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{SO_4^{2-}}(aq) \qquad K_\mathrm{a} = 1.2 \times 10^{-2}$$

Another measure of the strength of an acid is its *percent ionization*. The percent ionization of a weak acid is the ratio of the concentration of the ionized acid to the initial acid concentration, times 100:

$$\%\ \text{ionization} = \frac{[\mathrm{H_3O^+}]_\mathrm{eq}}{[\mathrm{HA}]_0} \times 100\% \tag{6.3.1}$$

Because the ratio includes the initial concentration, the percent ionization for a solution of a given weak acid varies depending on the original concentration of the acid, and actually decreases with increasing acid concentration.

Example 6.3.1: 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:

$$\frac{[\mathrm{H_3O^+}]_\mathrm{eq}}{[\mathrm{HNO_2}]_0} \times 100$$

The chemical equation for the dissociation of the nitrous acid is:

$$\mathrm{HNO_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NO_2^-}(aq) + \mathrm{H_3O^+}(aq).$$

Since $10^{-pH} = [\mathrm{H_3O^+}]$, we find that $10^{-2.09} = 8.1 \times 10^{-3}\ M$, so that percent ionization (Equation 6.3.1) is:

$$\frac{8.1 \times 10^{-3}}{0.125} \times 100 = 6.5\%$$

Remember, the logarithm 2.09 indicates a hydronium ion concentration with only two significant figures.

Exercise 6.3.1

Calculate the percent ionization of a 0.10 *M* solution of acetic acid with a pH of 2.89.

Answer

1.3% ionized

We can rank the strengths of bases by their tendency to form hydroxide ions in aqueous solution. The reaction of a Brønsted-Lowry base with water is given by:

$$\mathrm{B}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HB^+}(aq) + \mathrm{OH^-}(aq)$$

Water is the acid that reacts with the base, $\mathrm{HB^+}$ is the conjugate acid of the base B, and the hydroxide ion is the conjugate base of water. A strong base yields 100% (or very nearly so) of $\mathrm{OH^-}$ and $\mathrm{HB^+}$ when it reacts with water; Figure $6.3.1$ lists several strong bases. A weak base yields a small proportion of hydroxide ions. Soluble ionic hydroxides such as NaOH are considered strong bases because they dissociate completely when dissolved in water.

As we did with acids, we can measure the relative strengths of bases by measuring their 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:

$$\mathrm{B}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HB^+}(aq) + \mathrm{OH^-}(aq),$$

we write the equation for the ionization constant as:

$$K_\text{b} = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$$

where the concentrations are those at equilibrium. Again, we do not see water in the equation because water is the solvent and has an activity of 1. The chemical reactions and ionization constants of the three bases shown are:

$$\text{NO}_2^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HNO}_2(aq) + \text{OH}^-(aq) \qquad K_\text{b} = 2.17 \times 10^{-11}$$

$$\text{CH}_3\text{CO}_2^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{CO}_2\text{H}(aq) + \text{OH}^-(aq) \qquad K_\text{b} = 5.6 \times 10^{-10}$$

$$\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq) \qquad K_\text{b} = 1.8 \times 10^{-5}$$

A table of ionization constants of weak bases appears in Table E2. As with acids, percent ionization can be measured for basic solutions, but will vary depending on the base ionization constant and the initial concentration of the solution.

Consider the ionization reactions for a conjugate acid-base pair, $\text{HA} - \text{A}^-$:

$$\text{HA}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq)$$

with $K_\text{a} = \dfrac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$.

$$\text{A}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{HA}(aq)$$

with $K_\text{b} = \dfrac{[\text{HA}][\text{OH}]}{[\text{A}^-]}$.

Adding these two chemical equations yields the equation for the autoionization for water:

$$\cancel{\text{HA}(aq)} + \text{H}_2\text{O}(l) + \cancel{\text{A}^-(aq)} + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \cancel{\text{A}^-(aq)} + \text{OH}^-(aq) + \cancel{\text{HA}(aq)}$$

$$2\,\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)$$

As shown in the previous chapter on equilibrium, the K expression for a chemical equation derived from adding two or more other equations is the mathematical product of the other equations' K expressions. Multiplying the mass-action expressions together and cancelling common terms, we see that:

$$K_\text{a} \times K_\text{b} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \times \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = [\text{H}_3\text{O}^+][\text{OH}^-] = K_\text{w}$$

For example, the acid ionization constant of acetic acid (CH_3COOH) is 1.8×10^{-5}, and the base ionization constant of its conjugate base, acetate ion (CH_3COO^-), is 5.6×10^{-10}. The product of these two constants is indeed equal to K_w:

$$K_\text{a} \times K_\text{b} = (1.8 \times 10^{-5}) \times (5.6 \times 10^{-10}) = 1.0 \times 10^{-14} = K_\text{w}$$

The extent to which an acid, HA, donates protons to water molecules depends on the strength of the conjugate base, A^-, of the acid. If A^- is a strong base, any protons that are donated to water molecules are recaptured by A^-. Thus there is relatively little A^- and H_3O^+ in solution, and the acid, HA, is weak. If A^- is a weak base, water binds the protons more strongly, and the solution contains primarily A^- and H_3O^+—the acid is strong. Strong acids form very weak conjugate bases, and weak acids form stronger conjugate bases (Figure 6.3.2).

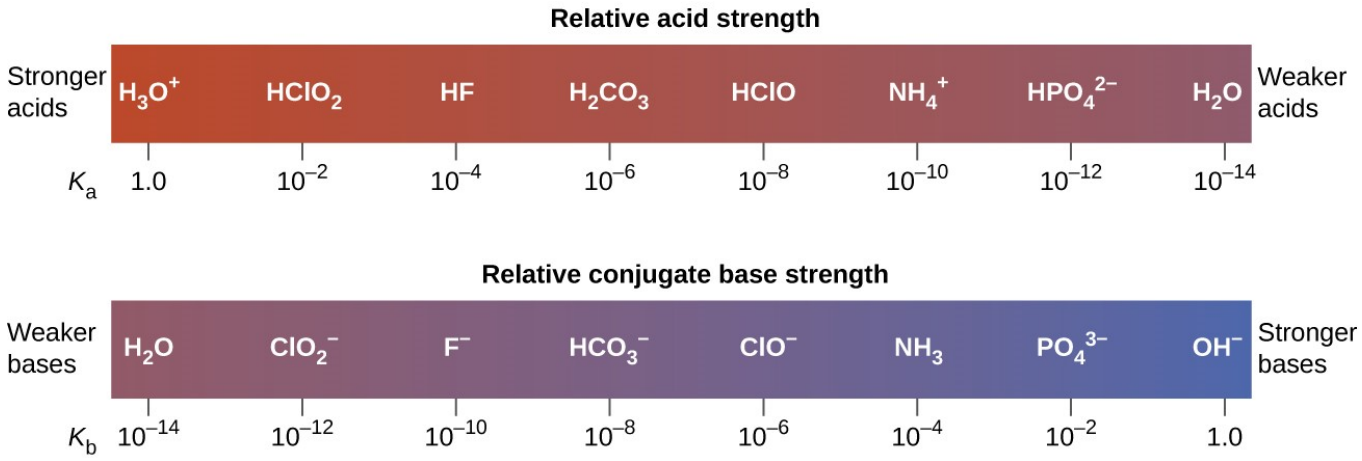


Figure 6.3.1: This diagram shows the relative strengths of conjugate acid-base pairs, as indicated by their ionization constants in aqueous solution.

Figure 6.3.2 lists a series of acids and bases in order of the decreasing strengths of the acids and the corresponding increasing strengths of the bases. The acid and base in a given row are conjugate to each other.

The first six acids in Figure 6.3.2 are the most common strong acids. These acids are completely dissociated in aqueous solution. The conjugate bases of these acids are weaker bases than water. When one of these acids dissolves in water, their protons are completely transferred to water, the stronger base.

Those acids that lie between the hydronium ion and water in Figure 6.3.2 form conjugate bases that can compete with water for possession of a proton. Both hydronium ions and nonionized acid molecules are present in equilibrium in a solution of one of these acids. Compounds that are weaker acids than water (those found below water in the column of acids) in Figure 6.3.2 exhibit no observable acidic behavior when dissolved in water. Their conjugate bases are stronger than the hydroxide ion, and if any conjugate base were formed, it would react with water to re-form the acid.

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

Increasing acid strength

Increasing base strength

Figure 6.3.2: The chart shows the relative strengths of conjugate acid-base pairs.

The extent to which a base forms hydroxide ion in aqueous solution depends on the strength of the base relative to that of the hydroxide ion, as shown in the last column in Figure 6.3.2. A strong base, such as one of those lying below hydroxide ion, accepts protons from water to yield 100% of the conjugate acid and hydroxide ion. Those bases lying between water and hydroxide ion accept protons from water, but a mixture of the hydroxide ion and the base results. Bases that are weaker than water (those that lie above water in the column of bases) show no observable basic behavior in aqueous solution.

Example 6.3.2: The Product $K_a \times K_b = K_w$

Use the K_b for the nitrite ion, NO_2^-, to calculate the K_a for its conjugate acid.

Solution

K_b for NO_2^- is given in this section as 2.17×10^{-11}. The conjugate acid of NO_2^- is HNO_2; K_a for HNO_2 can be calculated using the relationship:

$$K_a \times K_b = 1.0 \times 10^{-14} = K_w$$

Solving for K_a, we get:

$$K_a = \frac{K_w}{K_b}$$
$$= \frac{1.0 \times 10^{-14}}{2.17 \times 10^{-11}}$$
$$= 4.6 \times 10^{-4}$$

This answer can be verified by finding the K_a for HNO_2 in Table E1

? Exercise 6.3.2

We can determine the relative acid strengths of NH_4^+ and HCN by comparing their ionization constants. The ionization constant of HCN is given in Table E1 as 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}. Determine the ionization constant of NH_4^+, and decide which is the stronger acid, HCN or NH_4^+.

Answer

NH_4^+ is the slightly stronger acid (K_a for NH_4^+ = 5.6×10^{-10}).

The Ionization of Weak Acids and Weak Bases

Many acids and bases are weak; that is, they do not ionize fully in aqueous solution. A solution of a weak acid in water is a mixture of the nonionized acid, hydronium ion, and the conjugate base of the acid, with the nonionized acid present in the greatest concentration. Thus, a weak acid increases the hydronium ion concentration in an aqueous solution (but not as much as the same amount of a strong acid).

Acetic acid (CH_3CO_2H) is a weak acid. When we add acetic acid to water, it ionizes to a small extent according to the equation:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

giving an equilibrium mixture with most of the acid present in the nonionized (molecular) form. This equilibrium, like other equilibria, is dynamic; acetic acid molecules donate hydrogen ions to water molecules and form hydronium ions and acetate ions at the same rate that hydronium ions donate hydrogen ions to acetate ions to reform acetic acid molecules and water molecules. We can tell by measuring the pH of an aqueous solution of known concentration that only a fraction of the weak acid is ionized at any moment (Figure 6.3.4). The remaining weak acid is present in the nonionized form.

For acetic acid, at equilibrium:

$$K_a = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3CO_2H]} = 1.8 \times 10^{-5}$$



Figure 6.3.3: pH paper indicates that a 0.l-M solution of HCl (beaker on left) has a pH of 1. The acid is fully ionized and $[H_3O^+]$ = 0.1 M. A 0.1-M solution of CH_3CO_2H (beaker on right) has a pH of 3 ($[H_3O^+]$ = 0.001 M) because the weak acid CH_3CO_2H is only partially ionized. In this solution, $[H_3O^+] < [CH_3CO_2H]$. (credit: modification of work by Sahar Atwa)

Table 6.3.1: Ionization Constants of Some Weak Acids

Ionization Reaction	K_a at 25 °C
$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$	1.2×10^{-2}
$HF + H_2O \rightleftharpoons H_3O^+ + F^-$	3.5×10^{-4}
$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$	4.6×10^{-4}
$HNCO + H_2O \rightleftharpoons H_3O^+ + NCO^-$	2×10^{-4}
$HCO_2H + H_2O \rightleftharpoons H_3O^+ + HCO_2^-$	1.8×10^{-4}
$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$	1.8×10^{-5}
$HClO + H_2O \rightleftharpoons H_3O^+ + ClO^-$	2.9×10^{-8}
$HBrO + H_2O \rightleftharpoons H_3O^+ + BrO^-$	2.8×10^{-9}
$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	4.9×10^{-10}

Table 6.3.1 gives the ionization constants for several weak acids; additional ionization constants can be found in Table E1.

At equilibrium, a solution of a weak base in water is a mixture of the nonionized base, the conjugate acid of the weak base, and hydroxide ion with the nonionized base present in the greatest concentration. Thus, a weak base increases the hydroxide ion concentration in an aqueous solution (but not as much as the same amount of a strong base).

For example, a solution of the weak base trimethylamine, $(CH_3)_3N$, in water reacts according to the equation:

$$(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq)$$

This gives an equilibrium mixture with most of the base present as the nonionized amine. This equilibrium is analogous to that described for weak acids.

We can confirm by measuring the pH of an aqueous solution of a weak base of known concentration that only a fraction of the base reacts with water (Figure 14.4.5). The remaining weak base is present as the unreacted form. The equilibrium constant for the ionization of a weak base, K_b, is called the **ionization constant** of the weak base, and is equal to the reaction quotient when the reaction is at equilibrium. For trimethylamine, at equilibrium:

$$K_b = \frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]}$$



Figure 6.3.4: pH paper indicates that a 0.1-M solution of NH_3 (left) is weakly basic. The solution has a pOH of 3 ($[OH^-]$ = 0.001 M) because the weak base NH_3 only partially reacts with water. A 0.1-M solution of NaOH (right) has a pOH of 1 because NaOH is a strong base (credit: modification of work by Sahar Atwa).

The ionization constants of several weak bases are given in Table 6.3.2 and Table E2.

Table 6.3.2: Ionization Constants of Some Weak Bases

Ionization Reaction	K_b at 25 °C
$(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + OH^-$	5.9×10^{-4}

Ionization Reaction	K_b at 25 °C
$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$	4.4×10^{-4}
$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$	6.3×10^{-5}
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}
$C_6H_5NH_2 + H_2O \rightleftharpoons C_6N_5NH_3^+ + OH^-$	4.3×10^{-10}

Example 6.3.3: Determination of K_a from Equilibrium Concentrations

Acetic acid is the principal ingredient in vinegar; that's why it tastes sour. At equilibrium, a solution contains $[CH_3CO_2H]$ = 0.0787 *M* and $[H_3O^+] = [CH_3CO_2^-] = 0.00118$ *M*. What is the value of K_a for acetic acid?



Vinegar is a solution of acetic acid, a weak acid. (credit: modification of work by "HomeSpot HQ"/Flickr)

Solution

We are asked to calculate an equilibrium constant from equilibrium concentrations. At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

$$K_a = \frac{[H_3O^+][CH_3CO_2^-]}{[CH_3CO_2H]}$$

$$= \frac{(0.00118)(0.00118)}{0.0787}$$

$$= 1.77 \times 10^{-5}$$

Exercise 6.3.3

What is the equilibrium constant for the ionization of the HSO_4^- ion, the weak acid used in some household cleansers:

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$$

In one mixture of $NaHSO_4$ and Na_2SO_4 at equilibrium, $[H_3O^+]$ = 0.027 *M*; $[HSO_4^-] = 0.29$ *M*; and $[SO_4^{2-}] = 0.13$ *M*.

Answer

K_a for $HSO_4^- = 1.2 \times \times 10^{-2}$

Example 6.3.4: Determination of K_b from Equilibrium Concentrations

Caffeine, $C_8H_{10}N_4O_2$ is a weak base. What is the value of K_b for caffeine if a solution at equilibrium has $[C_8H_{10}N_4O_2]$ = 0.050 *M*, $[C_8H_{10}N_4O_2H^+]$ = 5.0×10^{-3} *M*, and $[OH^-]$ = 2.5×10^{-3} *M*?

Solution

At equilibrium, the value of the equilibrium constant is equal to the reaction quotient for the reaction:

$$C_8H_{10}N_4O_2(aq) + H_2O(l) \rightleftharpoons C_8H_{10}N_4O_2H^+(aq) + OH^-(aq)$$

so

$$K_b = \frac{[C_8H_{10}N_4O_2H^+][OH^-]}{[C_8H_{10}N_4O_2]} = \frac{(5.0 \times 10^{-3})(2.5 \times 10^{-3})}{0.050} = 2.5 \times 10^{-4}$$

Exercise 6.3.4

What is the equilibrium constant for the ionization of the HPO_4^{2-} ion, a weak base:

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + OH^-(aq)$$

In a solution containing a mixture of NaH_2PO_4 and Na_2HPO_4 at equilibrium with:

- $[OH^-] = 1.3 \times 10^{-6} M$
- $[H_2PO_4^-]$=0 · 042 M and
- $[HPO_4^{2-}]$=0 · 341 M.

Answer

K_b for $HPO_4^{2-} = 1.6 \times 10^{-7}$

Example 6.3.5: Determination of K_a or K_b from pH

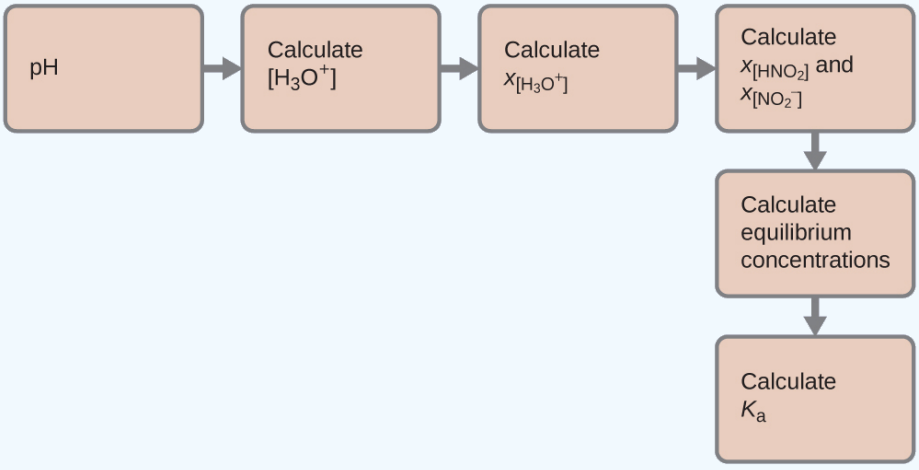
The pH of a 0.0516-*M* solution of nitrous acid, HNO_2, is 2.34. What is its K_a?

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$$

Solution

We determine an equilibrium constant starting with the initial concentrations of HNO_2, H_3O^+, and NO_2^- as well as one of the final concentrations, the concentration of hydronium ion at equilibrium. (Remember that pH is simply another way to express the concentration of hydronium ion.)

We can solve this problem with the following steps in which *x* is a change in concentration of a species in the reaction:



We can summarize the various concentrations and changes as shown here. Because water is the solvent, it has a fixed activity equal to 1. Any small amount of water produced or used up during the reaction will not change water's role as the solvent, so the value of its activity remains equal to 1 throughout the reaction.

	HNO_2 +	H_2O ⇌	H_3O^+ +	NO_2^-
Initial concentration (*M*)	0.0516		~0	0
Change (*M*)	−*x*	+	*x*	*x*
Equilibrium concentration (*M*)	$[HNO_2]_i$ + (−*x*) = 0.0516 + (−*x*)		$[H_3O]^+$ + *x* $[NO_2]^-$ + *x* ~0 + *x*	0.0046

To get the various values in the ICE (Initial, Change, Equilibrium) table, we first calculate $[H_3O^+]$, the equilibrium concentration of H_3O^+, from the pH:

$$[H_3O^+] = 10^{-2.34} = 0.0046\ M$$

The change in concentration of H_3O^+, $x_{[H_3O^+]}$, is the difference between the equilibrium concentration of H_3O^+, which we determined from the pH, and the initial concentration, $[H_3O^+]_i$. The initial concentration of H_3O^+ is its concentration in pure water, which is so much less than the final concentration that we approximate it as zero (~0).

The change in concentration of NO_2^- is equal to the change in concentration of $[H_3O^+]$. For each 1 mol of H_3O^+ that forms, 1 mol of NO_2^- forms. The equilibrium concentration of HNO_2 is equal to its initial concentration plus the change in its concentration.

Now we can fill in the ICE table with the concentrations at equilibrium, as shown here:

	HNO_2 +	H_2O ⇌	H_3O^+ +	NO_2^-
Initial concentration (*M*)	0.0516		~0	0
Change (*M*)	−*x*	+	*x* = 0.0046	*x* = 0.0046
Equilibrium concentration (*M*)	0.0470		0.0046	0.0046

Finally, we calculate the value of the equilibrium constant using the data in the table:

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = \frac{(0.0046)(0.0046)}{(0.0470)} = 4.5 \times 10^{-4}$$

Exercise 6.3.5

The pH of a solution of household ammonia, a 0.950-*M* solution of NH_3, is 11.612. What is K_b for NH_3.

Answer

$K_b = 1.8 \times 10^{-5}$

Example 6.3.6: Equilibrium Concentrations in a Solution of a Weak Acid

Formic acid, HCO_2H, is the irritant that causes the body's reaction to ant stings.



The pain of an ant's sting is caused by formic acid. (credit: John Tann)

What is the concentration of hydronium ion and the pH in a 0.534-*M* solution of formic acid?

$$\mathrm{HCO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_2^-}(aq) \quad K_\mathrm{a} = 1.8 \times 10^{-4}$$

Solution

1. Determine x and equilibrium concentrations. The equilibrium expression is:

$$\mathrm{HCO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_2^-}(aq)$$

Because water is the solvent, it has a fixed activity equal to 1. Any small amount of water produced or used up during the reaction will not change water's role as the solvent, so the value of its activity remains equal to 1 throughout the reaction so we do not need to consider it when setting up the ICE table.

The table shows initial concentrations (concentrations before the acid ionizes), changes in concentration, and equilibrium concentrations follows (the data given in the problem appear in color):

	$\mathrm{HCO_2H}$ +	$\mathrm{H_2O}$ $\rightleftharpoons$	$\mathrm{H_3O^+}$
Initial concentration (*M*)	0.534	~0	0
Change (*M*)	−*x*	*x*	*x*
Equilibrium concentration (*M*)	0.534 + (−*x*)	0 + *x* = *x*	0 + *x* = *x*

2. Solve for x and the equilibrium concentrations. At equilibrium:

$$K_\mathrm{a} = 1.8 \times 10^{-4} = \frac{[\mathrm{H_3O^+}][\mathrm{HCO_2^-}]}{[\mathrm{HCO_2H}]}$$

$$= \frac{(x)(x)}{0.534 - x} = 1.8 \times 10^{-4}$$

Now solve for x. Because the initial concentration of acid is reasonably large and K_a is very small, we assume that $x << 0.534$, which *permits* us to simplify the denominator term as $(0.534 - x) = 0.534$. This gives:

$$K_\mathrm{a} = 1.8 \times 10^{-4} = \frac{x^2}{0.534}$$

Solve for x as follows:

$$x^2 = 0.534 \times (1.8 \times 10^{-4})$$

$$= 9.6 \times 10^{-5}$$

$$x = \sqrt{9.6 \times 10^{-5}}$$

$$= 9.8 \times 10^{-3}$$

To check the assumption that x is small compared to 0.534, we calculate:

$$\frac{x}{0.534} = \frac{9.8 \times 10^{-3}}{0.534}$$

$$= 1.8 \times 10^{-2}\ (1.8\%\ \text{of}\ 0.534)$$

x is less than 5% of the initial concentration; the assumption is valid.

We find the equilibrium concentration of hydronium ion in this formic acid solution from its initial concentration and the change in that concentration as indicated in the last line of the table:

$$[\mathrm{H_3O^+}] = 0 + x = 0 + 9.8 \times 10^{-3}\ M.$$

$$= 9.8 \times 10^{-3}\ M$$

The pH of the solution can be found by taking the negative log of the $[\mathrm{H_3O^+}]$, so:

$$pH = -\log(9.8 \times 10^{-3}) = 2.01$$

Exercise 6.3.6: acetic acid

Only a small fraction of a weak acid ionizes in aqueous solution. What is the percent ionization of acetic acid in a 0.100-*M* solution of acetic acid, CH_3CO_2H?

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq) \quad K_a = 1.8 \times 10^{-5}$$

Hint

Determine $[CH_3CO_2^-]$ at equilibrium.) Recall that the percent ionization is the fraction of acetic acid that is ionized × 100, or $\dfrac{[CH_3CO_2^-]}{[CH_3CO_2H]_{\text{initial}}} \times 100$.

Answer

percent ionization = 1.3%

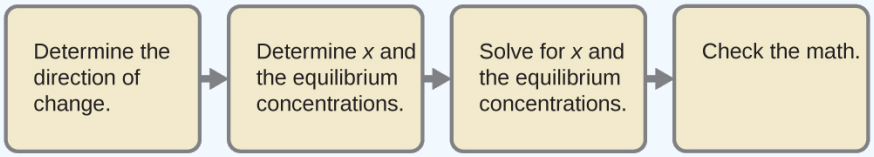
The following example shows that the concentration of products produced by the ionization of a weak base can be determined by the same series of steps used with a weak acid.

Example 6.3.7: Equilibrium Concentrations in a Solution of a Weak Base

Find the concentration of hydroxide ion in a 0.25-*M* solution of trimethylamine, a weak base:

$$(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq) \quad K_b = 6.3 \times 10^{-5}$$

Solution This problem requires that we calculate an equilibrium concentration by determining concentration changes as the ionization of a base goes to equilibrium. The solution is approached in the same way as that for the ionization of formic acid in Example 6.3.6. The reactants and products will be different and the numbers will be different, but the logic will be the same:



1. Determine x and equilibrium concentrations. The table shows the changes and concentrations:

	$(CH_3)_3N$ + H_2O ⇌ $(CH_3)_3NH^+$ + OH^-			
Initial concentration (*M*)	0.25		0	~0
Change (*M*)	−*x*		*x*	*x*
Equilibrium concentration (*M*)	0.25 + (−*x*)		0 + *x*	~0 + *x*

2. Solve for x and the equilibrium concentrations. At equilibrium:

$$K_b = \frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]} = \frac{(x)(x)}{0.25 - x =} 6.3 \times 10^{-5}$$

If we assume that *x* is small relative to 0.25, then we can replace (0.25 − *x*) in the preceding equation with 0.25. Solving the simplified equation gives:

$$x = 4.0 \times 10^{-3}$$

This change is less than 5% of the initial concentration (0.25), so the assumption is justified.

Recall that, for this computation, x is equal to the equilibrium concentration of *hydroxide ion* in the solution (see earlier tabulation):

$$([\mathrm{OH^-}] = 0 + x = x = 4.0 \times 10^{-3}\ M$$
$$= 4.0 \times 10^{-3}\ M$$

Then calculate pOH as follows:

$$\mathrm{pOH} = -\log(4.3 \times 10^{-3}) = 2.40$$

Using the relation introduced in the previous section of this chapter:

$$\mathrm{pH} + \mathrm{pOH} = \mathrm{p}K_\mathrm{w} = 14.00$$

permits the computation of pH:

$$\mathrm{pH} = 14.00 - \mathrm{pOH} = 14.00 - 2.37 = 11.60$$

Check the work. A check of our arithmetic shows that $K_b = 6.3 \times 10^{-5}$.

? Exercise 6.3.7

a. Show that the calculation in Step 2 of this example gives an *x* of 4.3 × 10^{-3} and the calculation in Step 3 shows K_b = 6.3 × 10^{-5}.

b. Find the concentration of hydroxide ion in a 0.0325-*M* solution of ammonia, a weak base with a K_b of 1.76 × 10^{-5}.

Calculate the percent ionization of ammonia, the fraction ionized × 100, or $\frac{[\mathrm{NH_4^+}]}{[\mathrm{NH_3}]} \times 100\%$

Answer a

$7.56 \times 10^{-4}\ M$, 2.33%

Answer b

2.33%

Some weak acids and weak bases ionize to such an extent that the simplifying assumption that *x* is small relative to the initial concentration of the acid or base is inappropriate. As we solve for the equilibrium concentrations in such cases, we will see that we cannot neglect the change in the initial concentration of the acid or base, and we must solve the equilibrium equations by using the quadratic equation.

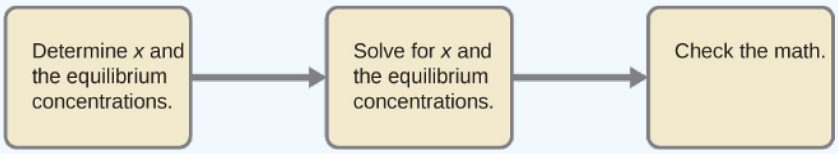
✓ Example 6.3.8: Equilibrium Concentrations in a Solution of a Weak Acid

Sodium bisulfate, $\mathrm{NaHSO_4}$, is used in some household cleansers because it contains the $\mathrm{HSO_4^-}$ ion, a weak acid. What is the pH of a 0.50-*M* solution of $\mathrm{HSO_4^-}$?

$$\mathrm{HSO_4^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{SO_4^{2-}}(aq) \quad K_\mathrm{a} = 1.2 \times 10^{-2}$$

Solution

We need to determine the equilibrium concentration of the hydronium ion that results from the ionization of $\mathrm{HSO_4^-}$ so that we can use $[\mathrm{H_3O^+}]$ to determine the pH. As in the previous examples, we can approach the solution by the following steps:



1. Determine x and equilibrium concentrations. This table shows the changes and concentrations:

	HSO_4^- + H_2O ⇌	H_3O^+	+ SO_4^{2-}
Initial concentration (*M*)	0.50	~0	0
Change (*M*)	−*x*	*x*	*x*
Equilibrium concentration (*M*)	0.50 + (−*x*) = 0.50 − *x*)	0 + *x* = *x*	0 + *x* = *x*

2. Solve for x and the concentrations.

As we begin solving for x, we will find this is more complicated than in previous examples. As we discuss these complications we should not lose track of the fact that it is still the purpose of this step to determine the value of x.

At equilibrium:

$$K_a = 1.2 \times 10^{-2} = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(x)(x)}{0.50 - x}$$

If we assume that *x* is small and approximate (0.50 − *x*) as 0.50, we find:

$$x = 7.7 \times 10^{-2}$$

When we check the assumption, we confirm:

$$\frac{x}{[HSO_4^-]_i} \overset{?}{\leq} 0.05$$

which for this system is

$$\frac{x}{0.50} = \frac{7.7 \times 10^{-2}}{0.50} = 0.15(15\%)$$

The value of x is not less than 5% of 0.50, so the assumption is not valid. We need the quadratic formula to find x.

The equation:

$$K_a = 1.2 \times 10^{-2} = \frac{(x)(x)}{0.50 - x}$$

gives

$$6.0 \times 10^{-3} - 1.2 \times 10^{-2} x = x^{2+}$$

or

$$x^{2+} + 1.2 \times 10^{-2} x - 6.0 \times 10^{-3} = 0$$

This equation can be solved using the quadratic formula. For an equation of the form

$$ax^{2+} + bx + c = 0,$$

x is given by the quadratic equation:

$$x = \frac{-b \pm \sqrt{b^{2+} - 4ac}}{2a}$$

In this problem, $a = 1$, $b = 1.2 \times 10^{-3}$, and $c = -6.0 \times 10^{-3}$.

Solving for x gives a negative root (which cannot be correct since concentration cannot be negative) and a positive root:

$$x = 7.2 \times 10^{-2}$$

Now determine the hydronium ion concentration and the pH:

$$[H_3O^+] = 0 + x = 0 + 7.2 \times 10^{-2}\ M$$
$$= 7.2 \times 10^{-2}\ M$$

The pH of this solution is:

$$pH = -\log[H_3O^+] = -\log 7.2 \times 10^{-2} = 1.14$$

? Exercise 6.3.8

a. Show that the quadratic formula gives $x = 7.2 \times 10^{-2}$.
b. Calculate the pH in a 0.010-*M* solution of caffeine, a weak base:

$$C_8H_{10}N_4O_2(aq) + H_2O(l) \rightleftharpoons C_8H_{10}N_4O_2H^+(aq) + OH^-(aq) \quad K_b = 2.5 \times 10^{-4}$$

Hint

It will be necessary to convert $[OH^-]$ to $[H_3O^+]$ or pOH to pH toward the end of the calculation.

Answer

pH 11.16

The Relative Strengths of Strong Acids and Bases

Strong acids, such as HCl, HBr, and HI, all exhibit the same strength in water. The water molecule is such a strong base compared to the conjugate bases Cl^-, Br^-, and I^- that ionization of these strong acids is essentially complete in aqueous solutions. In solvents less basic than water, we find HCl, HBr, and HI differ markedly in their tendency to give up a proton to the solvent. For example, when dissolved in ethanol (a weaker base than water), the extent of ionization increases in the order $HCl < HBr < HI$, and so HI is demonstrated to be the strongest of these acids. The inability to discern differences in strength among strong acids dissolved in water is known as the leveling effect of water.

Water also exerts a leveling effect on the strengths of strong bases. For example, the oxide ion, O^{2-}, and the amide ion, NH_2^-, are such strong bases that they react completely with water:

$$O^{2-}(aq) + H_2O(l) \longrightarrow OH^-(aq) + OH^-(aq)$$
$$NH_2^-(aq) + H_2O(l) \longrightarrow NH_3(aq) + OH^-(aq)$$

Thus, O^{2-} and NH_2^- appear to have the same base strength in water; they both give a 100% yield of hydroxide ion.

In the absence of any leveling effect, the acid strength of binary compounds of hydrogen with nonmetals (A) increases as the H-A bond strength decreases down a group in the periodic table. For group 17, the order of increasing acidity is $HF < HCl < HBr < HI$. Likewise, for group 16, the order of increasing acid strength is $H_2O < H_2S < H_2Se < H_2Te$. Across a row in the periodic table, the acid strength of binary hydrogen compounds increases with increasing electronegativity of the nonmetal atom because the polarity of the H-A bond increases. Thus, the order of increasing acidity (for removal of one proton) across the second row is $CH_4 < NH_3 < H_2O < HF$; across the third row, it is $SiH_4 < PH_3 < H_2S < HCl$ (see Figure 6.3.6).

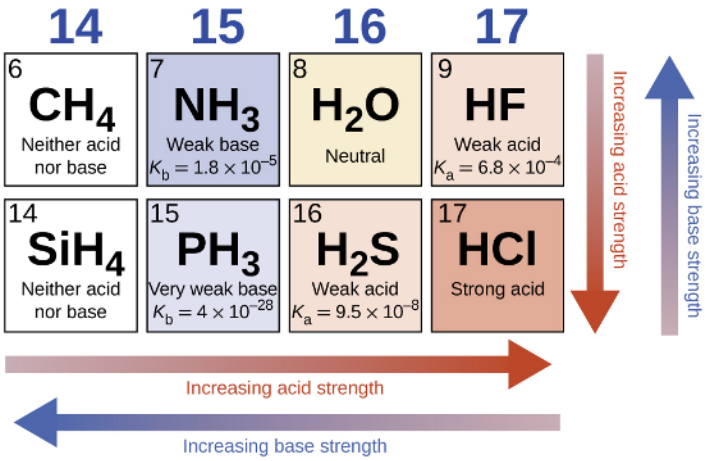
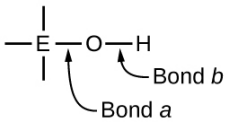


Figure 6.3.5: As you move from left to right and down the periodic table, the acid strength increases. As you move from right to left and up, the base strength increases.

Compounds containing oxygen and one or more hydroxyl (OH) groups can be acidic, basic, or amphoteric, depending on the position in the periodic table of the central atom E, the atom bonded to the hydroxyl group. Such compounds have the general formula $O_nE(OH)_m$, and include sulfuric acid, $O_2S(OH)_2$, sulfurous acid, $OS(OH)_2$, nitric acid, O_2NOH, perchloric acid, O_3ClOH, aluminum hydroxide, $Al(OH)_3$, calcium hydroxide, $Ca(OH)_2$, and potassium hydroxide, KOH:



If the central atom, E, has a low electronegativity, its attraction for electrons is low. Little tendency exists for the central atom to form a strong covalent bond with the oxygen atom, and bond *a* between the element and oxygen is more readily broken than bond *b* between oxygen and hydrogen. Hence bond *a* is ionic, hydroxide ions are released to the solution, and the material behaves as a base—this is the case with $Ca(OH)_2$ and KOH. Lower electronegativity is characteristic of the more metallic elements; hence, the metallic elements form ionic hydroxides that are by definition basic compounds.

If, on the other hand, the atom E has a relatively high electronegativity, it strongly attracts the electrons it shares with the oxygen atom, making bond *a* relatively strongly covalent. The oxygen-hydrogen bond, bond *b*, is thereby weakened because electrons are displaced toward E. Bond *b* is polar and readily releases hydrogen ions to the solution, so the material behaves as an acid. High electronegativities are characteristic of the more nonmetallic elements. Thus, nonmetallic elements form covalent compounds containing acidic −OH groups that are called oxyacids.

Increasing the oxidation number of the central atom E also increases the acidity of an oxyacid because this increases the attraction of E for the electrons it shares with oxygen and thereby weakens the O-H bond. Sulfuric acid, H_2SO_4, or $O_2S(OH)_2$ (with a sulfur oxidation number of +6), is more acidic than sulfurous acid, H_2SO_3, or $OS(OH)_2$ (with a sulfur oxidation number of +4). Likewise nitric acid, HNO_3, or O_2NOH (N oxidation number = +5), is more acidic than nitrous acid, HNO_2, or $ONOH$ (N oxidation number = +3). In each of these pairs, the oxidation number of the central atom is larger for the stronger acid (Figure 6.3.7).

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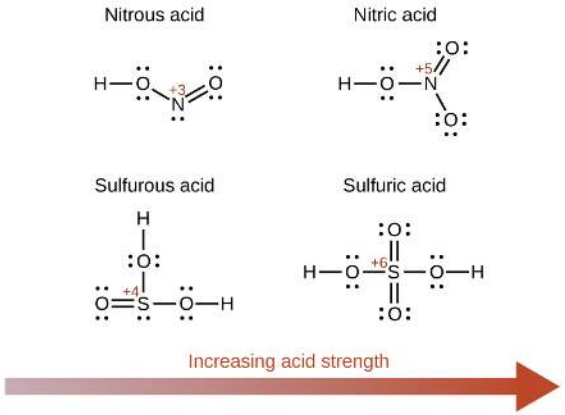


Figure 6.3.6: As the oxidation number of the central atom E increases, the acidity also increases.

Hydroxy compounds of elements with intermediate electronegativities and relatively high oxidation numbers (for example, elements near the diagonal line separating the metals from the nonmetals in the periodic table) are usually amphoteric. This means that the hydroxy compounds act as acids when they react with strong bases and as bases when they react with strong acids. The amphoterism of aluminum hydroxide, which commonly exists as the hydrate $\mathrm{Al(H_2O)_3(OH)_3}$, is reflected in its solubility in both strong acids and strong bases. In strong bases, the relatively insoluble hydrated aluminum hydroxide, $\mathrm{Al(H_2O)_3(OH)_3}$, is converted into the soluble ion, $\mathrm{[Al(H_2O)_2(OH)_4]^-}$, by reaction with hydroxide ion:

$$\mathrm{[Al(H_2O)_3(OH)_3](\mathit{aq}) + OH^-(\mathit{aq}) \rightleftharpoons H_2O(\mathit{l}) + [Al(H_2O)_2(OH)_4]^-(\mathit{aq})}$$

In this reaction, a proton is transferred from one of the aluminum-bound $\mathrm{H_2O}$ molecules to a hydroxide ion in solution. The $\mathrm{Al(H_2O)_3(OH)_3}$ compound thus acts as an acid under these conditions. On the other hand, when dissolved in strong acids, it is converted to the soluble ion $\mathrm{[Al(H_2O)_6]^{3+}}$ by reaction with hydronium ion:

$$\mathrm{3\,H_3O^+(\mathit{aq}) + Al(H_2O)_3(OH)_3(\mathit{aq}) \rightleftharpoons Al(H_2O)_6^{3+}(\mathit{aq}) + 3\,H_2O(\mathit{l})}$$

In this case, protons are transferred from hydronium ions in solution to $\mathrm{Al(H_2O)_3(OH)_3}$, and the compound functions as a base.

Summary

The strengths of Brønsted-Lowry acids and bases in aqueous solutions can be determined by their acid or base ionization constants. Stronger acids form weaker conjugate bases, and weaker acids form stronger conjugate bases. Thus strong acids are completely ionized in aqueous solution because their conjugate bases are weaker bases than water. Weak acids are only partially ionized because their conjugate bases are strong enough to compete successfully with water for possession of protons. Strong bases react with water to quantitatively form hydroxide ions. Weak bases give only small amounts of hydroxide ion. The strengths of the binary acids increase from left to right across a period of the periodic table ($\mathrm{CH_4 < NH_3 < H_2O < HF}$), and they increase down a group ($\mathrm{HF < HCl < HBr < HI}$). The strengths of oxyacids that contain the same central element increase as the oxidation number of the element increases ($\mathrm{H_2SO_3 < H_2SO_4}$). The strengths of oxyacids also increase as the electronegativity of the central element increases [$\mathrm{H_2SeO_4 < H_2SO_4}$].

Key Equations

- $\mathrm{K_a = \dfrac{[H_3O^+][A^-]}{[HA]}}$
- $\mathrm{K_b = \dfrac{[HB^+][OH^-]}{[B]}}$
- $K_a \times K_b = 1.0 \times 10^{-14} = K_w \text{ (at room temperature)}$
- $\text{Percent ionization} = \dfrac{[\mathrm{H_3O^+}]_{\mathrm{eq}}}{[\mathrm{HA}]_0} \times 100$

Glossary

acid ionization constant (K_a)
equilibrium constant for the ionization of a weak acid

base ionization constant (K_b)
equilibrium constant for the ionization of a weak base

leveling effect of water
any acid stronger than H_3O^+, or any base stronger than OH^- will react with water to form H_3O^+, or OH^-, respectively; water acts as a base to make all strong acids appear equally strong, and it acts as an acid to make all strong bases appear equally strong

oxyacid
compound containing a nonmetal and one or more hydroxyl groups

percent ionization
ratio of the concentration of the ionized acid to the initial acid concentration, times 100

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6.4: Polyprotic Acids

Learning Objectives

- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton

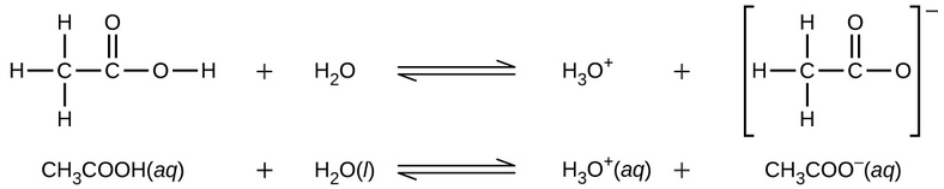
We can classify acids by the number of protons per molecule that they can give up in a reaction. Acids such as HCl, HNO_3, and HCN that contain one ionizable hydrogen atom in each molecule are called monoprotic acids. Their reactions with water are:

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

$$HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$$

$$HCN(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + CN^-(aq)$$

Even though it contains four hydrogen atoms, acetic acid, CH_3CO_2H, is also monoprotic because only the hydrogen atom from the carboxyl group ($-COOH$) reacts with bases:



Similarly, monoprotic bases are bases that will accept a single proton.

6.4.1: Diprotic Acids

Diprotic acids contain two ionizable hydrogen atoms per molecule; ionization of such acids occurs in two steps. The first ionization always takes place to a greater extent than the second ionization. For example, sulfuric acid, a strong acid, ionizes as follows:

- **The first ionization is**

$$H_2SO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_4^-(aq)$$

with $K_{a1} > 10^2$; *complete dissociation*.

- **The second ionization is**

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$$

with $K_{a2} = 1.2 \times 10^{-2}$.

This stepwise ionization process occurs for all polyprotic acids. When we make a solution of a weak diprotic acid, we get a solution that contains a mixture of acids. Carbonic acid, H_2CO_3, is an example of a weak diprotic acid. The first ionization of carbonic acid yields hydronium ions and bicarbonate ions in small amounts.

- **First Ionization**

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

with

$$K_{H_2CO_3} = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = 4.3 \times 10^{-7}$$

The bicarbonate ion can also act as an acid. It ionizes and forms hydronium ions and carbonate ions in even smaller quantities.

- **Second Ionization**

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

with

$$K_{\mathrm{HCO_3^-}} = \frac{[\mathrm{H_3O^+}][\mathrm{CO_3^{2-}}]}{[\mathrm{HCO_3^-}]} = 4.7 \times 10^{-11}$$

$K_{\mathrm{H_2CO_3}}$ is larger than $K_{\mathrm{HCO_3^-}}$ by a factor of 10^4, so H_2CO_3 is the dominant producer of hydronium ion in the solution. This means that little of the $\mathrm{HCO_3^-}$ formed by the ionization of H_2CO_3 ionizes to give hydronium ions (and carbonate ions), and the concentrations of H_3O^+ and $\mathrm{HCO_3^-}$ are practically equal in a pure aqueous solution of H_2CO_3.

If the first ionization constant of a weak diprotic acid is larger than the second by a factor of at least 20, it is appropriate to treat the first ionization separately and calculate concentrations resulting from it before calculating concentrations of species resulting from subsequent ionization. This can simplify our work considerably because we can determine the concentration of H_3O^+ and the conjugate base from the first ionization, then determine the concentration of the conjugate base of the second ionization in a solution with concentrations determined by the first ionization.

Example 6.4.1: Ionization of a Diprotic Acid

When we buy soda water (carbonated water), we are buying a solution of carbon dioxide in water. The solution is acidic because CO_2 reacts with water to form carbonic acid, H_2CO_3. What are $[\mathrm{H_3O^+}]$, $[\mathrm{HCO_3^-}]$, and $[\mathrm{CO_3^{2-}}]$ in a saturated solution of CO_2 with an initial $[H_2CO_3]$ = 0.033 *M*?

$$\mathrm{H_2CO_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_3^-}(aq) \quad K_{\mathrm{a1}} = 4.3 \times 10^{-7} \qquad (\text{equilibrium step 1})$$

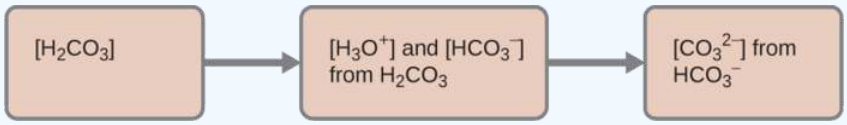
$$\mathrm{HCO_3^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CO_3^{2-}}(aq) \quad K_{\mathrm{a2}} = 4.7 \times 10^{-11} \qquad (\text{equilibrium step 2})$$

Solution

As indicated by the ionization constants, H_2CO_3 is a much stronger acid than $\mathrm{HCO_3^-}$, so $\mathrm{H_2CO_3}$ is the dominant producer of hydronium ion in solution. Thus there are two parts in the solution of this problem:

1. Using the customary four steps, we determine the concentration of H_3O^+ and $\mathrm{HCO_3^-}$ produced by ionization of H_2CO_3.
2. Then we determine the concentration of $\mathrm{CO_3^{2-}}$ in a solution with the concentration of H_3O^+ and $\mathrm{HCO_3^-}$ determined in (1).

To summarize:

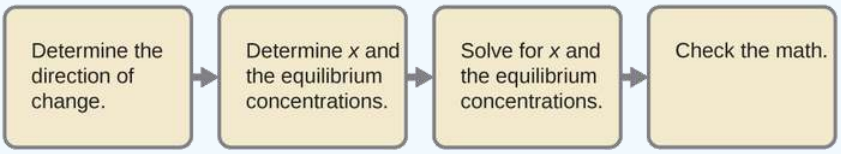


1. First Ionization: Determine the concentrations of $\mathrm{H_3O^+}$ *and* $\mathrm{HCO_3^-}$.

Since equilibrium step 1 is has a much bigger $K_{a1} = 4.3 \times 10^{-7}$ than $K_{a2} = 4.7 \times 10^{-11}$ for equilibrium step 2, we can safely ignore the second ionization step and focus only on the first step (but address it in next part of problem).

$$\mathrm{H_2CO_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_3^-}(aq) \quad K_{\mathrm{a1}} = 4.3 \times 10^{-7}$$

As for the ionization of any other weak acid:



An abbreviated table of changes and concentrations shows:

Abbreviated table of changes and concentrations

ICE Table	$\mathrm{H_2CO_3}(aq)$	$\mathrm{H_2O}(l)$	$\mathrm{H_3O^+}(aq)$	$\mathrm{HCO_3^-}(aq)$
Initial (M)	0.033 *M*	-	0	0
Change (M)	$-x$	-	$+x$	$+x$
Equilibrium (M)	$0.033\ M - x$	-	x	x

Substituting the equilibrium concentrations into the equilibrium constant gives us:

$$K_{H_2CO_3} = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = \frac{(x)(x)}{0.033 - x} = 4.3 \times 10^{-7}$$

Solving the preceding equation making our standard assumptions gives:

$$x = 1.2 \times 10^{-4}$$

Thus:

$$[H_2CO_3] = 0.033\ M$$

$$[H_3O^+] = [HCO_3^-] = 1.2 \times 10^{-4}\ M$$

2. Second Ionization: Determine the concentration of CO_3^{2-} in a solution at equilibrium.

Since the equilibrium step 1 is has a much bigger K_a than equilibrium step 2, we can the equilibrium conditions calculated from first part of example as the initial conditions for an ICER Table for the equilibrium step 2:

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

ICER Table for the equilibrium step 2:

ICE Table	$HCO_3^-(aq)$	$H_2O(l)$	$H_3O^+(aq)$	$CO_3^{2-}(aq)$
Initial (M)	$1.2 \times 10^{-4}\ M$	-	$1.2 \times 10^{-4}\ M$	0
Change (M)	$-y$	-	$+y$	$+y$
Equilibrium (M)	$1.2 \times 10^{-4}\ M - y$	-	$1.2 \times 10^{-4}\ M + y$	y

$$K_{HCO_3^-} = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]} = \frac{(1.2 \times 10^{-4}\ M + y)(y)}{(1.2 \times 10^{-4}\ M - y)}$$

To avoid solving a quadratic equation, we can assume $y \ll 1.2 \times 10^{-4}\ M$ so

$$K_{HCO_3^-} = 4.7 \times 10^{-11} \approx \frac{(1.2 \times 10^{-4}\ M)(y)}{(1.2 \times 10^{-4}\ M)}$$

Rearranging to solve for y

$$y \approx \frac{(4.7 \times 10^{-11})(1.2 \times 10^{-4}\ M)}{1.2 \times 10^{-4}\ M}$$

$$[CO_3^{2-}] = y \approx 4.7 \times 10^{-11}$$

To summarize:

In part 1 of this example, we found that the H_2CO_3 in a 0.033-M solution ionizes slightly and at equilibrium $[H_2CO_3] = 0.033\ M$, $[H_3O^+] = 1.2 \times 10^{-4}$, and $[HCO_3^-] = 1.2 \times 10^{-4}\ M$. In part 2, we determined that $[CO_3^{2-}] = 5.6 \times 10^{-11}\ M$.

? Exercise 6.4.2: Hydrogen Sulfide

The concentration of H_2S in a saturated aqueous solution at room temperature is approximately 0.1 M. Calculate $[H_3O^+]$, $[HS^-]$, and $[S^{2-}]$ in the solution:

$$H_2S(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HS^-(aq) \quad K_{a1} = 8.9 \times 10^{-8}$$

$$HS^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + S^{2-}(aq) \quad K_{a2} = 1.0 \times 10^{-19}$$

Answer

$[H_2S] = 0.1M$, $[H_3O^+] = [HS^-] = 0.0001\ M$, $[S^{2-}] = 1 \times 10^{-19}\ M$

We note that the concentration of the sulfide ion is the same as K_{a2}. This is due to the fact that each subsequent dissociation occurs to a lesser degree (as acid gets weaker).

6.4.2: Triprotic Acids

A triprotic acid is an acid that has three dissociable protons that undergo stepwise ionization: Phosphoric acid is a typical example:

- **The first ionization is**

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$$

with $K_{a1} = 7.5 \times 10^{-3}$.

- **The second ionization is**

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$$

with $K_{a2} = 6.2 \times 10^{-8}$.

- **The third ionization is**

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$$

with $K_{a3} = 4.2 \times 10^{-13}$.

As with the diprotic acids, the differences in the ionization constants of these reactions tell us that in each successive step the degree of ionization is significantly weaker. This is a general characteristic of polyprotic acids and successive ionization constants often differ by a factor of about 10^5 to 10^6. This set of three dissociation reactions may appear to make calculations of equilibrium concentrations in a solution of H_3PO_4 complicated. However, because the successive ionization constants differ by a factor of 10^5 to 10^6, the calculations can be broken down into a series of parts similar to those for diprotic acids.

Polyprotic bases can accept more than one hydrogen ion in solution. The carbonate ion is an example of a diprotic base, since it can accept up to two protons. Solutions of alkali metal carbonates are quite alkaline, due to the reactions:

$$H_2O(l) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

and

$$H_2O(l) + HCO_3^-(aq) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

Summary

An acid that contains more than one ionizable proton is a polyprotic acid. The protons of these acids ionize in steps. The differences in the acid ionization constants for the successive ionizations of the protons in a polyprotic acid usually vary by roughly five orders of magnitude. As long as the difference between the successive values of K_a of the acid is greater than about a factor of 20, it is appropriate to break down the calculations of the concentrations of the ions in solution into a series of steps.

Glossary

diprotic acid

acid containing two ionizable hydrogen atoms per molecule. A diprotic acid ionizes in two steps

diprotic base

base capable of accepting two protons. The protons are accepted in two steps

monoprotic acid

acid containing one ionizable hydrogen atom per molecule

stepwise ionization

process in which an acid is ionized by losing protons sequentially

triprotic acid

acid that contains three ionizable hydrogen atoms per molecule; ionization of triprotic acids occurs in three steps

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6.5: Hydrolysis of Salt Solutions

Learning Objectives

- Predict whether a salt solution will be acidic, basic, or neutral
- Calculate the concentrations of the various species in a salt solution
- Describe the process that causes solutions of certain metal ions to be acidic

As we have seen in the section on chemical reactions, when an acid and base are mixed, they undergo a neutralization reaction. The word “neutralization” seems to imply that a stoichiometrically equivalent solution of an acid and a base would be neutral. This is sometimes true, but the salts that are formed in these reactions may have acidic or basic properties of their own, as we shall now see.

6.5.1: Acid-Base Neutralization

A solution is neutral when it contains equal concentrations of hydronium and hydroxide ions. When we mix solutions of an acid and a base, an acid-base neutralization reaction occurs. However, even if we mix stoichiometrically equivalent quantities, we may find that the resulting solution is not neutral. It could contain either an excess of hydronium ions or an excess of hydroxide ions because the nature of the salt formed determines whether the solution is acidic, neutral, or basic. The following four situations illustrate how solutions with various pH values can arise following a neutralization reaction using stoichiometrically equivalent quantities:

1. A strong acid and a strong base, such as HCl(*aq*) and NaOH(*aq*) will react to form a neutral solution since the conjugate partners produced are of negligible strength:

$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \rightleftharpoons \mathrm{NaCl}(aq) + \mathrm{H_2O}(l)$$

2. A strong acid and a weak base yield a weakly acidic solution, not because of the strong acid involved, but because of the conjugate acid of the weak base.
3. A weak acid and a strong base yield a weakly basic solution. A solution of a weak acid reacts with a solution of a strong base to form the conjugate base of the weak acid and the conjugate acid of the strong base. The conjugate acid of the strong base is a weaker acid than water and has no effect on the acidity of the resulting solution. However, the conjugate base of the weak acid is a weak base and ionizes slightly in water. This increases the amount of hydroxide ion in the solution produced in the reaction and renders it slightly basic.
4. A weak acid plus a weak base can yield either an acidic, basic, or neutral solution. This is the most complex of the four types of reactions. When the conjugate acid and the conjugate base are of unequal strengths, the solution can be either acidic or basic, depending on the relative strengths of the two conjugates. Occasionally the weak acid and the weak base will have the *same* strength, so their respective conjugate base and acid will have the same strength, and the solution will be neutral. To predict whether a particular combination will be acidic, basic or neutral, tabulated *K* values of the conjugates must be compared.

6.5.2: 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.

6.5.3: Culinary Aspects of Chemistry

Cooking is essentially synthetic chemistry that happens to be safe to eat. There are a number of examples of acid-base chemistry in the culinary world. One example is the use of baking soda, or sodium bicarbonate in baking. $NaHCO_3$ is a base. When it reacts with an acid such as lemon juice, buttermilk, or sour cream in a batter, bubbles of carbon dioxide gas are formed from decomposition of the resulting carbonic acid, and the batter "rises." Baking powder is a combination of sodium bicarbonate, and one or more acid salts that react when the two chemicals come in contact with water in the batter.

Many people like to put lemon juice or vinegar, both of which are acids, on cooked fish (Figure 6.5.1). It turns out that fish have volatile amines (bases) in their systems, which are neutralized by the acids to yield involatile ammonium salts. This reduces the odor of the fish, and also adds a "sour" taste that we seem to enjoy.

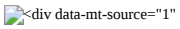


Figure 6.5.1: A neutralization reaction takes place between citric acid in lemons or acetic acid in vinegar, and the bases in the flesh of fish.

Pickling is a method used to preserve vegetables using a naturally produced acidic environment. The vegetable, such as a cucumber, is placed in a sealed jar submerged in a brine solution. The brine solution favors the growth of beneficial bacteria and suppresses the growth of harmful bacteria. The beneficial bacteria feed on starches in the cucumber and produce lactic acid as a waste product in a process called fermentation. The lactic acid eventually increases the acidity of the brine to a level that kills any harmful bacteria, which require a basic environment. Without the harmful bacteria consuming the cucumbers they are able to last much longer than if they were unprotected. A byproduct of the pickling process changes the flavor of the vegetables with the acid making them taste sour.

6.5.4: Salts of Weak Bases and Strong Acids

When we neutralize a weak base with a strong acid, the product is a salt containing the conjugate acid of the weak base. This conjugate acid is a weak acid. For example, ammonium chloride, NH_4Cl, is a salt formed by the reaction of the weak base ammonia with the strong acid HCl:

$$\mathrm{NH_3}(aq) + \mathrm{HCl}(aq) \longrightarrow \mathrm{NH_4Cl}(aq)$$

A solution of this salt contains ammonium ions and chloride ions. The chloride ion has no effect on the acidity of the solution since HCl is a strong acid. Chloride is a very weak base and will not accept a proton to a measurable extent. However, the ammonium ion, the conjugate acid of ammonia, reacts with water and increases the hydronium ion concentration:

$$\mathrm{NH_4^+}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{NH_3}(aq)$$

The equilibrium equation for this reaction is simply the ionization constant. K_a, for the acid $\mathrm{NH_4^+}$:

$$\frac{[\mathrm{H_3O^+}][\mathrm{NH_3}]}{[\mathrm{NH_4^+}]} = K_a$$

We will not find a value of K_a for the ammonium ion in Table E1. However, it is not difficult to determine K_a for $\mathrm{NH_4^+}$ from the value of the ionization constant of water, K_w, and K_b, the ionization constant of its conjugate base, NH_3, using the following relationship:

$$K_w = K_a \times K_b$$

This relation holds for any base and its conjugate acid or for any acid and its conjugate base.

Example 6.5.1: pH of a Solution of a Salt of a Weak Base and a Strong Acid

Aniline is an amine that is used to manufacture dyes. It is isolated as aniline hydrochloride, $[C_6H_5NH_3^+]Cl$, a salt prepared by the reaction of the weak base aniline and hydrochloric acid. What is the pH of a 0.233 *M* solution of aniline hydrochloride?

$$C_6H_5NH_3^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_6H_5NH_2(aq)$$

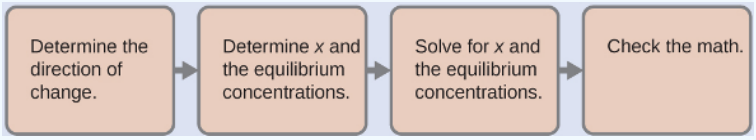
Solution

The new step in this example is to determine K_a for the $C_6H_5NH_3^+$ ion. The $C_6H_5NH_3^+$ ion is the conjugate acid of a weak base. The value of K_a for this acid is not listed in Table E1, but we can determine it from the value of K_b for aniline, $C_6H_5NH_2$, which is given as 4.6×10^{-10} :

$$K_a(\text{for } C_6H_5NH_3^+) \times K_b(\text{for } C_6H_5NH_2) = K_w = 1.0 \times 10^{-14}$$

$$K_a(\text{for } C_6H_5NH_3^+) = \frac{K_w}{K_b(\text{for } C_6H_5NH_2)} = \frac{1.0 \times 10^{-14}}{4.6 \times 10^{-10}} = 2.3 \times 10^{-5}$$

Now we have the ionization constant and the initial concentration of the weak acid, the information necessary to determine the equilibrium concentration of H_3O^+, and the pH:



With these steps we find $[H_3O^+] = 2.3 \times 10^{-3}$ *M* and pH = 2.64

Exercise 6.5.1

a. Do the calculations and show that the hydronium ion concentration for a 0.233-*M* solution of $C_6H_5NH_3^+$ is 2.3×10^{-3} and the pH is 2.64.

b. What is the hydronium ion concentration in a 0.100-*M* solution of ammonium nitrate, NH_4NO_3, a salt composed of the ions NH_4^+ and NO_3^-. Use the data in Table E1 to determine K_b for the ammonium ion. Which is the stronger acid $C_6H_5NH_3^+$ or NH_4^+?

Answer a

$K_a(\text{for } NH_4^+) = 5.6 \times 10^{-10}$, $[H_3O^+] = 7.5 \times 10{-}6$ M

Answer b

$C_6H_5NH_3^+$ is the stronger acid (a) (b) .

6.5.5: Salts of Weak Acids and Strong Bases

When we neutralize a weak acid with a strong base, we get a salt that contains the conjugate base of the weak acid. This conjugate base is usually a weak base. For example, sodium acetate, $NaCH_3CO_2$, is a salt formed by the reaction of the weak acid acetic acid with the strong base sodium hydroxide:

$$CH_3CO_2H(aq) + NaOH(aq) \longrightarrow NaCH_3CO_2(aq) + H_2O(aq)$$

A solution of this salt contains sodium ions and acetate ions. The sodium ion has no effect on the acidity of the solution. However, the acetate ion, the conjugate base of acetic acid, reacts with water and increases the concentration of hydroxide ion:

$$CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)$$

The equilibrium equation for this reaction is the ionization constant, K_b, for the base $CH_3CO_2^-$. The value of K_b can be calculated from the value of the ionization constant of water, K_w, and K_a, the ionization constant of the conjugate acid of the anion using the equation:

$$_w = K_a \times K_b$$

For the acetate ion and its conjugate acid we have:

$$K_b(\text{for } CH_3CO_2^-) = \frac{K_w}{K_a(\text{for } CH_3CO_2H)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Some handbooks do not report values of K_b. They only report ionization constants for acids. If we want to determine a K_b value using one of these handbooks, we must look up the value of K_a for the conjugate acid and convert it to a K_b value.

Example 6.5.2: Equilibrium of a Salt of a Weak Acid and a Strong Base

Determine the acetic acid concentration in a solution with $[CH_3CO_2^-] = 0.050\ M$ and $[OH^-] = 2.5 \times 10^{-6}\ M$ at equilibrium. The reaction is:

$$CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)$$

Solution

We are given two of three equilibrium concentrations and asked to find the missing concentration. If we can find the equilibrium constant for the reaction, the process is straightforward.

The acetate ion behaves as a base in this reaction; hydroxide ions are a product. We determine K_b as follows:

$$K_b(\text{for } CH_3CO_2^-) = \frac{K_w}{K_a(\text{for } CH_3CO_2H)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Now find the missing concentration:

$$K_b = \frac{[CH_3CO_2H][OH^-]}{[CH_3CO_2^-]} = 5.6 \times 10^{-10}$$

$$= \frac{[CH_3CO_2H](2.5 \times 10^{-6})}{(0.050)} = 5.6 \times 10^{-10}$$

Solving this equation we get $[CH_3CO_2H] = 1.1 \times 10^{-5}\ M$.

Exercise 6.5.2

What is the pH of a 0.083-*M* solution of CN^-? Use 4.9×10^{-10} as K_a for HCN. Hint: We will probably need to convert pOH to pH or find $[H_3O^+]$ using $[OH^-]$ in the final stages of this problem.

Answer

11.16

6.5.6: Equilibrium in a Solution of a Salt of a Weak Acid and a Weak Base

In a solution of a salt formed by the reaction of a weak acid and a weak base, to predict the pH, we must know both the K_a of the weak acid and the K_b of the weak base. If $K_a > K_b$, the solution is acidic, and if $K_b > K_a$, the solution is basic.

Example 6.5.3: Determining the Acidic or Basic Nature of Salts

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

a. KBr
b. $NaHCO_3$
c. NH_4Cl
d. Na_2HPO_4
e. NH_4F

Solution

Consider each of the ions separately in terms of its effect on the pH of the solution, as shown here:

a. The K^+ cation and the Br^- anion are both spectators, since they are the cation of a strong base (KOH) and the anion of a strong acid (HBr), respectively. The solution is neutral.
b. The Na^+ cation is a spectator, and will not affect the pH of the solution; the HCO_3^- anion is amphiprotic.The K_a of HCO_3^- is 4.7×10^{-11}, so the K_b of its conjugate base is $\frac{1.0 \times 10^{-14}}{4.7 \times 10^{-11}} = 2.1 \times 10^{-4}$. Since $K_b >> K_a$, the solution is basic.
c. The NH_4^+ ion is acidic and the Cl^- ion is a spectator. The solution will be acidic.
d. The Na^+ ion is a spectator and will not affect the pH of the solution, while the HPO_4^{2-} ion is amphiprotic. The K_a of HPO_4^{2-} is 4.2×10^{-13} and its K_b is $\frac{1.0 \times 10^{-14}}{4.2 \times 10^{-13}} = 2.4 \times 10^{-2}$. Because $K_b >> K_a$, the solution is basic.
e. The NH_4^+ ion is listed as being acidic, and the F^- ion is listed as a base, so we must directly compare the K_a and the K_b of the two ions. K_a of NH_4^+ is 5.6×10^{-10}, which seems very small, yet the K_b of F^- is 1.4×10^{-11}, so the solution is acidic, since $K_a > K_b$.

? Exercise 6.5.3

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

a. K_2CO_3
b. $CaCl_2$
c. KH_2PO_4
d. $(NH_4)_2CO_3$
e. $AlBr_3$

Answer a

basic

Answer b

neutral

Answer c

acidic

Answer d

basic

Answer e

acidic

6.5.7: The Ionization of Hydrated Metal Ions

If we measure the pH of the solutions of a variety of metal ions we will find that these ions act as weak acids when in solution. The aluminum ion is an example. When aluminum nitrate dissolves in water, the aluminum ion reacts with water to give a hydrated aluminum ion, $Al(H_2O)_6^{3+}$, dissolved in bulk water. What this means is that the aluminum ion has the strongest interactions with the six closest water molecules (the so-called first solvation shell), even though it does interact with the other water molecules surrounding this $Al(H_2O)_6^{3+}$ cluster as well:

$$Al(NO_3)_3(s) + 6\,H_2O(l) \longrightarrow Al(H_2O)_6^{3+}(aq) + 3\,NO_3^-(aq)$$

We frequently see the formula of this ion simply as "$Al^{3+}(aq)$", without explicitly noting the six water molecules that are the closest ones to the aluminum ion and just describing the ion as being solvated in water (hydrated). This is similar to the simplification of the formula of the hydronium ion, H_3O^+ to H^+. However, in this case, the hydrated aluminum ion is a weak acid (Figure 6.5.2) and donates a proton to a water molecule. Thus, the hydration becomes important and we may use formulas that show the extent of hydration:

$$Al(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Al(H_2O)_5(OH)^{2+}(aq) \quad K_a = 1.4 \times 10^{-5}$$

As with other polyprotic acids, the hydrated aluminum ion ionizes in stages, as shown by:

$$\mathrm{Al(H_2O)_6^{3+}}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{Al(H_2O)_5(OH)^{2+}}(aq)$$

$$\mathrm{Al(H_2O)_5(OH)^{2+}}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{Al(H_2O)_4(OH)_2^{+}}(aq)$$

$$\mathrm{Al(H_2O)_4(OH)_2^{+}}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{Al(H_2O)_3(OH)_3}(aq)$$

Note that some of these aluminum species are exhibiting amphiprotic behavior, since they are acting as acids when they appear on the left side of the equilibrium expressions and as bases when they appear on the right side.

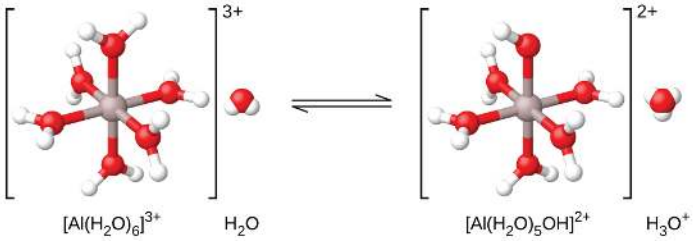


Figure 6.5.2: When an aluminum ion reacts with water, the hydrated aluminum ion becomes a weak acid.

However, the ionization of a cation carrying more than one charge is usually not extensive beyond the first stage. Additional examples of the first stage in the ionization of hydrated metal ions are:

$$\mathrm{Fe(H_2O)_6^{3+}}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{Fe(H_2O)_5(OH)^{2+}}(aq) \quad K_\mathrm{a} = 2.74$$

$$\mathrm{Cu(H_2O)_6^{2+}}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{Cu(H_2O)_5(OH)^{+}}(aq) \quad K_\mathrm{a} = 6.3$$

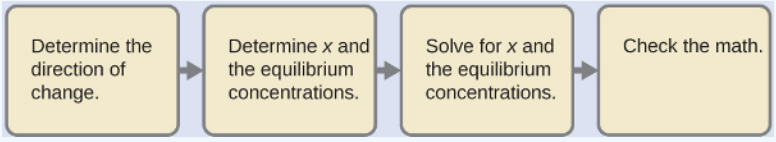
$$\mathrm{Zn(H_2O)_4^{2+}}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{Zn(H_2O)_3(OH)^{+}}(aq) \quad K_\mathrm{a} = 9.6$$

Example 6.5.4: Hydrolysis of $[Al(H_2O)_6]^{3+}$

Calculate the pH of a 0.10-*M* solution of aluminum chloride, which dissolves completely to give the hydrated aluminum ion $\mathrm{[Al(H_2O)_6]^{3+}}$ in solution.

Solution

In spite of the unusual appearance of the acid, this is a typical acid ionization problem.



1. *Determine the direction of change*. The equation for the reaction and K_a are:

$$\mathrm{Al(H_2O)_6^{3+}}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{Al(H_2O)_5(OH)^{2+}}(aq) \quad K_\mathrm{a} = 1.4 \times 10^{-5}$$

The reaction shifts to the right to reach equilibrium.

2. *Determine x and equilibrium concentrations.* Use the table

:

	$Al(H_2O)_6^{3+} + H_2O \rightleftharpoons H_3O^+ + Al(H_2O)_5(OH)^{2+}$		
Initial concentration (*M*)	0.10	~0	0
Change (*M*)	$-x$	x	x
Equilibrium constant (*M*)	$0.10 - x$	x	x

Solve for x and the equilibrium concentrations. Substituting the expressions for the equilibrium concentrations into the equation for the ionization constant yields:

1. $$K_a = \frac{[H_3O^+][Al(H_2O)_5(OH)^{2+}]}{[Al(H_2O)_6^{3+}]}$$

$$= \frac{(x)(x)}{0.10 - x} = 1.4 \times 10^{-5}$$

Solving this equation gives:

$$x = 1.2 \times 10^{-3}\ M$$

From this we find:

$$[H_3O^+] = 0 + x = 1.2 \times 10^{-3}\ M$$

$$pH = -\log[H_3O^+] = 2.92 (\text{an acidic solution})$$

Check the work. The arithmetic checks; when 1.2×10^{-3} *M* is substituted for *x*, the result = K_a.

Exercise 6.5.4

What is $[Al(H_2O)_5(OH)^{2+}]$ in a 0.15-*M* solution of $Al(NO_3)_3$ that contains enough of the strong acid HNO_3 to bring $[H_3O^+]$ to 0.10 *M*?

Answer

$2.1 \times 10^{-5}\ M$

The constants for the different stages of ionization are not known for many metal ions, so we cannot calculate the extent of their ionization. However, practically all hydrated metal ions other than those of the alkali metals ionize to give acidic solutions. Ionization increases as the charge of the metal ion increases or as the size of the metal ion decreases.

Summary

The characteristic properties of aqueous solutions of Brønsted-Lowry acids are due to the presence of hydronium ions; those of aqueous solutions of Brønsted-Lowry bases are due to the presence of hydroxide ions. The neutralization that occurs when aqueous solutions of acids and bases are combined results from the reaction of the hydronium and hydroxide ions to form water. Some salts formed in neutralization reactions may make the product solutions slightly acidic or slightly basic. Solutions that contain salts or hydrated metal ions have a pH that is determined by the extent of the hydrolysis of the ions in the solution. The pH of the solutions may be calculated using familiar equilibrium techniques, or it may be qualitatively determined to be acidic, basic, or neutral depending on the relative K_a and K_b of the ions involved.

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6.6: Lewis Acids and Bases

Learning Objectives

Make sure you thoroughly understand the following essential ideas which have been presented above. It is especially important that you know the precise meanings of all the highlighted terms in the context of this topic.

- Write the equation for the proton transfer reaction involving a Brønsted-Lowry acid or base, and show how it can be interpreted as an electron-pair transfer reaction, clearly identifying the donor and acceptor.
- Give an example of a *Lewis acid-base reaction* that does not involve protons.
- Write equations illustrating the behavior of a given non-aqueous acid-base system.

The Brønsted-Lowry proton donor-acceptor concept has been one of the most successful theories of Chemistry. But as with any such theory, it is fair to ask if this is not just a special case of a more general theory that could encompass an even broader range of chemical science. In 1916, G.N. Lewis of the University of California proposed that the *electron pair* is the dominant actor in acid-base chemistry. The Lewis theory did not become very well known until about 1923 (the same year that Brønsted and Lowry published their work), but since then it has been recognized as a very powerful tool for describing chemical reactions of widely different kinds and is widely used in organic and inorganic chemistry. According to Lewis,

- An *acid* is a substance that **accepts** a pair of electrons, and in doing so, forms a covalent bond with the entity that supplies the electrons.
- A *base* is a substance that **donates** an unshared pair of electrons to a recipient species with which the electrons can be shared.

> *In modern chemistry, electron donors are often referred to as nucleophiles, while acceptors are electrophiles.*

Proton-Transfer Reactions Involve Electron-Pair Transfer

Just as any Arrhenius acid is also a Brønsted acid, any Brønsted acid is also a Lewis acid, so the various acid-base concepts are all "upward compatible". Although we do not really need to think about electron-pair transfers when we deal with ordinary aqueous-solution acid-base reactions, it is important to understand that it is the opportunity for electron-pair sharing that enables proton transfer to take place.

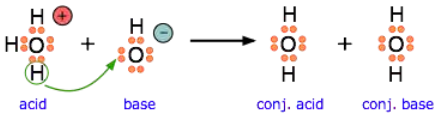


Figure 6.6.1: Lewis acid-base neutralization

This equation for a simple acid-base neutralization shows how the Brønsted and Lewis definitions are really just different views of the same process. Take special note of the following points:

- The arrow shows the movement of a proton from the hydronium ion to the hydroxide ion.
- Note carefully that the electron-pairs themselves do not move; they remain attached to their central atoms. The electron pair on the base is "donated" to the acceptor (the proton) only in the sense that it ends up being *shared* with the acceptor, rather than being the exclusive property of the oxygen atom in the hydroxide ion.
- Although the hydronium ion is the nominal Lewis acid here, it does not itself accept an electron pair, but acts merely as the source of the proton that coordinates with the Lewis base.

The point about the electron-pair remaining on the donor species is especially important to bear in mind. For one thing, it distinguishes a *Lewis acid-base reaction* from an *oxidation-reduction reaction*, in which a physical transfer of one or more electrons from donor to acceptor does occur. The product of a Lewis acid-base reaction is known formally as an "adduct" or "complex", although we do not ordinarily use these terms for simple proton-transfer reactions such as the one in the above example. Here, the proton combines with the hydroxide ion to form the "adduct" H_2O. The following examples illustrate these points for some other proton-transfer reactions that you should already be familiar with.

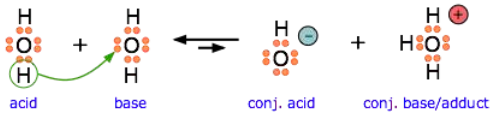


Figure 6.6.2: autoprotolysis of water

Another example, showing the autoprotolysis of water. Note that the conjugate base is also the adduct.

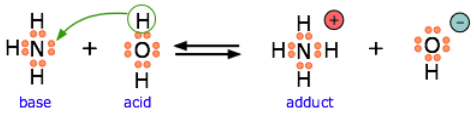


Figure 6.6.3: h*ydrolysis* of the ammonium ion.

Ammonia is both a Brønsted and a Lewis base, owing to the unshared electron pair on the nitrogen. The reverse of this reaction represents the *hydrolysis* of the ammonium ion.

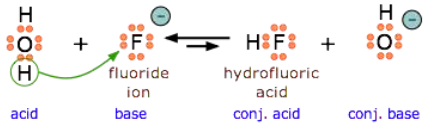


Figure 6.6.4: acid-base reaction

Because HF is a weak acid, fluoride salts behave as bases in aqueous solution. As a Lewis base, F^- accepts a proton from water, which is transformed into a hydroxide ion.

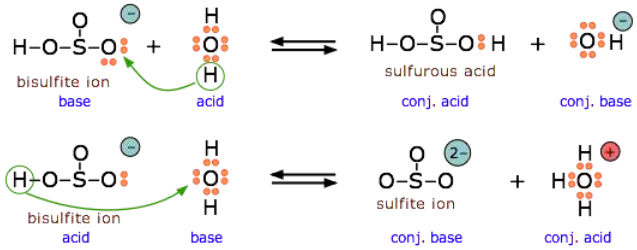


Figure 6.6.5: amphiprotic example

The bisulfite ion is *amphiprotic* and can act as an electron donor or acceptor.

Acid-base Reactions without Transferring Protons

The major utility of the Lewis definition is that it extends the concept of acids and bases beyond the realm of proton transfer reactions. The classic example is the reaction of boron trifluoride with ammonia to form an *adduct*:

$$BF_3 + NH_3 \rightarrow F_3B{-}NH_3 \tag{6.6.1}$$

One of the most commonly-encountered kinds of Lewis acid-base reactions occurs when electron-donating ligands form coordination complexes with transition-metal ions.

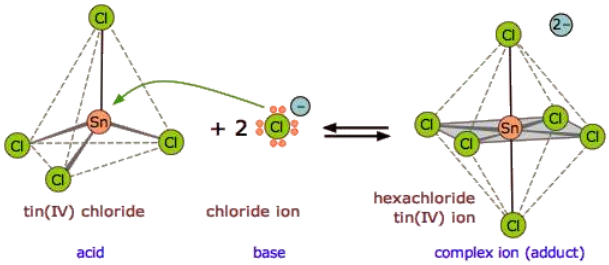


Figure 6.6.6: The tin atom in $SnCl_4$ can expand its valence shell by utilizing a pair of d-orbitals, changing its hybridization from sp^3 to sp^3d^2.

https://chem.libretexts.org/@go/page/393575

? Exercise 6.6.1

Here are several more examples of Lewis acid-base reactions that **cannot** be accommodated within the Brønsted or Arrhenius models. Identify the Lewis acid and Lewis base in each reaction.

a. $Al(OH)_3 + OH^- \rightarrow Al(OH)_4-$
b. $SnS_2 + S^{2-} \rightarrow SnS_3^{2-}$
c. $Cd(CN)_2 + 2\,CN- \rightarrow Cd(CN)_4^{2+}$
d. $AgCl + 2\,NH_3 \rightarrow Ag(NH_3)_2^+ + Cl-$
e. $Fe^{2+} + NO \rightarrow Fe(NO)^{2+}$
f. $Ni^{2+} + 6\,NH_3 \rightarrow Ni(NH_3)_5^{2+}$

Although organic chemistry is beyond the scope of these lessons, it is instructive to see how electron donors and acceptors play a role in chemical reactions. The following two diagrams show the mechanisms of two common types of reactions initiated by simple inorganic Lewis acids:

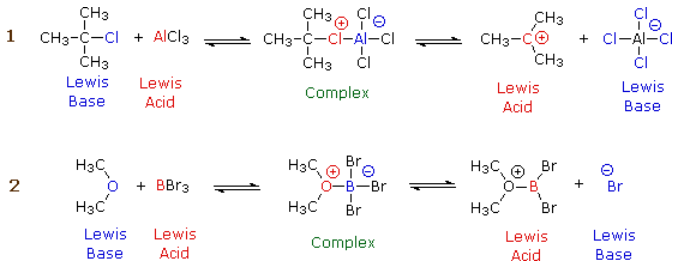


Figure 6.6.7: organic reaction examples

In each case, the species labeled "Complex" is an intermediate that decomposes into the products, which are conjugates of the original acid and base pairs. The electric charges indicated in the complexes are formal charges, but those in the products are "real".

In reaction 1, the incomplete octet of the aluminum atom in $AlCl_3$ serves as a better electron acceptor to the chlorine atom than does the isobutyl part of the base. In reaction 2, the pair of non-bonding electrons on the dimethyl ether coordinates with the electron-deficient boron atom, leading to a complex that breaks down by releasing a bromide ion.

Non-aqueous Protonic Acid-Base Systems

We ordinarily think of Brønsted-Lowry acid-base reactions as taking place in aqueous solutions, but this need not always be the case. A more general view encompasses a variety of acid-base *solvent systems*, of which the *water system* is only one (Table 6.6.1). Each of these has as its basis an amphiprotic solvent (one capable of undergoing autoprotolysis), in parallel with the familiar case of water.

The ammonia system is one of the most common non-aqueous system in Chemistry. Liquid ammonia boils at –33° C, and can conveniently be maintained as a liquid by cooling with dry ice (–77° C). It is a good solvent for substances that also dissolve in water, such as ionic salts and organic compounds since it is capable of forming hydrogen bonds. However, many other familiar substances can also serve as the basis of protonic solvent systems as Table 6.6.1 indicates:

Table 6.6.1: Popular Solvent systems

solvent	autoprotolysis reaction	pK_{ap}
water	$2\,H_2O \rightarrow H_3O^+ + OH^-$	14
ammonia	$2\,NH_3 \rightarrow NH_4^+ + NH_2^-$	33
acetic acid	$2\,CH_3COOH \rightarrow CH_3COOH_2^+ + CH_3COO^-$	13
ethanol	$2\,C_2H_5OH \rightarrow C_2H_5OH_2^+ + C_2H_5O^-$	19

solvent	autoprotolysis reaction	pK_{ap}
hydrogen peroxide	$2\ HO\text{-}OH \rightarrow HO\text{-}OH_2^+ + HO\text{-}O^-$	13
hydrofluoric acid	$2\ HF \rightarrow H_2F^+ + F^-$	10
sulfuric acid	$2\ H_2SO_4 \rightarrow H_3SO_4^+ + HSO_4^-$	3.5

One use of nonaqueous acid-base systems is to examine the relative strengths of the strong acids and bases, whose strengths are "leveled" by the fact that they are all totally converted into H_3O^+ or OH^- ions in water. By studying them in appropriate non-aqueous solvents which are poorer acceptors or donors of protons, their relative strengths can be determined.

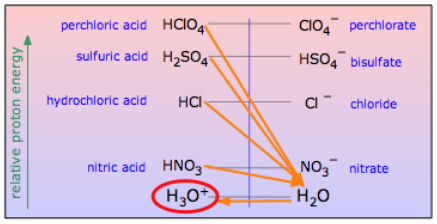


Figure 6.6.8: Use of non-aqueous solvents allows the study of strong acids that are hindered by the "leveling" of the solvent.

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6.E: Acid-Base Equilibrium (Exercises)

6.1: Brønsted-Lowry Acids and Bases

Exercise 6.E.1

Write equations that show NH_3 as both a conjugate acid and a conjugate base.

Answer

One example for NH_3 as a conjugate acid: $NH_2^-(aq) + H_3O^+(aq) \longrightarrow NH_3(aq) + H_2O(l)$; as a conjugate base: $NH_4^+(aq) + OH^-(aq) \longrightarrow NH_3(aq) + H_2O(l)$

Exercise 6.E.2

Show by suitable reaction equations that each of the following species can act as a Brønsted-Lowry acid:

a. HCl (aq)
b. CH_3CO_2H (aq)
c. NH_4^+ (aq)
d. HSO_4^- (aq)

Answer

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

b. $CH_3CO_2H(aq) + H_2O(l) \longrightarrow CH_3CO_2^-(aq) + H_3O^+(aq)$

c. $NH_4^+(aq) + H_2O(l) \longrightarrow NH_3(aq) + H_3O^+(aq)$

d. $HSO_4^-(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + SO_{42}^-(aq)$

Exercise 6.E.3

Show by suitable reaction equations that each of the following species can act as a Brønsted-Lowry base:

a. H_2O (l)
b. NH_3 (aq)
c. S^{2-} (aq)
d. $H_2PO_4^-$ (aq)

Answer

a. $H_2O(l) + H_2O(l) \longrightarrow H_3O^+(aq) + OH^-(aq)$

b. $NH_3(aq) + H_2O(l) \longrightarrow NH_4^+(aq) + OH^-(aq)$

c. $S_2^-(aq) + H_2O(l) \longrightarrow HS^-(aq) + OH^-(aq)$

d. $H_2PO_4^-(aq) + H_2O(l) \longrightarrow H_3PO_4(aq) + OH^-(aq)$

Exercise 6.E.4

Decide if each of the following are a conjugate acid-base pair:

a. H_2O (l), H_3O^+(aq)

b. OH^- (aq), H_3O^+ (aq)

c. NH_3 (aq), OH^-(aq)

d. H_2CO_3 (aq), HCO_3^- (aq)

Answer

a. Yes, H_2O (l) is the base and H_3O^+ is the conjugate acid.

b. No.

c. No.

d. Yes, H_2CO_3 s the acid and HCO_3^- is the conjugate base.

Exercise 6.E.5

What is the conjugate acid of each of the following? What is the conjugate base of each?

a. OH^-
b. H_2O
c. HCO_3^-
d. NH_3
e. HSO_4^-
f. H_2O_2
g. HS^-
h. $H_5N_2^+$

Answer

H_2O, O^{2-}; H_3O^+, OH^- ; H_2CO_3, CO_3^{2-}; NH_4^+, NH_2^-; H_2SO_4, SO_4^{2-}; $H_3O_2^+$, HO_2^-; H_2S; S^{2-}; $H_6N_2^{2+}$, H_4N_2

Exercise 6.E.6

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. $HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$
b. $CN^-(aq) + H_2O(l) \longrightarrow HCN(aq) + OH^-(aq)$
c. $H_2SO_4(aq) + Cl^-(aq) \longrightarrow HCl(aq) + HSO_4^-(aq)$
d. $HSO_4^-(aq) + OH^-(aq) \longrightarrow SO_{42}^-(aq) + H_2O(l)$
e. $O_2^-(aq) + H_2O(l) \longrightarrow 2\,OH^-(aq)$
f. $H_2S(aq) + NH_2^-(aq) \longrightarrow HS^-(aq) + NH_3(aq)$

Answer

The labels are Brønsted-Lowry acid = BA; its conjugate base = CB; Brønsted-Lowry base = BB; its conjugate acid = CA.

a. HNO_3(BA), H_2O(BB), H_3O^+(CA), NO_3^- (CB)

b. CN^-(BB), H_2O(BA), HCN(CA), OH^- (CB)

c. H_2SO_4(BA), Cl^-(BB), HCl(CA), HSO_4^- (CB)

d. HSO_4^- (BA), OH^-(BB), SO_4^{2-} (CB), H_2O(CA)

e. O^{2-}(BB), H_2O(BA) OH^- (CB and CA)

f. H_2S(BA), NH_2^- (BB), HS^-(CB), NH_3(CA)

Exercise 6.E.7

What is the $[H_3O^+]$ if an aqueous solution has an $[OH^-]$ concentration of 1.65 x 10^{-5} at 100°C? K_w at 100°C is 5.6×10^{-13}

Answer

3.39 x 10^{-8} M

Exercise 6.E.8

What are amphiprotic species? Illustrate with suitable equations.

Answer

Amphiprotic species may either gain or lose a proton in a chemical reaction, thus acting as a base or an acid. An example is H_2O.

As an acid: $H_2O(l) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$. As a base: $H_2O(l) + HCl(aq) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$

Exercise 6.E.9

State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species.

a. NH_3
b. HPO_4^-
c. Br^-
d. NH_4^+
e. ASO_4^{3-}

Answer

amphiprotic: $NH_3 + H_3O^+ \longrightarrow NH_4OH + H_2O$, $NH_3 + OCH_3^- \longrightarrow NH_2^- + CH_3OH$; $HPO_4^{2-} + OH^- \longrightarrow PO_4^{3-} + H_2O$, $HPO_4^{2-} + HClO_4 \longrightarrow H_2PO_4^- + ClO_4^-$; not amphiprotic: Br^-; NH_4^+; AsO_4^{3-}

6.2: pH and pOH

Exercise 6.E.10

Explain why a sample of pure water at 40 °C is neutral even though $[H_3O^+] = 1.7 \times 10^{-7}$ *M*. K_w is 2.9×10^{-14} at 40 °C.

Answer

In a neutral solution $[H_3O^+] = [OH^-]$. At 40 °C,

$[H_3O^+] = [OH^-] = (2.910^{-14})^{1/2} = 1.7 \times 10^{-7}$.

Exercise 6.E.11

The ionization constant for water (K_w) is 2.90×10^{-14} at 40 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 40 °C.

Answer

x = 1.70×10^{-7} M = $[H_3O^+] = [OH^-]$

pH = -log (1.70×10^{-7}) = −(−6.769) = 6.769

pOH = pH = 6.769

Exercise 6.E.12

Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:

a. 0.000259 *M* $HClO_4$
b. 0.21 *M* NaOH

c. 0.000071 *M* $Ba(OH)_2$
d. 2.5 *M* KOH

Answer

pH = 3.587; pOH = 10.413; pH = 0.68; pOH = 13.32; pOH = 3.85; pH = 10.15; pH = −0.40; pOH = 14.4

Exercise 6.*E*.13

What are the hydronium and hydroxide ion concentrations in a solution whose pH is 6.52?

Answer

$[H_3O^+] = 3.0 \times 10^{-7}\ M$; $[OH^-] = 3.3 \times 10^{-8}\ M$

Exercise 6.*E*.14

The hydroxide ion concentration in household ammonia is $3.2 \times 10^{-3}\ M$ at 25 °C. What is the concentration of hydronium ions in the solution?

Answer

$[OH^-] = 3.1 \times 10^{-12}\ M$

6.3: Relative Strengths of Acids and Bases

Exercise 6.*E*.15

1. Arrange these acids in order of increasing strength.
   - acid A: pKa=1.52
   - acid B: pKa=6.93
   - acid C: pKa=3.86

Given solutions with the same initial concentration of each acid, which would have the highest percent ionization?

Answer

Acids in order of increasing strength: acidB<acidC<acidA.

Given the same initial concentration of each acid, the highest percent of ionization is acid A because it is the strongest acid.

Exercise 6.*E*.16

The odor of vinegar is due to the presence of acetic acid, CH_3CO_2H, a weak acid. List, in order of descending concentration, all of the ionic and molecular species present in a 1-*M* aqueous solution of this acid.

Answer

$[H_2O] > [CH_3CO_2H] > [H_3O^+] \approx [CH_3CO_2^-] > [OH^-]$

Exercise 6.*E*.17

Gastric juice, the digestive fluid produced in the stomach, contains hydrochloric acid, HCl. Milk of Magnesia, a suspension of solid $Mg(OH)_2$ in an aqueous medium, is sometimes used to neutralize excess stomach acid. Write a complete balanced equation for the neutralization reaction, and identify the conjugate acid-base pairs.

Answer

$$\underset{\text{BB}}{\text{Mg(OH)}_2}(s) + \underset{\text{BA}}{\text{HCl}}(aq) \longrightarrow \underset{\text{CB}}{\text{Mg}^{2+}}(aq) + 2\,\underset{\text{CA}}{\text{Cl}^-}(aq) + 2\,\text{H}_2\text{O}(l)$$

Exercise 6.E.18

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 × 10^{-4}.

Answer

$K_a = 2.3 \times 10^{-11}$

Exercise 6.E.19

Which base, CH_3NH_2 or $(CH_3)_2NH$, is the strongest base? Which conjugate acid, $(\text{CH}_3)_2\text{NH}_2^+$ or $(CH_3)_2NH$, is the strongest acid?

Answer

The strongest base or strongest acid is the one with the larger K_b or K_a, respectively. In these two examples, they are $(CH_3)_2NH$ and CH_3NH_3^+.

Exercise 6.E.20

What two common assumptions can simplify calculation of equilibrium concentrations in a solution of a weak acid?

Answer

Assume that the change in initial concentration of the acid as the equilibrium is established can be neglected, so this concentration can be assumed constant and equal to the initial value of the total acid concentration.

Assume we can neglect the contribution of water to the equilibrium concentration of H_3O^+.

Exercise 6.E.21

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

The equation for the equilibrium is:

$$\text{NO}_2^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HNO}_2(aq) + \text{OH}^-(aq) \tag{6.E.1}$$

Answer

Adding HCl will add H_3O^+ ions, which will then react with the OH^- ions, lowering their concentration. The equilibrium will shift to the right, increasing the concentration of HNO_2, and decreasing the concentration of NO_2^- ions. Adding HNO_2 increases the concentration of HNO_2 and shifts the equilibrium to the left, increasing the concentration of NO_2^- ions and decreasing the concentration of OH^- ions. Adding NaOH adds OH^- ions, which shifts the equilibrium to the left, increasing the concentration of NO_2^- ions and decreasing the concentrations of HNO_2. Adding NaCl has no effect on the concentrations of the ions. Adding KNO_2 adds NO_2^- ions and shifts the equilibrium to the right, increasing the HNO_2 and OH^- ion concentrations.

Exercise 6.E.22

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?

Answer

This is a case in which the solution contains a mixture of acids of different ionization strengths. In solution, the HCO_2H exists primarily as HCO_2H molecules because the ionization of the weak acid is suppressed by the strong acid. Therefore, the HCO_2H contributes a negligible amount of hydronium ions to the solution. The stronger acid, HCl, is the dominant producer of hydronium ions because it is completely ionized. In such a solution, the stronger acid determines the concentration of hydronium ions, and the ionization of the weaker acid is fixed by the $[H_3O^+]$ produced by the stronger acid.

Exercise 6.E.23

From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.

NH_3: $[OH^-] = 3.1 \times 10^{-3}$ *M*;

$[NH_4^+] = 3.1 \times 10^{-3}$ *M*;

$[NH_3] = 0.533$ *M*;

HNO_2: $[H_3O^+] = 0.011$ *M*;

$[NO_2^-] = 0.0438$ *M*;

$[HNO_2] = 1.07$ *M*;

$(CH_3)_3N$: $[(CH_3)_3N] = 0.25$ *M*;

$[(CH_3)_3NH^+] = 4.3 \times 10^{-3}$ *M*;

$[OH^-] = 4.3 \times 10^{-3}$ *M*;

NH_4^+ : $[NH_4^+] = 0.100$ *M*;

$[NH_3] = 7.5 \times 10^{-6}$ *M*;

$[H_3O^+] = 7.5 \times 10^{-6}$ *M*

Answer

$K_b = 1.8 \times 10^{-5}$; $K_a = 4.5 \times 10^{-4}$; $K_b = 7.4 \times 10^{-5}$; $K_a = 5.6 \times 10^{-10}$

Exercise 6.E.24

Determine K_a for hydrogen sulfate ion, HSO_4^-. In a 0.10-*M* solution the acid is 29% ionized.

Answer

$K_a = 1.2 \times 10^{-2}$

Exercise 6.E.25

Calculate the concentration of all solute species in each of the following solutions of acids or bases. Assume that the ionization of water can be neglected, and show that the change in the initial concentrations can be neglected. Ionization constants can be found in the text or Resource Tables.

a. 0.0092 *M* HClO, a weak acid
b. 0.0784 *M* $C_6H_5NH_2$, a weak base
c. 0.0810 *M* HCN, a weak acid

d. 0.11 *M* $(CH_3)_3N$, a weak base

e. 0.120 *M* $Fe(H_2O)_6^{2+}$ a weak acid, $K_a = 1.6 \times 10^{-7}$

Answer

a. $$\frac{[H_3O^+][ClO^-]}{[HClO]} = \frac{(x)(x)}{(0.0092 - x)} \approx \frac{(x)(x)}{0.0092} = 3.5 \times 10^{-8}$$

Solving for *x* gives 1.79×10^{-5} *M*. This value is less than 5% of 0.0092, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are:

$[H_3O^+] = [ClO] = 1.8 \times 10^{-5}$ *M*$[HClO] = 0.00092$ *M* $[OH^-] = 5.6 \times 10^{-10}$ *M*;

b. $$\frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]} = \frac{(x)(x)}{(0.0784 - x)} \approx \frac{(x)(x)}{0.0784} = 4.6 \times 10^{-10}$$

Solving for *x* gives 6.01×10^{-6} *M*.

This value is less than 5% of 0.0784, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are: $[CH_3CO_2^-] = [OH^-] = 6.0 \times 10^{-6}$ *M* $[C_6H_5NH_2] = 0.00784$ $[H_3O^+] = 1.7 \times 10^{-9}$ *M*

c. $\frac{[H_3O^+][CN^-]}{[HCN]} = \frac{(x)(x)}{(0.0810 - x)} \approx \frac{(x)(x)}{0.0810} = 4 \times 10^{-10}$ Solving for *x* gives 5.69×10^{-6} *M*. This value is less than 5% of 0.0810, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are: $[H_3O^+] = [CN^-] = 5.7 \times 10^{-6}$ *M* $[HCN] = 0.0810$ *M* $[OH^-] = 1.8 \times 10^{-9}$ *M*

d. $\frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]} = \frac{(x)(x)}{(0.11 - x)} \approx \frac{(x)(x)}{0.11} = 7.4 \times 10^{-5}$ Solving for *x* gives 2.85×10^{-3} *M*. This value is less than 5% of 0.11, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are: $[(CH_3)_3NH^+] = [OH^-] = 2.9 \times 10^{-3}$ *M* $[(CH_3)_3N] = 0.11$ *M* $[H_3O^+] = 3.5 \times 10^{-12}$ *M*

e. $\frac{[Fe(H_2O)_5(OH)^+][H_3O^+]}{[Fe(H_2O)_6^{2+}]} = \frac{(x)(x)}{(0.120 - x)} \approx \frac{(x)(x)}{0.120} = 1.6 \times 10^{-7}$ Solving for *x* gives 1.39×10^{-4} *M*. This value is less than 5% of 0.120, so the assumption that it can be neglected is valid. Thus, the concentrations of solute species at equilibrium are: $[Fe(H_2O)_5(OH)^+] = [H_3O^+] = 1.4 \times 10^{-4}$ *M* $[Fe(H_2O)_6^{2+}] = 0.120$ *M* $[OH^-] = 7.2 \times 10^{-11}$ *M*

Exercise 6.E.26

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?

Answer

pH = 2.41

Exercise 6.E.27

The pH of a 0.15-*M* solution of HSO_4^- is 1.43. Determine K_a for HSO_4^- from these data.

Answer

$K_a = 1.2 \times 10^{-2}$

Exercise 6.E.28

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.

Answer

$K_b = 1.77 \times 10^{-5}$

6.4: Diprotic & Polyprotic Acids

Exercise 6.E.29

Which of the following concentrations would be practically equal in a calculation of the equilibrium concentrations in a 0.134-*M* solution of H_2CO_3, a diprotic acid: $[H_3O^+]$,$[H_3O^+]$, $[OH^-]$, $[H_2CO_3]$, $[HCO_3^-]$,$[HCO_3^-]$, $[CO_3^{2-}]$?$[CO_3^{2-}]$? No calculations are needed to answer this question.

Answer

$[H_3O^+]$ and $[HCO_3^-]$ are practically equal.

Exercise 6.E.30

Nicotine, $C_{10}H_{14}N_2$, is a base that will accept two protons ($K_1 = 7 \times 10^{-7}$, $K_2 = 1.4 \times 10^{-11}$). What is the concentration of each species present in a 0.050-*M* solution of nicotine?

Answer

$[C_{10}H_{14}N_2] = 0.049\ M$

$[C_{10}H_{14}N_2H^+] = 1.9 \times 10^{-4}\ M\ [C_{10}H_{14}N_2H_2^{2+}] = 1.4 \times 10^{-11}\ M\ [OH^-] = 1.9 \times 10^{-4}\ M\ [H_3O^+] = 5.3 \times 10^{-11}\ M$

Exercise 6.E.31

The ion HTe^- is an amphiprotic species; it can act as either an acid or a base.

K_{a2} for the reation of HTe^- with H_2O is 1.5 x 10^{-11}

What is K_b for the reaction in which HTe^- functions as a base in water is 4.3 x 10^{-12}

Demonstrate whether or not the second ionization of H_2Te can be neglected in the calculation of $[HTe^-]$ in a 0.10 M solution of H_2Te.

Answer

$$\frac{\left[Te^{2-}\right]\left[H_3O^+\right]}{\left[HTe^-\right]} = \frac{(x)(0.0141+x)}{(0.0141-x)} \approx \frac{(x)(0.0141)}{0.0141} = 1.5 \times 10^{-11}$$

Solving for *x* gives 1.5×10^{-11} *M*. Therefore, compared with 0.014 *M*, this value is negligible (1.1 ×× 10^{-7}%).

6.5 Hydrolysis of Salt Solutions

Exercise 6.E.32

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

a. $FeCl_3$
b. K_2CO_3
c. NH_4Br
d. $KClO_4$

Answer

a. acidic

b. basic

c. acidic

d. neutral

Exercise 6.E.33

1. Why are aqueous solutions of salts such as $CaCl_2$ neutral? Why is an aqueous solution of $NaNH_2$ basic?

Answer

Aqueous solutions of salts such as $CaCl_2$ are neutral because it is created from hydrochloric acid (a strong acid) and calcium hydroxide (a strong base). An aqueous solution of $NaNH_2$ is basic because it can deprotonate alkynes, alcohols, and a host of other functional groups with acidic protons such as esters and ketones.

Exercise 6.E.34

Predict whether the aqueous solutions of the following are acidic, basic, or neutral.

1. Li_3N
2. NaH
3. KBr
4. $C_2H_5NH_3Cl$

Answer

a. Li_3N is a base because the lone pair on the nitrogen can accept a proton.

b. NaH is a base because the hydrogen has a negative charge with a lone pai that can accept a proton.

c. KBr is neutral because it is formed from HBr (a strong acid) and KOH (a strong base) so no reaction.

d. $C_2H_5NH_3Cl$ is acidic because it can donate a proton.

(make sure you can write out reactions to explain each answer!)

6.5 Lewis Acids & Bases

Exercise 6.E.35

Identify the nature of each of the following as either a Lewis Acid or a Lewis Base:

a. NH_3

b. H_2O

c. SO_2

Answer

a. NH_3 is a lewis base because nitrogen has a lone pair of electrons to "donate."

b. H_2O is a lewis base because oxygen has two lone pairs of electrons to "donate."

c. SO_2 is a lewis acid because sulfur has an unfilled octet and thus is able to accept a pair of electrons.

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6.S: Acid–Base Equilibrium (Study Guide)

6.1: Brønsted–Lowry Acids and Bases

- Brønsted-Lowry definition of acids an bases

- Acid is a proton donor
- Base is a proton acceptor
- Can be applied to non-aqueous solutions
- Brønsted-Lowry acid must be able to lose a H^+ ion
- Brønsted-Lowry base must have at least one non-bonding pair (lone pair) of electrons to bind to H^+ ion
- Amphoteric - substance that can act as an acid or base
- Conjugate Acid-Base Pairs
    - conjugate acid - product formed by adding a proton to base
    - conjugate base - product formed by removal of a proton from acid
- autoionization of water - dissociation of H_2O molecules to H^+ and OH^- ions
- at room temperature only 1 out of 10^9 molecules are ionized
- exclude water from equilibrium expressions involving aqueous solutions
- ion-product constant
- $k_w = k[H_2O] = [H^+][OH^-] = 1.0 \times 10^{-14}$ (at 25° C)
- solution is neutral when $[H^+] = [OH^-]$
- solution is acidic when $[H^+] > [OH^-]$
- solution is basic when $[H^+] < [OH^-]$

6.2: pH and pOH

- concentration of $[H^+]$ expressed in terms of pH
- $pH = -\log [H^+]$
- acidic solutions $[H^+] > 1.0 \times 10^{-7}$ $[OH^-] < 1.0 \times 10^{-7}$ $pH < 7.00$
- neutral solutions $[H^+] = [OH^-] = 1.0 \times 10^{-7}$ $pH = 7$
- basic solutions $[H^+] < 1.0 \times 10^{-7}$ $[OH^-] > 1.0 \times 10^{-7}$ $pH > 7$

Other "p" Series

- $pOH = -\log [OH^-]$
- $pH + pOH = -\log K_w = 14.00$

6.3 **Relative** Strengths of Acids and Bases

- the stronger the acid, the weaker the conjugate base
- the stronger the base, the weaker the conjugate acid
- equilibrium favors transfer of proton from stronger acid to stronger base

Weak Acids

- $HA_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+ + A^-_{(aq)}$
- $HA_{(aq)} \rightarrow H^+_{(aq)} + A^-_{(aq)}$
- $K_a = \frac{[H^+][A^-]}{[HA]}$
- K_a = acid - dissociation constant
- The lager the K_a the stronger the acid
- K_a usually less than 10^{-3}

Weak Bases

- base-dissociation constant, K_b
- equilibrium at which base reacts with H_2O to form a conjugate acid and OH^-
- contain 1 or more lone pair of electrons

Relationship Between K_a and K_b

- when two reactions are added together then equilibrium constant of third reaction is equal to the product of the equilibrium constants of the added reactions
- reaction 1 + reaction 2 = reaction 3
- $K_1 \times K_2 = K_3$
- $K_a \times K_b = [H^+][OH^-] = K_w$
- Acid-dissociation constant times base-dissociation constant equals the ion-product constant for water
- $K_a \times K_b = K_w = 1.0 \times 10^{-14}$
- $pK_a \times pK_b = pK_w = 14$; ($pK_a = -\log K_a$ and $pK_b = -\log K_b$)

Calculating Ka or Kb given initial and equilibrium concentration

1.Identify species, write dissociation equation

2.Obtain K expression

3.If pH or pOH given, calculate [H3O+] or [OH-]

4.Build the corresponding ICE table

5.Solve for all concentrations, answer question

Calculating pH for Solution of Weak Acid or Base

1) write ionization equilibrium

2) write equilibrium expression

3) I.C.E. Table

4) substitute equilibrium concentrations into equilibrium expression

- percent ionization = fraction of weak acid molecules that ionize * 100%
- in weak acids $[H^+]$ is small fraction of concentration of acid (can make assumptions)
- percent ionization depends on temperature, identity of acid and concentration
- as percent ionization decreases, concentration increases

6.4 Polyprotic Acids

- more than one ionizable H atom
- easier to remove first proton than second
- acid dissociation constants are K_{a1}, K_{a2}, etc…
- K_a values usually differ by 10^3

6.5 Acid-Base Properties of Salt Solutions

- hydrolysis - ions reacting with water to produce H^+ and OH^- ions
- anions from weak acids react with water to produce OH^- ions which is basic
- anions of strong acids are not basic and do not influence pH
- anions that have ionizable protons are amphoteric
- behavior depends on K_a and K_b
- all cations except those of alkali metals and heavier alkaline earth (Ca^{2+}, Sr^{2+} and Ba^{2+}) are weak acids in water
- alkali metal and alkaline earth cations do not hydrolyze
- do not affect pH
- strengths of acids and bases from salts
- 1) salts derived from strong acid and base

- no hydrolysis and solution has pH of 7

- 2) salts derived from strong base and weak acid
  - strong conjugate base
  - anion hydrolyzes and produces OH^- ions
  - cation does not hydrolyze
  - pH greater than 7
- 3) salts derived from weak base and strong acids
  - cation is strong conjugate acid
  - cation hydrolyzes to produce H^+
  - anion does not hydrolyze
  - solution has pH below 7
- 4) salts derived from weak acid and base
  - both cation and anion hydrolyze
  - pH depends on extent on hydrolysis of each ion]

6.6 Lewis Acids and Bases

- Lewis acid - electron pair acceptor
- Lewis base - electron pair donor
- Any Bronsted-Lowry base is a Lewis base
- Lewis acids contain at least one atom with an incomplete octet

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CHAPTER OVERVIEW

7: Buffers, Titrations and Solubility Equilibria

7.1: Acid-Base Buffers
7.2: Practical Aspects of Buffers
7.3: Acid-Base Titrations
7.4: Solving Titration Problems
7.5: Solubility Equilibria
7.E: Buffers, Titrations and Solubility Equilibria (Exercises)
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7.1: Acid-Base Buffers

Skills to Develop

- Describe the composition and function of acid–base buffers
- Calculate the pH of a buffer before and after the addition of added acid or base using the Henderson-Hasselbalch approximation

A mixture of a weak acid and its conjugate base (or a mixture of a weak base and its conjugate acid) 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 7.1.1). A solution of acetic acid (CH_3COOH and sodium acetate 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 ($NH_3(aq)$) and ammonium chloride ($NH_4Cl(aq)$).



Figure 7.1.1: (a) The unbuffered solution on the left and the buffered 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. (credit: modification of work by Mark Ott)

How Buffers Work

In order for a buffer to "resist" the effect of adding strong acid or strong base, it must have both an acidic and a basic component. However, you cannot mix any two acid/base combination together and get a buffer. If you mix HCl and NaOH, for example, you will simply neutralize the acid with the base and obtain a neutral salt, not a buffer. For a buffer to work, both the acid and the base component must be *part of the same equilibrium system* - that way, neutralizing one or the other component (by adding strong acid or base) will *transform* it into the other component, and maintain the buffer mixture.

> *Therefore, a buffer must consist of a mixture of a weak conjugate acid-base pair.*

The pH a buffer maintains is determined by the nature of the conjugate pair and the concentrations of both components. A mixture of acetic acid and sodium acetate is acidic because the K_a of acetic acid is greater than the K_b of its conjugate base acetate. It is a buffer because it contains both the weak acid and its salt. Hence, it acts to keep the hydronium ion concentration (and the pH) almost constant by the addition of either a small amount of a strong acid or a strong base. If we add a base such as sodium hydroxide, the hydroxide ions react with the few hydronium ions present. Then more of the acetic acid reacts with water, restoring the hydronium ion concentration almost to its original value:

$$CH_3CO_2H(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + CH_3CO_2^-(aq) \tag{7.1.1}$$

The pH changes very little. If we add an acid such as hydrochloric acid, most of the hydronium ions from the hydrochloric acid combine with acetate ions, forming acetic acid molecules:

$$H_3O^+(aq) + CH_3CO_2^-(aq) \longrightarrow CH_3CO_2H(aq) + H_2O(l) \tag{7.1.2}$$

Thus, there is very little increase in the concentration of the hydronium ion, and the pH remains practically unchanged (Figure 7.1.2).

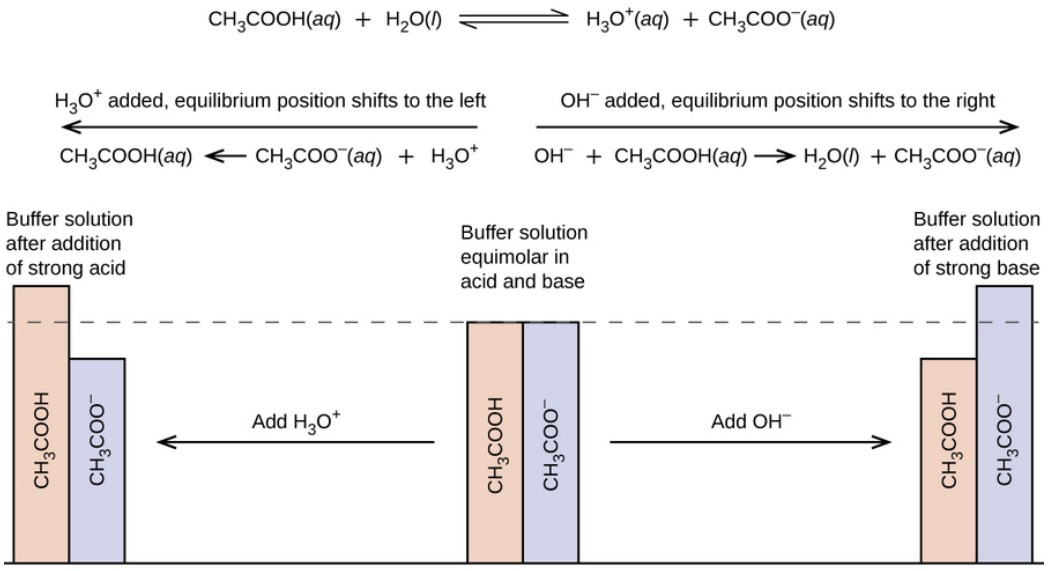


Figure 7.1.2: This diagram shows the buffer action of these reactions.

A mixture of ammonia and ammonium chloride is basic because the K_b for ammonia is greater than the K_a for the ammonium ion. It is a buffer because it also contains the salt of the weak base. If we add a base (hydroxide ions), ammonium ions in the buffer react with the hydroxide ions to form ammonia and water and reduce the hydroxide ion concentration almost to its original value:

$$\mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) \longrightarrow \mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \tag{7.1.3}$$

If we add an acid (hydronium ions), ammonia molecules in the buffer mixture react with the hydronium ions to form ammonium ions and reduce the hydronium ion concentration almost to its original value:

$$\mathrm{H_3O^+}(aq) + \mathrm{NH_3}(aq) \longrightarrow \mathrm{NH_4^+}(aq) + \mathrm{H_2O}(l) \tag{7.1.4}$$

The three parts of the following example illustrate the change in pH that accompanies the addition of base to a buffered solution of a weak acid and to an unbuffered solution of a strong acid.

Example 7.1.1: pH Changes in Buffered and Unbuffered Solutions

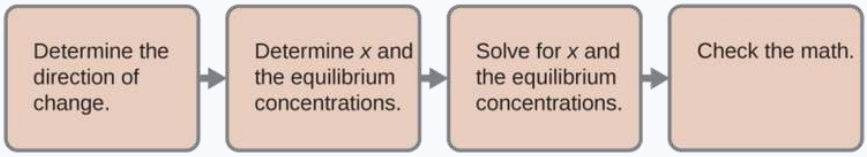
Acetate buffers are used in biochemical studies of enzymes and other chemical components of cells to prevent pH changes that might change the biochemical activity of these compounds.

a. Calculate the pH of an acetate buffer that is a mixture with 0.10 *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, giving a solution with a volume of 101 mL.
c. For comparison, calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of a solution of an unbuffered solution with a pH of 4.74 (e.g. a 1.8×10^{-5}-*M* solution of HCl). The volume of the final solution is 101 mL.

Solution

a. Calculate the pH of an acetate buffer that is a mixture with 0.10 *M* acetic acid and 0.10 *M* sodium acetate.

To determine the pH of the buffer solution we use a typical equilibrium calculation (as illustrated in earlier Examples):



1. *Determine the direction of change.* The equilibrium in a mixture of $\mathrm{H_3O^+}$, $\mathrm{CH_3CO_2^-}$, and $\mathrm{CH_3CO_2H}$ is:

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq) \tag{7.1.5}$$

The equilibrium constant for $\mathrm{CH_3CO_2H}$ is not given, so we look it up in Table E1: $K_a = 1.8 \times 10^{-5}$. With $[\mathrm{CH_3CO_2H}] = [\mathrm{CH_3CO_2^-}] = 0.10$ *M* and $[\mathrm{H_3O^+}] = \sim 0$ *M*, the reaction shifts to the right to form $\mathrm{H_3O^+}$.

2. *Determine* x *and equilibrium concentrations*. A table of changes and concentrations follows:

	$[CH_3CO_2H]$ + $[H_2O]$ $\rightleftharpoons$ H_3O^+ + $[CH_3CO_2^-]$		
Initial concentration (*M*)	0.10	~0	0.10
Change (*M*)	$-x$	x	x
Equilibrium constant (*M*)	$0.10 - x$	x	$0.10 + x$

3. *Solve for x and the equilibrium concentrations*. We find:

$$x = 1.8 \times 10^{-5}\ M \tag{7.1.6}$$

and

$$[\mathrm{H_3O^+}] = 0 + x = 1.8 \times 10^{-5}\ M \tag{7.1.7}$$

Thus:

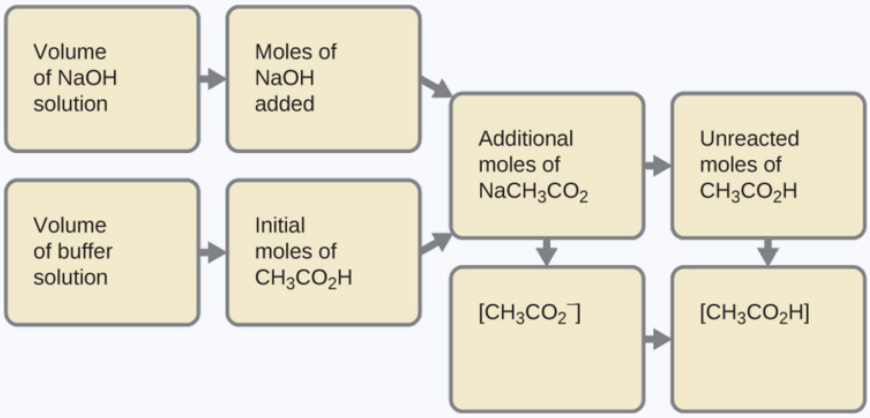
$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log(1.8 \times 10^{-5}) \tag{7.1.8}$$

$$= 4.74 \tag{7.1.9}$$

4. *Check the work*. If we calculate all calculated equilibrium concentrations, we find that the equilibrium value of the reaction coefficient, $Q = K_a$.

(b) Calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of this buffer, giving a solution with a volume of 101 mL.

First, we calculate the concentrations of an intermediate mixture resulting from the complete reaction between the acid in the buffer and the added base. Then we determine the concentrations of the mixture at the new equilibrium:



1. *Determine the moles of NaOH*. One milliliter (0.0010 L) of 0.10 *M* NaOH contains:

$$0.0010\ \cancel{\mathrm{L}} \times \left(\frac{0.10\ \mathrm{mol\ NaOH}}{1\ \cancel{\mathrm{L}}}\right) = 1.0 \times 10^{-4}\ \mathrm{mol\ NaOH} \tag{7.1.10}$$

2. *Determine the moles of CH_3CO_2H*. Before reaction, 0.100 L of the buffer solution contains:

$$0.100\ \cancel{\mathrm{L}} \times \left(\frac{0.100\ \mathrm{mol\ CH_3CO_2H}}{1\ \cancel{\mathrm{L}}}\right) = 1.00 \times 10^{-2}\ \mathrm{mol\ CH_3CO_2H} \tag{7.1.11}$$

3. *Solve for the amount of $NaCH_3CO_2$ produced*. The 1.0×10^{-4} mol of NaOH neutralizes 1.0×10^{-4} mol of CH_3CO_2H, leaving:

$$(1.0 \times 10^{-2}) - (0.01 \times 10^{-2}) = 0.99 \times 10^{-2}\ \mathrm{mol\ CH_3CO_2H} \tag{7.1.12}$$

and producing 1.0×10^{-4} mol of $NaCH_3CO_2$. This makes a total of:

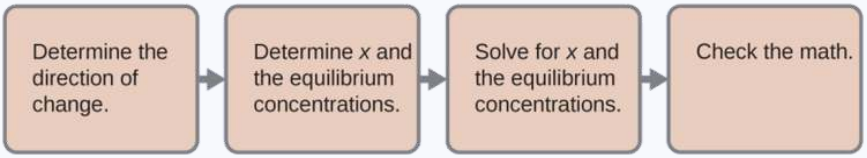
[\mathrm{(1.0×10^{−2})+(0.01×10^{−2})=1.01×10^{−2}\:mol\:NaCH_3CO_2} \]

4. *Find the molarity of the products*. After reaction, CH_3CO_2H and $NaCH_3CO_2$ are contained in 101 mL of the intermediate solution, so:

$$[CH_3CO_2H] = \frac{9.9 \times 10^{-3}\ \text{mol}}{0.101\ \text{L}} = 0.098\ M \tag{7.1.13}$$

$$[NaCH_3CO_2] = \frac{1.01 \times 10^{-2}\ \text{mol}}{0.101\ \text{L}} = 0.100\ M \tag{7.1.14}$$

Now we calculate the pH after the intermediate solution, which is 0.098 *M* in CH_3CO_2H and 0.100 *M* in $NaCH_3CO_2$, comes to equilibrium. The calculation is very similar to that in part (a) of this example:



This series of calculations gives a pH = 4.75. Thus the addition of the base barely changes the pH of the solution.

(c) This 1.8 × 10^{-5}-*M* solution of HCl has the same hydronium ion concentration as the 0.10-*M* solution of acetic acid-sodium acetate buffer described in part (a) of this example. The solution contains:

$$0.100\ \text{L} \times \left(\frac{1.8 \times 10^{-5}\ \text{mol HCl}}{1\ \text{L}}\right) = 1.8 \times 10^{-6}\ \text{mol HCl}$$

As shown in part (b), 1 mL of 0.10 *M* NaOH contains 1.0 × 10^{-4} mol of NaOH. When the NaOH and HCl solutions are mixed, the HCl is the limiting reagent in the reaction. All of the HCl reacts, and the amount of NaOH that remains is:

$$(1.0 \times 10^{-4}) - (1.8 \times 10^{-6}) = 9.8 \times 10^{-5}\ M$$

The concentration of NaOH is:

$$\frac{9.8 \times 10^{-5}\ M\ \text{NaOH}}{0.101\ \text{L}} = 9.7 \times 10^{-4}\ M$$

The pOH of this solution is:

$$\text{pOH} = -\log[OH^-] = -\log(9.7 \times 10^{-4}) = 3.01$$

The pH is:

$$\text{pH} = 14.00 - \text{pOH} = 10.99$$

The pH changes from 4.74 to 10.99 in this unbuffered solution. This compares to the change of 4.74 to 4.75 that occurred when the same amount of NaOH was added to the buffered solution described in part (b).

Exercise 7.1.1

Show that adding 1.0 mL of 0.10 *M* HCl changes the pH of 100 mL of a 1.8 × 10^{-5} *M* HCl solution from 4.74 to 3.00.

Answer

Initial pH of 1.8 × 10^{-5} *M* HCl; pH = −log[H_3O^+] = −log[1.8 × 10^{-5}] = 4.74

Moles of H_3O^+ added by addition of 1.0 mL of 0.10 *M* HCl: 0.10 moles/L × 0.0010 L = 1.0 × 10^{-4} moles; final pH after addition of 1.0 mL of 0.10 *M* HCl:

$$\text{pH} = -\log[H_3O^+] = -\log\left(\frac{\text{total moles } H_3O^+}{\text{total volume}}\right) = -\log\left(\frac{1.0 \times 10^{-4}\ \text{mol} + 1.8 \times 10^{-6}\ \text{mol}}{101\ \text{mL}\left(\frac{1\ \text{L}}{1000\ \text{mL}}\right)}\right) = 3.00 \tag{7.1.15}$$

The Henderson-Hasselbalch Approximation

We have seen in Example 7.1.1 how the pH of a buffer may be calculated using the ICE table method. The method requires knowing the concentrations of the conjugate acid-base pair and the K_a or K_b of the weak acid or weak base. However, there is a simpler method

using the same information in a convenient formula, based on a rearrangement of the equilibrium equation for the dissociation of a weak acid.

The simplified ionization reaction of any weak acid is $HA \leftrightharpoons H^+ + A^-$, for which the equilibrium constant expression is as follows:

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{7.1.16}$$

This equation can be rearranged as follows:

$$[H^+] = K_a \frac{[HA]}{[A^-]} \tag{7.1.17}$$

Taking the logarithm of both sides and multiplying both sides by −1,

$$-\log[H^+] = -\log K_a - \log\left(\frac{[HA]}{[A^-]}\right) \tag{7.1.18}$$

$$= -\log K_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{7.1.19}$$

Replacing the negative logarithms in Equation 7.1.19 to obtain pH, we get,

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{7.1.20}$$

or, more generally,

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right) \tag{7.1.21}$$

Equation 7.1.20 and Equation 7.1.21 are both forms of the **Henderson-Hasselbalch approximation**, named after the two early 20th-century chemists who first noticed that this rearranged version of the equilibrium constant expression provides an easy way to calculate the pH of a buffer solution. In general, the validity of the Henderson-Hasselbalch approximation may be limited to solutions whose concentrations are at least 100 times greater than their K_a values (the "x is small" assumption).

There are three special cases where the Henderson-Hasselbalch approximation is easily interpreted without the need for calculations:

- $[base] = [acid]$: Under these conditions,

  $$\frac{[base]}{[acid]} = 1 \tag{7.1.22}$$

  in Equation 7.1.21. Because $\log 1 = 0$,

  $$pH = pK_a \tag{7.1.23}$$

  regardless of the actual concentrations of the acid and base.
- $[base]/[acid] = 10$: In Equation 7.1.21, because $\log 10 = 1$,

  $$pH = pK_a + 1. \tag{7.1.24}$$
- $[base]/[acid] = 100$: In Equation 7.1.21, because $\log 100 = 2$,

  $$pH = pK_a + 2. \tag{7.1.25}$$

Each time we increase the [base]/[acid] ratio by 10, the pH of the solution increases by 1 pH unit. Conversely, if the [base]/[acid] ratio is 0.1, then pH = pK_a − 1. Each additional factor-of-10 decrease in the [base]/[acid] ratio causes the pH to decrease by 1 pH unit.

> *If [base] = [acid] for a buffer, then pH = pK_a. Changing the ratio by a factor of 10 changes the pH by ±1 unit.*

Example 7.1.2

What is the pH of a solution that contains

a. 0.135 M HCO_2H and 0.215 M HCO_2Na? (The pK_a of formic acid is 3.75.)

b. 0.0135 M HCO_2H and 0.0215 M HCO_2Na?
c. 0.119 M pyridine and 0.234 M pyridine hydrochloride? (The pK_b of pyridine is 8.77.)

Given: concentration of acid, conjugate base, and pK_a; concentration of base, conjugate acid, and pK_b

Asked for: pH

Strategy:

Substitute values into either form of the Henderson-Hasselbalch approximation (Equation 7.1.20 or Equation 7.1.21) to calculate the pH.

Solution:

According to the Henderson-Hasselbalch approximation (Equation 7.1.20), the pH of a solution that contains both a weak acid and its conjugate base is

$$pH = pK_a + \log([A-]/[HA]). \tag{7.1.26}$$

A

Inserting the given values into the equation,

$$\begin{aligned} pH &= 3.75 + \log\left(\frac{0.215}{0.135}\right) \\ &= 3.75 + \log 1.593 \\ &= 3.95 \end{aligned}$$

This result makes sense because the $[A^-]/[HA]$ ratio is between 1 and 10, so the pH of the buffer must be between the pK_a (3.75) and $pK_a + 1$, or 4.75.

B

This is identical to part (a), except for the concentrations of the acid and the conjugate base, which are 10 times lower. Inserting the concentrations into the Henderson-Hasselbalch approximation,

$$\begin{aligned} pH &= 3.75 + \log\left(\frac{0.0215}{0.0135}\right) \\ &= 3.75 + \log 1.593 \\ &= 3.95 \end{aligned}$$

This result is identical to the result in part (a), which emphasizes the point that the pH of a buffer depends only on the ratio of the concentrations of the conjugate base and the acid, not on the magnitude of the concentrations. Because the [A⁻]/[HA] ratio is the same as in part (a), the pH of the buffer must also be the same (3.95).

C

In this case, we have a weak base, pyridine (Py), and its conjugate acid, the pyridinium ion (HPy^+). We will therefore use Equation 7.1.21, the more general form of the Henderson-Hasselbalch approximation, in which "base" and "acid" refer to the appropriate species of the conjugate acid–base pair. We are given [base] = [Py] = 0.119 M and $[acid] = [HPy^+] = 0.234\ M$. We also are given $pK_b = 8.77$ for pyridine, but we need pK_a for the pyridinium ion. Recall that the pK_b of a weak base and the pK_a of its conjugate acid are related:

$$pK_a + pK_b = pK_w. \tag{7.1.27}$$

Thus pK_a for the pyridinium ion is $pK_w - pK_b = 14.00 - 8.77 = 5.23$. Substituting this pK_a value into the Henderson-Hasselbalch approximation,

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right)$$
$$= 5.23 + \log\left(\frac{0.119}{0.234}\right)$$
$$= 5.23\ -0.294$$
$$= 4.94$$

Once again, this result makes sense: the $[B]/[BH^+]$ ratio is about 1/2, which is between 1 and 0.1, so the final pH must be between the pK_a (5.23) and $pK_a - 1$, or 4.23.

Exercise 7.1.2

What is the pH of a solution that contains

a. 0.333 M benzoic acid and 0.252 M sodium benzoate?
b. 0.050 M trimethylamine and 0.066 M trimethylamine hydrochloride?

The pK_a of benzoic acid is 4.20, and the pK_b of trimethylamine is also 4.20.

Answer a

4.08

Answer b

9.68

The Henderson-Hasselbalch approximation ((Equation 7.1.20) can also be used to calculate the pH of a buffer solution after adding a given amount of strong acid or strong base, as demonstrated in Example 7.1.3.

Example 7.1.3

The buffer solution in Example 7.1.2 contained 0.135 M HCO_2H and 0.215 M HCO_2Na and had a pH of 3.95.

a. What is the final pH if 5.00 mL of 1.00 M HCl are added to 100 mL of this solution?
b. What is the final pH if 5.00 mL of 1.00 M $NaOH$ are added?

Given: composition and pH of buffer; concentration and volume of added acid or base

Asked for: final pH

Strategy:

A. Calculate the amounts of formic acid and formate present in the buffer solution. Then calculate the amount of acid or base added.
B. Construct a table showing the amounts of all species after the neutralization reaction. Use the final volume of the solution to calculate the concentrations of all species. Finally, substitute the appropriate values into the Henderson-Hasselbalch approximation (Equation 7.1.21) to obtain the pH.

Solution:

The added HCl (a strong acid) or $NaOH$ (a strong base) will react completely with formate (a weak base) or formic acid (a weak acid), respectively, to give formic acid or formate and water. We must therefore calculate the amounts of formic acid and formate present after the neutralization reaction.

A We begin by calculating the millimoles of formic acid and formate present in 100 mL of the initial pH 3.95 buffer:

The millimoles of H^+ in 5.00 mL of 1.00 M HCl is as follows:

B Next, we construct an ICE table:

$$HCO^{2-}(aq) + H^+(aq) \rightarrow HCO_2H(aq) \tag{7.1.28}$$

	$HCO^{2-}(aq)$	$H^+(aq)$	$HCO_2H(aq)$
Initial	21.5 mmol	5.00 mmol	13.5 mmol
Change	−5.00 mmol	−5.00 mmol	+5.00 mmol

	$HCO^{2-}(aq)$	$H^+(aq)$	$HCO_2H(aq)$
Equilibrium	16.5 mmol	~0 mmol	18.5 mmol

The final amount of H^+ in solution is given as "~0 mmol." For the purposes of the stoichiometry calculation, this is essentially true, but remember that the point of the problem is to calculate the final $[H^+]$ and thus the pH. We now have all the information we need to calculate the pH. We can use either the lengthy procedure of Example 7.1.1 or the Henderson–Hasselbach approximation. The latter approach is much simpler. The Henderson-Hasselbalch approximation requires the concentrations of HCO_2^- and HCO_2H, which can be calculated using the number of millimoles (n) of each and the total volume (VT). Substituting these values into the Henderson-Hasselbalch approximation,

$$pH = pK_a + \log\left(\frac{[HCO_2^-]}{[HCO_2H]}\right) = pK_a + \log\left(\frac{n_{HCO_2^-}/V_f}{n_{HCO_2H}/V_f}\right) = pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) \tag{7.1.29}$$

Because the total volume appears in both the numerator and denominator, it cancels. We therefore need to use only the ratio of the number of millimoles of the conjugate base to the number of millimoles of the weak acid. So

$$pH = pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) = 3.75 + \log\left(\frac{16.5\ mmol}{18.5\ mmol}\right) = 3.75\ -0.050 = 3.70 \tag{7.1.30}$$

Once again, this result makes sense on two levels. First, the addition of HClhas decreased the pH from 3.95, as expected. Second, the ratio of HCO_2^- to HCO_2H is slightly less than 1, so the pH should be between the pK_a and pK_a − 1.

A The procedure for solving this part of the problem is exactly the same as that used in part (a). We have already calculated the numbers of millimoles of formic acid and formate in 100 mL of the initial pH 3.95 buffer: 13.5 mmol of HCO_2H and 21.5 mmol of HCO_2^-. The number of millimoles of OH^- in 5.00 mL of 1.00 M $NaOH$ is as follows:

B With this information, we can construct an ICE table.

$$HCO_2H(aq) + OH^-(aq) \rightarrow HCO_2^-(aq) + H_2O(l) \tag{7.1.31}$$

	$HCO_2H(aq)$	OH^-	$HCO_2^-(aq)$
Initial	13.5 mmol	5.00 mmol	21.5 mmol
Change	−5.00 mmol	−5.00 mmol	+5.00 mmol
Equilibrium	8.5 mmol	~0 mmol	26.5 mmol

The final amount of OH^- in solution is not actually zero; this is only approximately true based on the stoichiometric calculation. We can calculate the final pH by inserting the numbers of millimoles of both HCO_2^- and HCO_2H into the simplified Henderson-Hasselbalch expression used in part (a) because the volume cancels:

$$pH = pK_a + \log\left(\frac{n_{HCO_2^-}}{n_{HCO_2H}}\right) = 3.75 + \log\left(\frac{26.5\ mmol}{8.5\ mmol}\right) = 3.75 + 0.494 = 4.24 \tag{7.1.32}$$

Once again, this result makes chemical sense: the pH has increased, as would be expected after adding a strong base, and the final pH is between the pK_a and pK_a + 1, as expected for a solution with a HCO_2^-/HCO_2H ratio between 1 and 10.

Exercise 7.1.3

The buffer solution from Example 7.1.2 contained 0.119 M pyridine and 0.234 M pyridine hydrochloride and had a pH of 4.94.

a. What is the final pH if 12.0 mL of 1.5 M $NaOH$ are added to 250 mL of this solution?
b. What is the final pH if 12.0 mL of 1.5 M HCl are added?

Answer a

5.30

Answer b

4.42

Note

Either concentrations OR amounts (in moles or millimoles) of the acidic and basic components of a buffer may be used in the Henderson-Hasselbalch approximation, because the volume cancels out in the ratio of [base]/[acid].

The results obtained in Example 7.1.3 and its corresponding exercise demonstrate how little the pH of a well-chosen buffer solution changes despite the addition of a significant quantity of strong acid or strong base. Suppose we had added the same amount of HCl or $NaOH$ solution to 100 mL of an unbuffered solution at pH 3.95 (corresponding to 1.1×10^{-4} M HCl). In this case, adding 5.00 mL of 1.00 M HCl would lower the final pH to 1.32 instead of 3.70, whereas adding 5.00 mL of 1.00 M $NaOH$ would raise the final pH to 12.68 rather than 4.24. (Try verifying these values by doing the calculations yourself.) Thus the presence of a buffer significantly increases the ability of a solution to maintain an almost constant pH.

Medicine: The Buffer System in Blood

The normal pH of human blood is about 7.4. The carbonate buffer system in the blood uses the following equilibrium reaction:

$$\mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2CO_3}(aq) \rightleftharpoons \mathrm{HCO_3^-}(aq) + \mathrm{H_3O^+}(aq) \tag{7.1.33}$$

The concentration of carbonic acid, H_2CO_3 is approximately 0.0012 *M*, and the concentration of the hydrogen carbonate ion, HCO_3^-, is around 0.024 *M*. Using the Henderson-Hasselbalch equation and the pK_a of carbonic acid at body temperature, we can calculate the pH of blood:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{base}]}{[\mathrm{acid}]} = 6.1 + \log\frac{0.024}{0.0012} = 7.4 \tag{7.1.34}$$

The fact that the H_2CO_3 concentration is significantly lower than that of the HCO_3^- ion may seem unusual, but this imbalance is due to the fact that most of the by-products of our metabolism that enter our bloodstream are acidic. Therefore, there must be a larger proportion of base than acid, so that the capacity of the buffer will not be exceeded.

Lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the HCO_3^- ion, producing H_2CO_3. An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be eliminated by breathing. In fact, in addition to the regulating effects of the carbonate buffering system on the pH of blood, the body uses breathing to regulate blood pH. If the pH of the blood decreases too far, an increase in breathing removes CO_2 from the blood through the lungs driving the equilibrium reaction such that $[H_3O^+]$ is lowered. If the blood is too alkaline, a lower breath rate increases CO_2 concentration in the blood, driving the equilibrium reaction the other way, increasing $[H^+]$ and restoring an appropriate pH.

Summary

A solution containing a mixture of an acid and its conjugate base, or of a base and its conjugate acid, is called a buffer solution. Unlike in the case of an acid, base, or salt solution, the hydronium ion concentration of a buffer solution does not change greatly when a small amount of acid or base is added to the buffer solution. The base (or acid) in the buffer reacts with the added acid (or base).

Key Equations

- pK_a = −log K_a
- pK_b = −log K_b
- $\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}$

Glossary

buffer

mixture of a weak acid or a weak base and the salt of its conjugate; the pH of a buffer resists change when small amounts of acid or base are added

Henderson-Hasselbalch equation

equation used to calculate the pH of buffer solutions

Contributors

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7.2: Practical Aspects of Buffers

Skills to Develop

- Understand the factors that affect buffer range and capacity
- Calculate the amounts of acid and base needed to prepare a buffer of a given pH

Buffers are characterized by the pH range over which they can maintain a more or less constant pH and by their buffer capacity, the amount of strong acid or base that can be absorbed before the pH changes significantly. Although the useful pH range of a buffer depends strongly on the chemical properties of the weak acid and weak base used to prepare the buffer (i.e., on K), its buffer capacity depends solely on the concentrations of the species in the buffered solution.

Buffer Capacity

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant (Figure 7.2.1). If we add so much base to a buffer that the weak acid is exhausted, no more buffering action toward the base is possible. On the other hand, if we add an excess of acid, the weak base would be exhausted, and no more buffering action toward any additional acid would be possible. In fact, we do not even need to exhaust all of the acid or base in a buffer to overwhelm it; its buffering action will diminish rapidly as a given component nears depletion.

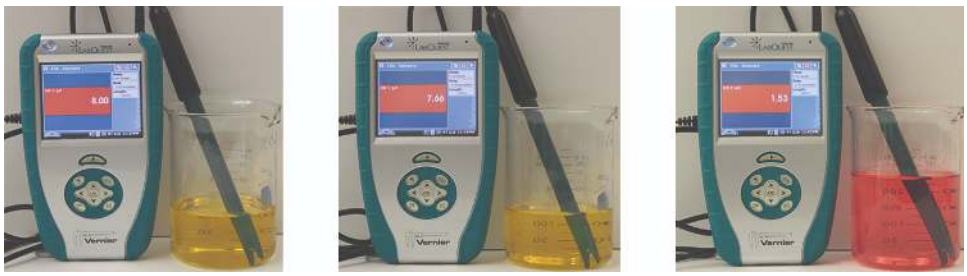


Figure 7.2.1: The indicator color (methyl orange) shows that a small amount of acid added to a buffered solution of pH 8 (beaker on the left) has little affect on the buffered system (middle beaker). However, a large amount of acid exhausts the buffering capacity of the solution and the pH changes dramatically (beaker on the right). (credit: modification of work by Mark Ott)

The buffer capacity is the amount of acid or base that can be added to a given volume of a buffer solution before the pH changes significantly, usually by one unit. Buffer capacity depends on the amounts of the weak acid and its conjugate base that are in a buffer mixture.

> *The more concentrated the buffer solution, the greater its buffer capacity.*

As illustrated in Figure 7.2.2, when $NaOH$ is added to solutions that contain different concentrations of an acetic acid/sodium acetate buffer, the observed change in the pH of the buffer is inversely proportional to the concentration of the buffer. If the buffer capacity is 10 times larger, then the buffer solution can absorb 10 times more strong acid or base before undergoing a significant change in pH.

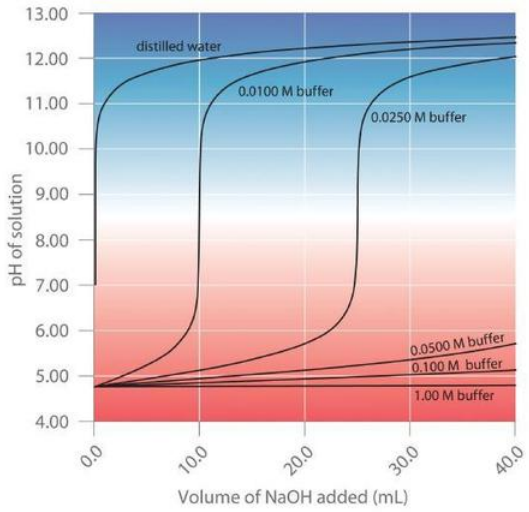


Figure 7.2.2: Effect of Buffer Concentration on the Capacity of a Buffer

A buffer maintains a relatively constant pH when acid or base is added to a solution. The addition of even tiny volumes of 0.10 M $NaOH$ to 100.0 mL of distilled water results in a very large change in pH. As the concentration of a 50:50 mixture of sodium acetate/acetic acid buffer in the solution is increased from 0.010 M to 1.00 M, the change in the pH produced by the addition of the same volume of $NaOH$ solution decreases steadily. For buffer concentrations of at least 0.500 M, the addition of even 25 mL of the $NaOH$ solution results in only a relatively small change in pH.

Buffer Range

The buffer range is the range of pH values over which a buffer is most effective (i.e. has the largest buffer capacity for its concentration). A good buffer mixture should have about equal concentrations of both of its components. As a rule of thumb, a buffer solution has generally lost its usefulness when one component of the buffer pair is less than about 10% of the other. Figure 7.2.3 shows an acetic acid-acetate ion buffer as base is added. The initial pH is 4.74 (the pK_a of acetic acid). A change of 1 pH unit occurs when the acetic acid concentration is reduced to 11% of the acetate ion concentration. Past this point, the pH begins to change more rapidly with additional base as the buffer is overwhelmed.

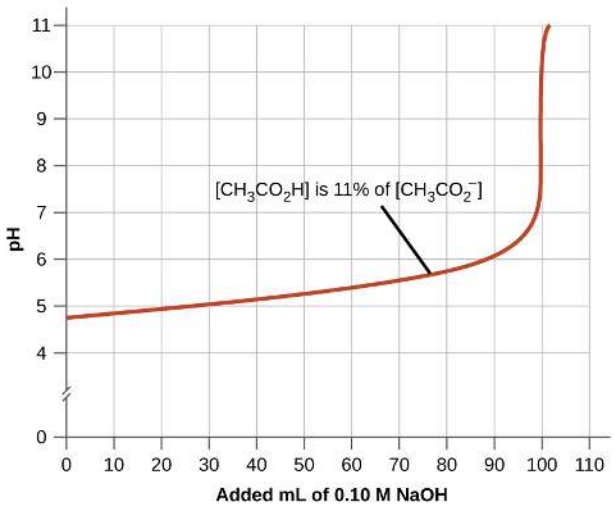


Figure 7.2.3: The graph, an illustration of buffering action, shows change of pH as an increasing amount of a 0.10-M NaOH solution is added to 100 mL of a buffer solution in which, initially, [CH_3CO_2H] = 0.10 M and $[CH_3CO_2^-] = 0.10\ M$

> *The most effective buffers contain equal concentrations of an acid and its conjugate base.*

A buffer that contains approximately equal amounts of a weak acid and its conjugate base in solution is equally effective at neutralizing either added base or added acid. This is shown in Figure 7.2.4 for an acetic acid/sodium acetate buffer. Adding a given

amount of strong acid shifts the system along the horizontal axis to the left, whereas adding the same amount of strong base shifts the system the same distance to the right. In either case, the change in the ratio of $CH_3CO_2^-$ to CH_3CO_2H from 1:1 reduces the buffer capacity of the solution.

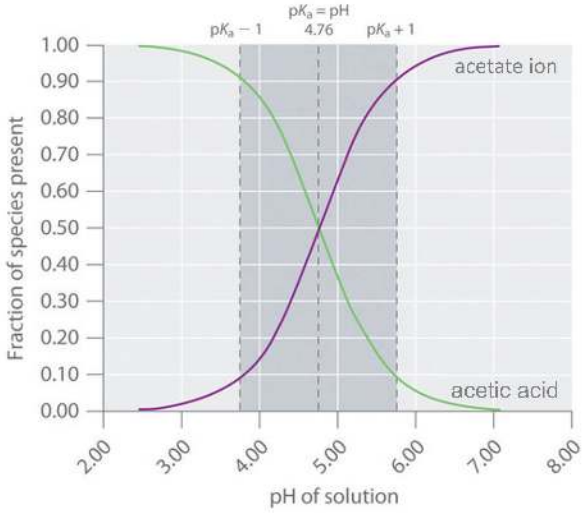


Figure 7.2.4: Distribution Curve Showing the Fraction of Acetic Acid Molecules and Acetate Ions as a Function of pH in a Solution of Acetic Acid. The pH range over which the acetic acid/sodium acetate system is an effective buffer (the darker shaded region) corresponds to the region in which appreciable concentrations of both species are present (pH 3.76–5.76, corresponding to $pH = pK_a \pm 1$).

Recall that according to the Henderson-Hasselbalch relationship, pH = pK_a when a buffer contains equal concentrations of conjugate acid and base. Thus, the effective range of a buffer is approximately the pK_a plus or minus one pH unit. This corresponds to a ten-to-one concentration of the two components either way, as illustrated above.

> *The buffer range is approximately* $pH = pK_a \pm 1$

Preparing Buffers

In many situations, chemists must prepare buffer solutions to maintain a desired pH. There are many different buffer systems to choose from, depending on the characteristics and pH required of the solution. The following steps may be used when preparing a buffer in the laboratory:

1. *Choose an appropriate buffer system.* Because the buffer capacity is highest where pH = pK_a, the ideal buffer will have a pK_a close to the desired pH. In general, weak acids and their salts are better as buffers for pHs less than 7; weak bases and their salts are better as buffers for pHs greater than 7.
2. *Use the total buffer concentration and pH desired to calculate the amounts of acid and base needed to create the buffer.* The Henderson-Hasselbalch equation can be used to determine the ratio of [base]/[acid] needed.
3. *Mix the components.* The weak acid can be added to a salt of the conjugate base directly; alternatively, enough strong base can be added to the weak acid to partially convert it to the conjugate base (or strong acid can be added to a weak base to partially neutralize it).
4. *Adjust the pH as desired.* In practice, experimental error and other factors often cause buffers not quite to be at the calculated pH, so the chemist can add small amounts of strong acid or strong base to fine-tune the pH, monitoring the solution with a pH meter.

Example 7.2.1 illustrates the method for calculating the amount of reagents needed to create a buffer at a desired pH.

Example 7.2.1

The pK_a of formic acid is 3.75. How many grams of formic acid (HCO_2H) and sodium formate (HCO_2Na) must be mixed to prepare 100.0 mL of a buffer with a total concentration of 0.100 M and a pH of 3.90?

Given: pK_a of formic acid, volume of buffer, total buffer concentration, desired pH

Asked For: grams of HCO_2H and HCO_2Na

Strategy: Use the Henderson-Hasselbalch approximation to determine the ratio of [base]/[acid] needed, then use the total concentration and volume to calculate the number of moles of each component needed, convert moles to grams

Solution:

According to the Henderson-Hasselbalch approximation,

$$pH = pK_a + \log([base]/[acid]) \tag{7.2.1}$$

In this case, the conjugate base is HCO_2Na and the conjugate acid is HCO_2H. Plugging the desired pH and pK_a into the equation:

$$3.90 = 3.75 + \log([HCO_2Na]/[HCO_2H]) \tag{7.2.2}$$

Solving for the [base]/[acid] ratio:

$$\log([HCO_2Na]/[HCO_2H]) = 0.15 \tag{7.2.3}$$

$$[HCO_2Na]/[HCO_2H] = e^{0.15} = 1.16 \tag{7.2.4}$$

This ratio means that the buffer must contain 1.16 times as many moles of HCO_2Na as HCO_2H to get a pH of 3.90. This makes sense because the desired pH is higher than the pK_a, so more of the conjugate base than acid is needed.

We know that we need to create 100.0 mL of buffer with a total concentration of 0.100 M:

$$100.0\text{mL} \times \frac{1\text{L}}{1000\text{mL}} \times \frac{0.100\text{mol}}{1\text{L}} = 0.0100 \text{ mol}$$

Thus, we need 0.0100 moles total of both buffer components. We can set up the following two equations:

$$\text{mol}(\text{HCO}_2\text{Na}) + \text{mol}(\text{HCO}_2\text{H}) = 0.0100 \text{ mol}$$

$$\text{mol}(\text{HCO}_2\text{Na})/\text{mol}(\text{HCO}_2\text{H}) = 1.16 \quad \text{or} \quad \text{mol}(\text{HCO}_2\text{Na}) = 1.16 \times \text{mol}(\text{HCO}_2\text{H})$$

With two equations and two unknowns, we substitute one expression into the other to solve for both components:

$$1.16 \times \text{mol}(\text{HCO}_2\text{H}) + \text{mol}(\text{HCO}_2\text{H}) = 2.16 \times \text{mol}(\text{HCO}_2\text{H}) = 0.0100 \text{ mol}$$

$$\text{mol}(\text{HCO}_2\text{H}) = 0.00463 \text{ mol HCO}_2\text{H}$$

$$\text{mol}(\text{HCO}_2\text{Na}) = 1.16 \times 0.00463 \text{ mol} = 0.00537 \text{ mol HCO}_2\text{Na}$$

Finally, we solve for grams using the molar mass of each component:

$$0.00463 \text{ mol HCO}_2\text{H} \times \frac{46.03 \text{ g}}{1 \text{ mol HCO}_2\text{H}} = 0.213 \text{ g HCO}_2\text{H}$$

$$0.00537 \text{ mol HCO}_2\text{Na} \times \frac{68.01 \text{ g}}{1 \text{ mol HCO}_2\text{Na}} = 0.365 \text{ g HCO}_2\text{Na}$$

Exercise 7.2.1

A biochemist requires 250 mL of a 0.15 M acetic acid-acetate buffer at pH 5.00. How many grams of CH_3CO_2H and CH_3CO_2Na must she add to create the buffer mixture (the pK_a of acetic acid is 4.74)?

Answer

0.98 g CH_3CO_2H and 1.74 g CH_3CO_2Na

Summary

Buffers are characterized by their pH range and buffer capacity. The useful pH range of a buffer depends on the chemical properties of the conjugate weak acid–base pair used to prepare the buffer and is generally the $pK_a \pm 1$. Buffer capacity depends on the concentrations of the species in the solution; the more concentrated the buffer mixture, the higher the buffer capacity. A buffer has its highest capacity at equal concentrations of weak acid and conjugate base, when $pH = pK_a$.

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7.3: Acid-Base Titrations

Learning Objectives

- To calculate the pH at any point in an acid–base titration.

In an acid–base titration, a buret is used to deliver measured volumes of an acid or a base solution of known concentration (the titrant) to a flask that contains a solution of a base or an acid, respectively, of unknown concentration (the unknown). If the concentration of the titrant is known, then the concentration of the unknown can be determined. The following discussion focuses on the pH changes that occur during an acid–base titration. Plotting the pH of the solution in the flask against the amount of acid or base added produces a titration curve. The shape of the curve provides important information about what is occurring in solution during the titration.

Titrations of Strong Acids and Bases

Figure $7.3.1a$ shows a plot of the pH as 0.20 M HCl is gradually added to 50.00 mL of pure water. The pH of the sample in the flask is initially 7.00 (as expected for pure water), but it drops very rapidly as HCl is added. Eventually the pH becomes constant at 0.70—a point well beyond its value of 1.00 with the addition of 50.0 mL of HCl (0.70 is the pH of 0.20 M HCl). In contrast, when 0.20 M NaOH is added to 50.00 mL of distilled water, the pH (initially 7.00) climbs very rapidly at first but then more gradually, eventually approaching a limit of 13.30 (the pH of 0.20 M NaOH), again well beyond its value of 13.00 with the addition of 50.0 mL of NaOH as shown in Figure $7.3.1b$ As you can see from these plots, the titration curve for adding a base is the mirror image of the curve for adding an acid.

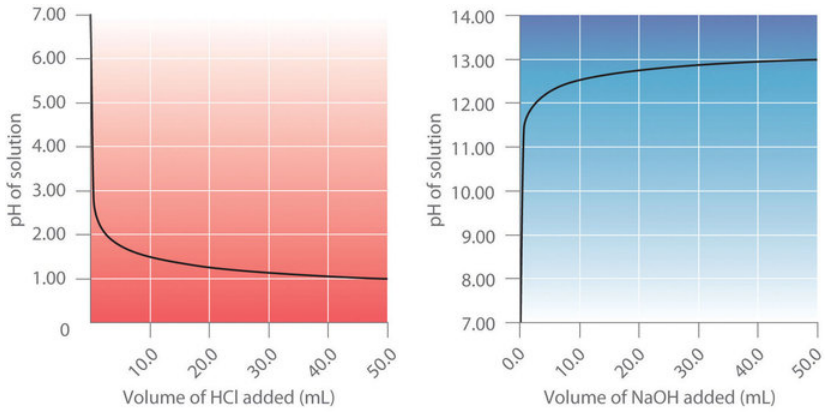


Figure 7.3.1: Solution pH as a Function of the Volume of a Strong Acid or a Strong Base Added to Distilled Water. (a) When 0.20 M HCl is added to 50.0 mL of distilled water, the pH rapidly decreases until it reaches a minimum at the pH of 0.20 M HCl. (b) Conversely, when 0.20 M NaOH is added to 50.0 mL of distilled water, the pH rapidly increases until it reaches a maximum at the pH of 0.20 M $NaOH$. (CC BY-SA-NC; Anonymous by request)

The graphs of water with strong acid added and water with strong base added are inverses of each other.

Suppose that we now add 0.20 M NaOH to 50.0 mL of a 0.10 M solution of HCl. Because HCl is a strong acid that is completely ionized in water, the initial $[H^+]$ is 0.10 M, and the initial pH is 1.00. Adding NaOH decreases the concentration of H+ because of the neutralization reaction (Figure $7.3.2a$):

$$OH^- + H^+ \rightleftharpoons H_2O.$$

Thus the pH of the solution increases gradually. Near the equivalence point, however, the point at which the number of moles of base (or acid) added equals the number of moles of acid (or base) originally present in the solution, the pH increases much more rapidly because most of the H^+ ions originally present have been consumed. For the titration of a monoprotic strong acid (HCl) with a monobasic strong base (NaOH), we can calculate the volume of base needed to reach the equivalence point from the following relationship:

$$moles\ of\ base = (volume)_b(molarity)_b V_b M_b = moles\ of\ acid = (volume)_a(molarity)_a = V_a M_a \qquad (7.3.1)$$

If 0.20 M NaOH is added to 50.0 mL of a 0.10 M solution of HCl, we solve for V_b:

$$V_b(0.20Me) = 0.025L = 25mL$$

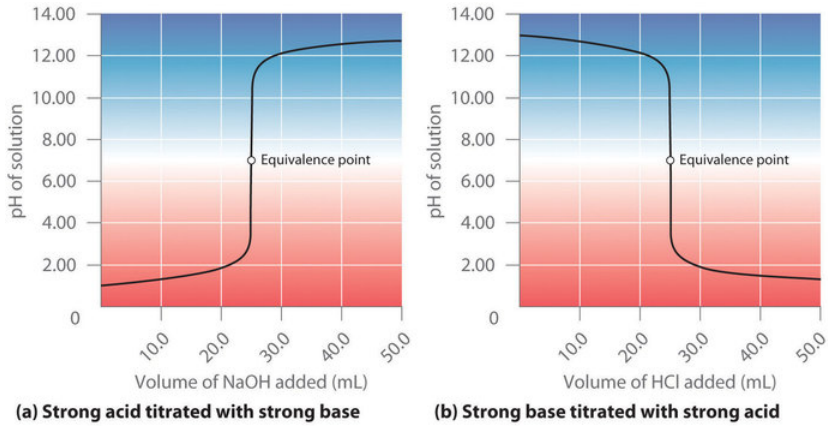


Figure 7.3.2: The Titration of (a) a Strong Acid with a Strong Base and (b) a Strong Base with a Strong Acid(a) As 0.20 M NaOH is slowly added to 50.0 mL of 0.10 M HCl, the pH increases slowly at first, then increases very rapidly as the equivalence point is approached, and finally increases slowly once more. (b) Conversely, as 0.20 M HCl is slowly added to 50.0 mL of 0.10 M $NaOH$, the pH decreases slowly at first, then decreases very rapidly as the equivalence point is approached, and finally decreases slowly once more. (CC BY-SA-NC; Anonymous by request)

The titration curves of strong acid titrated with strong base and strong base titrated with strong acid are inverses of each other.

At the equivalence point (when 25.0 mL of NaOH solution has been added), the neutralization is complete: only a salt remains in solution (NaCl), and the pH of the solution is 7.00. Adding more NaOH produces a rapid increase in pH, but eventually the pH levels off at a value of about 13.30, the pH of 0.20 M $NaOH$.

As shown in Figure $7.3.2b$, the titration of 50.0 mL of a 0.10 M solution of NaOH with 0.20 M HCl produces a titration curve that is nearly the mirror image of the titration curve in Figure $7.3.2a$. The pH is initially 13.00, and it slowly decreases as HCl is added. As the equivalence point is approached, the pH drops rapidly before leveling off at a value of about 0.70, the pH of 0.20 M HCl.

The titration of either a strong acid with a strong base or a strong base with a strong acid produces an S-shaped curve. The curve is somewhat asymmetrical because the steady increase in the volume of the solution during the titration causes the solution to become more dilute. Due to the leveling effect, the shape of the curve for a titration involving a strong acid and a strong base depends on only the concentrations of the acid and base, not their identities.

> The shape of the titration curve involving a strong acid and a strong base depends only on their concentrations, not their identities.

Example 7.3.1: Hydrochloric Acid

Calculate the pH of the solution after 24.90 mL of 0.200 M NaOH has been added to 50.00 mL of 0.100 M HCl.

Given: volumes and concentrations of strong base and acid

Asked for: pH

Strategy:

A. Calculate the number of millimoles of H^+ and OH^- to determine which, if either, is in excess after the neutralization reaction has occurred. If one species is in excess, calculate the amount that remains after the neutralization reaction.
B. Determine the final volume of the solution. Calculate the concentration of the species in excess and convert this value to pH.

Solution

A Because 0.100 mol/L is equivalent to 0.100 mmol/mL, the number of millimoles of H^+ in 50.00 mL of 0.100 M HCl can be calculated as follows:

$$50.00\ \cancel{mL}\left(\frac{0.100\ mmol\ HCl}{\cancel{mL}}\right) = 5.00\ mmol\ HCl = 5.00\ mmol\ H^+$$

The number of millimoles of NaOH added is as follows:

$$24.90\ \cancel{mL}\left(\frac{0.200\ mmol\ NaOH}{\cancel{mL}}\right) = 4.98\ mmol\ NaOH = 4.98\ mmol\ OH^-$$

Thus H^+ is in excess. To completely neutralize the acid requires the addition of 5.00 mmol of OH^- to the HCl solution. Because only 4.98 mmol of OH^- has been added, the amount of excess H^+ is 5.00 mmol − 4.98 mmol = 0.02 mmol of H^+.

B The final volume of the solution is 50.00 mL + 24.90 mL = 74.90 mL, so the final concentration of H^+ is as follows:

$$[H^+] = \frac{0.02\ mmol\ H^+}{74.90\ mL} = 3 \times 10^{-4}\ M$$

Hence,

$$pH \approx -\log[H^+] = -\log(3 \times 10^{-4}) = 3.5$$

This is significantly less than the pH of 7.00 for a neutral solution.

Exercise 7.3.1

Calculate the pH of a solution prepared by adding $40.00\ mL$ of $0.237\ M\ HCl$ to $75.00\ mL$ of a $0.133 M$ solution of $NaOH$.

Answer

11.6



pH after the addition of 10 ml of Strong Base to a Strong Acid:

https://youtu.be/_cM1_-kdJ20 (opens in new window)



pH at the Equivalence Point in a Strong Acid/Strong Base Titration:

https://youtu.be/7POGDA5Ql2M

Titrations of Weak Acids and Bases

In contrast to strong acids and bases, the shape of the titration curve for a weak acid or a weak base depends dramatically on the identity of the acid or the base and the corresponding K_a or K_b. As we shall see, the pH also changes much more gradually around the equivalence point in the titration of a weak acid or a weak base. As you learned previously, $[\mathrm{H}^+]$ of a solution of a weak acid (HA) is not equal to the concentration of the acid but depends on both its pK_a and its concentration. Because only a fraction of a weak acid dissociates, $[\backslash(\mathrm{H}^+]$ is less than $[\mathrm{HA}]$. Thus the pH of a solution of a weak acid is greater than the pH of a solution of a strong acid of the same concentration.

Figure $7.3.3a$ shows the titration curve for 50.0 mL of a 0.100 M solution of acetic acid with 0.200 M NaOH superimposed on the curve for the titration of 0.100 M HCl shown in part (a) in Figure $7.3.2$. Below the equivalence point, the two curves are very different. Before any base is added, the pH of the acetic acid solution is greater than the pH of the HCl solution, and the pH changes more rapidly during the first part of the titration. Note also that the pH of the acetic acid solution at the equivalence point is greater than 7.00. That is, at the equivalence point, the solution is basic. In addition, the change in pH around the equivalence point is only about half as large as for the HCl titration; the magnitude of the pH change at the equivalence point depends on the pK_a of the acid being titrated. Above the equivalence point, however, the two curves are identical. Once the acid has been neutralized, the pH of the solution is controlled only by the amount of excess NaOH present, regardless of whether the acid is weak or strong.

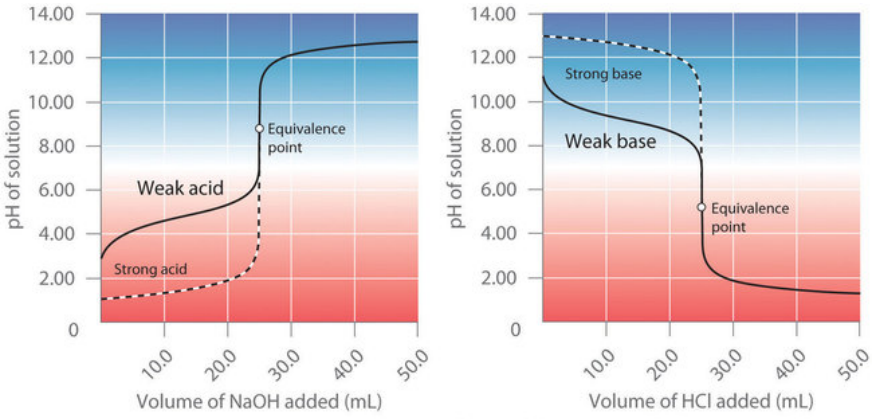


Figure 7.3.3: The Titration of (a) a Weak Acid with a Strong Base and (b) a Weak Base with a Strong Acid. (a) As 0.200 M NaOH is slowly added to 50.0 mL of 0.100 M acetic acid, the pH increases slowly at first, then increases rapidly as the equivalence point is approached, and then again increases more slowly. The corresponding curve for the titration of 50.0 mL of 0.100 M HCl with 0.200 M NaOH is shown as a dashed line. (b) As 0.200 M HCl is slowly added to 50.0 mL of 0.100 M NH3, the pH decreases slowly at first, then decreases rapidly as the equivalence point is approached, and then again decreases more slowly. The corresponding curve for the titration of 50.0 mL of 0.100 M NaOH with 0.200 M HCl is shown as a dashed line. (CC BY-SA-NC; Anonymous by request)

The titration curves of weak acid titrated with strong base and weak base titrated with strong acid are inverse of each other. These curves are shorter than the titration curves with strong acid and strong base.

> The shape of the titration curve of a weak acid or weak base depends heavily on their identities and the K_a or K_b.

The titration curve in Figure $7.3.3a$ was created by calculating the starting pH of the acetic acid solution before any NaOH is added and then calculating the pH of the solution after adding increasing volumes of $NaOH$. The procedure is illustrated in the following subsection and Example $7.3.2$ for three points on the titration curve, using the pK_a of acetic acid (4.76 at 25°C; $K_a = 1.7 \times 10^{-5}$.

Calculating the pH of a Solution of a Weak Acid or a Weak Base

As explained discussed, if we know K_a or K_b and the initial concentration of a weak acid or a weak base, we can calculate the pH of a solution of a weak acid or a weak base by setting up a ICE table (i.e, initial concentrations, changes in concentrations, and final concentrations). In this situation, the initial concentration of acetic acid is 0.100 M. If we define x as $[H^+]$ due to the dissociation of the acid, then the table of concentrations for the ionization of 0.100 M acetic acid is as follows:

$$CH_3CO_2H(aq) \rightleftharpoons H^+(aq) + CH_3CO_2^-$$

table of concentrations for the ionization of 0.100 M acetic acid

ICE	$[CH_3CO_2H]$	$[H^+]$	$[CH_3CO_2^-]$
initial	0.100	1.00×10^{-7}	0
change	−x	+x	+x
final	0.100 − x	x	x

In this and all subsequent examples, we will ignore $[H^+]$ and $[OH^-]$ due to the autoionization of water when calculating the final concentration. However, you should use Equation 16.45 and Equation 16.46 to check that this assumption is justified.

Inserting the expressions for the final concentrations into the equilibrium equation (and using approximations),

$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]}$$
$$= \frac{(x)(x)}{0.100 - x}$$
$$\approx \frac{x^2}{0.100}$$
$$\approx 1.74 \times 10^{-5}$$

Solving this equation gives $x = [H^+] = 1.32 \times 10^{-3}\ M$. Thus the pH of a 0.100 M solution of acetic acid is as follows:

$$pH = -\log(1.32 \times 10^{-3}) = 2.879$$



pH at the Start of a Weak Acid/Strong Base Titration: https://youtu.be/AtdBKfrfJNg

Calculating the pH during the Titration of a Weak Acid or a Weak Base

Now consider what happens when we add 5.00 mL of 0.200 M NaOH to 50.00 mL of 0.100 M CH_3CO_2H (part (a) in Figure 7.3.3). Because the neutralization reaction proceeds to completion, all of the OH^- ions added will react with the acetic acid to generate acetate ion and water:

$$CH_3CO_2H_{(aq)} + OH^-_{(aq)} \rightarrow CH_3CO^-_{2\ (aq)} + H_2O_{(l)} \tag{7.3.2}$$

All problems of this type must be solved in two steps: a stoichiometric calculation followed by an equilibrium calculation. In the first step, we use the stoichiometry of the neutralization reaction to calculate the amounts of acid and conjugate base present in solution after the neutralization reaction has occurred. In the second step, we use the equilibrium equation to determine $[H^+]$ of the resulting solution.

Step 1

To determine the amount of acid and conjugate base in solution after the neutralization reaction, we calculate the amount of CH_3CO_2H in the original solution and the amount of OH^- in the NaOH solution that was added. The acetic acid solution contained

$$50.00\ \cancel{mL}(0.100\ mmol(CH_3CO_2H)/\ \cancel{mL}) = 5.00\ mmol(CH_3CO_2H)$$

The NaOH solution contained

5.00 mL=1.00 mmol $NaOH$

Comparing the amounts shows that CH_3CO_2H is in excess. Because OH^- reacts with CH_3CO_2H in a 1:1 stoichiometry, the amount of excess CH_3CO_2H is as follows:

5.00 mmol CH_3CO_2H − 1.00 mmol OH^- = 4.00 mmol CH_3CO_2H

Each 1 mmol of OH^- reacts to produce 1 mmol of acetate ion, so the final amount of $CH_3CO_2^-$ is 1.00 mmol.

The stoichiometry of the reaction is summarized in the following ICE table, which shows the numbers of moles of the various species, not their concentrations.

$$\mathrm{CH_3CO_2H(aq) + OH^-(aq) \rightleftharpoons CH_3CO_2^-(aq) + H_2O(l)}$$

ICE table

ICE	$[\mathrm{CH_3CO_2H}]$	$[\mathrm{OH^-}]$	$[\mathrm{CH_3CO_2^-}]$
initial	5.00 mmol	1.00 mmol	0 mmol
change	−1.00 mmol	−1.00 mmol	+1.00 mmol
final	4.00 mmol	0 mmol	1.00 mmol

This ICE table gives the initial amount of acetate and the final amount of OH^- ions as 0. Because an aqueous solution of acetic acid always contains at least a small amount of acetate ion in equilibrium with acetic acid, however, the initial acetate concentration is not actually 0. The value can be ignored in this calculation because the amount of $CH_3CO_2^-$ in equilibrium is insignificant compared to the amount of OH^- added. Moreover, due to the autoionization of water, no aqueous solution can contain 0 mmol of OH^-, but the amount of OH^- due to the autoionization of water is insignificant compared to the amount of OH^- added. We use the initial amounts of the reactants to determine the stoichiometry of the reaction and defer a consideration of the equilibrium until the second half of the problem.

Step 2

To calculate $[\mathrm{H^+}]$ at equilibrium following the addition of $NaOH$, we must first calculate $[\mathrm{CH_3CO_2H}]$ and $[\mathrm{CH_3CO_2^-}]$ using the number of millimoles of each and the total volume of the solution at this point in the titration:

$$final\ volume = 50.00\ mL + 5.00\ mL = 55.00\ mL$$

$$[CH_3CO_2H] = \frac{4.00\ mmol\ CH_3CO_2H}{55.00\ mL} = 7.27 \times 10^{-2}\ M$$

$$\left[CH_3CO_2^-\right] = \frac{1.00\ mmol\ CH_3CO_2^-}{55.00\ mL} = 1.82 \times 10^{-2}\ M$$

Knowing the concentrations of acetic acid and acetate ion at equilibrium and K_a for acetic acid (1.74×10^{-5}), we can calculate $[H^+]$ at equilibrium:

$$K_a = \frac{\left[CH_3CO_2^-\right][H^+]}{[CH_3CO_2H]}$$

$$\left[H^+\right] = \frac{K_a\,[CH_3CO_2H]}{\left[CH_3CO_2^-\right]} = \frac{\left(1.72 \times 10^{-5}\right)\left(7.27 \times 10^{-2}\ M\right)}{\left(1.82 \times 10^{-2}\right)} = 6.95 \times 10^{-5}\ M$$

Calculating $-\log[\mathrm{H^+}]$ gives

$$pH = -\log(6.95 \times 10^{-5}) = 4.158.$$

Comparing the titration curves for HCl and acetic acid in Figure 7.3.3*a*, we see that adding the same amount (5.00 mL) of 0.200 M NaOH to 50 mL of a 0.100 M solution of both acids causes a much smaller pH change for HCl (from 1.00 to 1.14) than for acetic acid (2.88 to 4.16). This is consistent with the qualitative description of the shapes of the titration curves at the beginning of this section. In Example 7.3.2, we calculate another point for constructing the titration curve of acetic acid.



pH Before the Equivalence Point of a Weak Acid/Strong Base Titration:

https://youtu.be/znpwGCsefXc

Example 7.3.2

What is the pH of the solution after 25.00 mL of 0.200 M NaOH is added to 50.00 mL of 0.100 M acetic acid?

Given: volume and molarity of base and acid

Asked for: pH

Strategy:

A. Write the balanced chemical equation for the reaction. Then calculate the initial numbers of millimoles of OH^- and CH_3CO_2H. Determine which species, if either, is present in excess.

B. Tabulate the results showing initial numbers, changes, and final numbers of millimoles.

C. If excess acetate is present after the reaction with OH^-, write the equation for the reaction of acetate with water. Use a tabular format to obtain the concentrations of all the species present.

D. Calculate K_b using the relationship $K_w = K_a K_b$. Calculate [OH−] and use this to calculate the pH of the solution.

Solution

A Ignoring the spectator ion (Na^+), the equation for this reaction is as follows:

$$CH_3CO_2H_{(aq)} + OH^-(aq) \rightarrow CH_3CO_2^-(aq) + H_2O(l)$$

The initial numbers of millimoles of OH^- and CH_3CO_2H are as follows:

$$25.00 \text{ mL}(0.200 \text{ mmol OH}-\text{mL}=5.00 \text{ mmol } OH-$$

$$50.00\ mL(0.100 CH_3CO_2HL = 5.00 mmol\ CH_3CO_2H$$

The number of millimoles of OH^- equals the number of millimoles of CH_3CO_2H, so neither species is present in excess.

B Because the number of millimoles of OH^- added corresponds to the number of millimoles of acetic acid in solution, this is the equivalence point. The results of the neutralization reaction can be summarized in tabular form.

$$CH_3CO_2H_{(aq)} + OH^-_{(aq)} \rightleftharpoons CH_3CO_2^-(aq) + H_2O(l)$$

results of the neutralization reaction

ICE	$[CH_3CO_2H]$	$[OH^-]$	$[CH_3CO_2^-]$
initial	5.00 mmol	5.00 mmol	0 mmol
change	−5.00 mmol	−5.00 mmol	+5.00 mmol
final	0 mmol	0 mmol	5.00 mmol

C Because the product of the neutralization reaction is a weak base, we must consider the reaction of the weak base with water to calculate [H+] at equilibrium and thus the final pH of the solution. The initial concentration of acetate is obtained from the neutralization reaction:

$$[\mathrm{CH_3CO_2}] = \frac{5.00\ mmol\ CH_3CO_2^-}{(50.00+25.00)\ mL} = 6.67\times10^{-2}\ M$$

The equilibrium reaction of acetate with water is as follows:

$$\mathrm{CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)}$$

The equilibrium constant for this reaction is

$$K_b = \frac{K_w}{K_a} \tag{7.3.3}$$

where K_a is the acid ionization constant of acetic acid. We therefore define x as $[\mathrm{OH^-}]$ produced by the reaction of acetate with water. Here is the completed table of concentrations:

$$H_2O_{(l)} + CH_3CO_{2(aq)}^- \rightleftharpoons CH_3CO_2H_{(aq)} + OH_{(aq)}^-$$

completed table of concentrations

	$[\mathrm{CH_3CO_2^-}]$	$[\mathrm{CH_3CO_2H}]$	$[\mathrm{OH^-}]$
initial	0.0667	0	1.00 × 10−7
change	−x	+x	+x
final	(0.0667 − x)	x	x

D We can obtain K_b by substituting the known values into Equation 7.3.3:

$$K_b = \frac{K_w}{K_a} = \frac{1.01\times10^{-14}}{1.74\times10^{-5}} = 5.80\times10^{-10} \tag{7.3.4}$$

Substituting the expressions for the final values from the ICE table into Equation 7.3.4 and solving for x:

$$\frac{x^2}{0.0667} = 5.80\times10^{-10}$$

$$x = \sqrt{(5.80\times10^{-10})(0.0667)}$$

$$= 6.22\times10^{-6}$$

Thus $[OH^-] = 6.22\times10^{-6}\ M$ and the pH of the final solution is 8.794 (Figure 7.3.3*a*). As expected for the titration of a weak acid, the pH at the equivalence point is greater than 7.00 because the product of the titration is a base, the acetate ion, which then reacts with water to produce $\mathrm{OH^-}$.

? Exercise 7.3.2

Calculate the pH of a solution prepared by adding 45.0 mL of a 0.213 M HCl solution to 125.0 mL of a 0.150 M solution of ammonia. The pK_b of ammonia is 4.75 at 25°C.

Answer

9.23

As shown in part (b) in Figure 7.3.3, the titration curve for NH3, a weak base, is the reverse of the titration curve for acetic acid. In particular, the pH at the equivalence point in the titration of a weak base is less than 7.00 because the titration produces an acid.

The identity of the weak acid or weak base being titrated strongly affects the shape of the titration curve. Figure 7.3.4 illustrates the shape of titration curves as a function of the pK_a or the pK_b. As the acid or the base being titrated becomes weaker (its pK_a or pK_b becomes larger), the pH change around the equivalence point decreases significantly. With very dilute solutions, the curve becomes so shallow that it can no longer be used to determine the equivalence point.

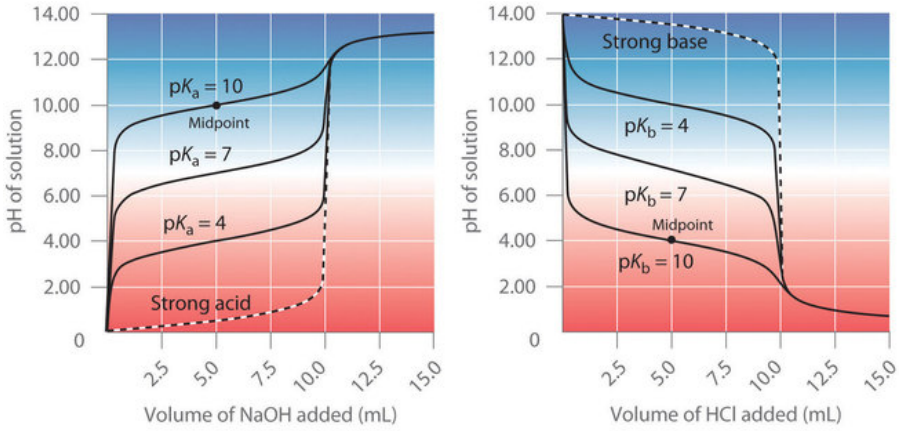


Figure 7.3.4: Effect of Acid or Base Strength on the Shape of Titration Curves. Unlike strong acids or bases, the shape of the titration curve for a weak acid or base depends on the pK_a or pK_b of the weak acid or base being titrated. (a) Solution pH as a function of the volume of 1.00 M NaOH added to 10.00 mL of 1.00 M solutions of weak acids with the indicated pK_a values. (b) Solution pH as a function of the volume of 1.00 M HCl added to 10.00 mL of 1.00 M solutions of weak bases with the indicated pK_b values. The shapes of the two sets of curves are essentially identical, but one is flipped vertically in relation to the other. Midpoints are indicated for the titration curves corresponding to pK_a = 10 and pK_b = 10. (CC BY-SA-NC; Anonymous by request)

The titration curves of weak acids with strong base and weak bases titrated with strong acid are inverses of each other. Three weak acids and three weak bases with pKa and pKb of 4, 7, and 10 are used.

One point in the titration of a weak acid or a weak base is particularly important: the midpoint of a titration is defined as the point at which exactly enough acid (or base) has been added to neutralize one-half of the acid (or the base) originally present and occurs halfway to the equivalence point. The midpoint is indicated in Figures 7.3.4*a* and 7.3.4*b* for the two shallowest curves. By definition, at the midpoint of the titration of an acid, [HA] = [A−]. Recall that the ionization constant for a weak acid is as follows:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

If $[HA] = [A^-]$, this reduces to $K_a = [H_3O^+]$. Taking the negative logarithm of both sides,

$$-\log K_a = -\log[H_3O+]$$

From the definitions of pK_a and pH, we see that this is identical to

$$pK_a = pH \tag{7.3.5}$$

Thus the pH at the midpoint of the titration of a weak acid is equal to the pK_a of the weak acid, as indicated in part (a) in Figure 7.3.4 for the weakest acid where we see that the midpoint for pK_a = 10 occurs at pH = 10. Titration methods can therefore be used to determine both the concentration and the pK_a (or the pK_b) of a weak acid (or a weak base).

> The pH at the midpoint of the titration of a weak acid is equal to the pK_a of the weak acid.

Titrations of Polyprotic Acids or Bases

When a strong base is added to a solution of a polyprotic acid, the neutralization reaction occurs in stages. The most acidic group is titrated first, followed by the next most acidic, and so forth. If the pK_a values are separated by at least three pK_a units, then the overall titration curve shows well-resolved “steps” corresponding to the titration of each proton. A titration of the triprotic acid H_3PO_4 with NaOH is illustrated in Figure 7.3.5 and shows two well-defined steps: the first midpoint corresponds to pK_a1, and the second midpoint corresponds to pK_{a2}. Because HPO_4^{2-} is such a weak acid, pK_{a3} has such a high value that the third step cannot be resolved using 0.100 M NaOH as the titrant.

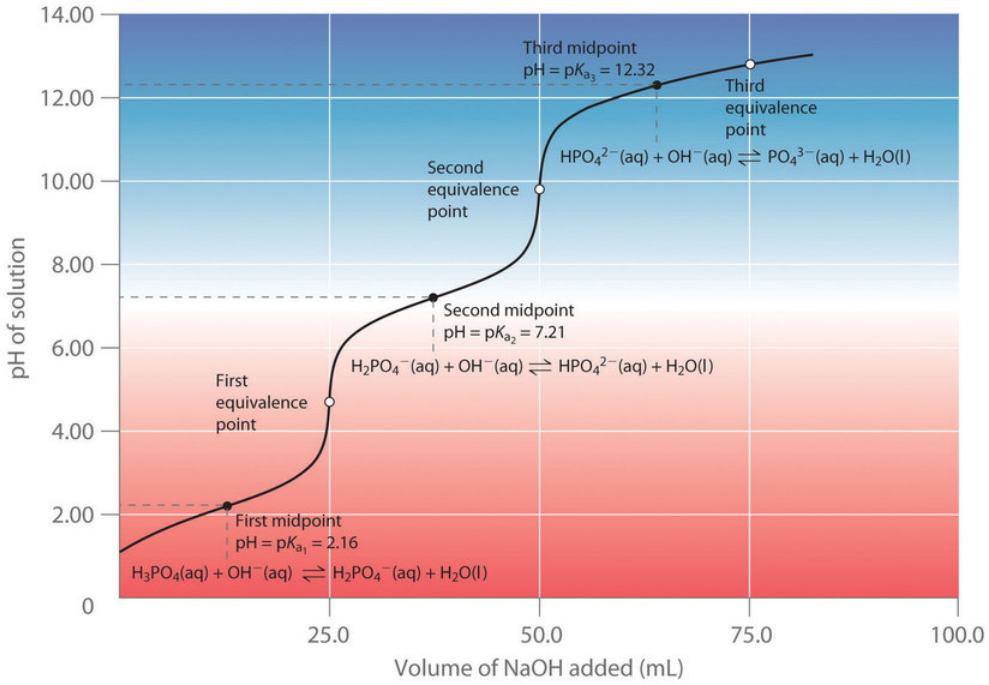
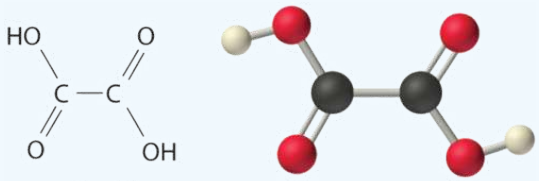


Figure 7.3.5: Titration Curve for Phosphoric Acid (H_3PO_4, a Typical Polyprotic Acid. The curve for the titration of 25.0 mL of a 0.100 M H_3PO_4 solution with 0.100 M NaOH along with the species in solution at each Ka is shown. Note the two distinct equivalence points corresponding to deprotonation of H_3PO_4 at pH ≈ 4.6 and $H_2PO_4^{2-}$ at pH ≈ 9.8. Because HPO_4^{2-} is a very weak acid, the third equivalence point, at pH ≈ 13, is not well defined. (CC BY-SA-NC; Anonymous by request)

The titration curve for the reaction of a polyprotic base with a strong acid is the mirror image of the curve shown in Figure 7.3.5. The initial pH is high, but as acid is added, the pH decreases in steps if the successive pK_b values are well separated. Table E1 lists the ionization constants and pK_a values for some common polyprotic acids and bases.

Example 7.3.3

Calculate the pH of a solution prepared by adding 55.0 mL of a 0.120 M NaOH solution to 100.0 mL of a 0.0510 M solution of oxalic acid (HO_2CCO_2H), a diprotic acid (abbreviated as H_2ox). Oxalic acid, the simplest dicarboxylic acid, is found in rhubarb and many other plants. Rhubarb leaves are toxic because they contain the calcium salt of the fully deprotonated form of oxalic acid, the oxalate ion ($O_2CCO_2^{2-}$, abbreviated ox^{2-}).Oxalate salts are toxic for two reasons. First, oxalate salts of divalent cations such as Ca^{2+} are insoluble at neutral pH but soluble at low pH. As a result, calcium oxalate dissolves in the dilute acid of the stomach, allowing oxalate to be absorbed and transported into cells, where it can react with calcium to form tiny calcium oxalate crystals that damage tissues. Second, oxalate forms stable complexes with metal ions, which can alter the distribution of metal ions in biological fluids.



oxalic acid

Given: volume and concentration of acid and base

Asked for: pH

Strategy:

A. Calculate the initial millimoles of the acid and the base. Use a tabular format to determine the amounts of all the species in solution.

B. Calculate the concentrations of all the species in the final solution. Determine $[H+]$ and convert this value to pH.

Solution:

A Table E5 gives the pK_a values of oxalic acid as 1.25 and 3.81. Again we proceed by determining the millimoles of acid and base initially present:

$$100.00\ \cancel{mL}\left(\frac{0.510\ mmol\ H_2ox}{\cancel{mL}}\right) = 5.10\ mmol\ H_2ox$$

$$55.00\ \cancel{mL}\left(\frac{0.120\ mmol\ NaOH}{\cancel{mL}}\right) = 6.60\ mmol\ NaOH$$

The strongest acid (H_2ox) reacts with the base first. This leaves (6.60 − 5.10) = 1.50 mmol of OH^- to react with Hox−, forming ox^{2-} and H_2O. The reactions can be written as follows:

$$\underset{5.10\ mmol}{H_2ox} + \underset{6.60\ mmol}{OH^-} \rightarrow \underset{5.10\ mmol}{Hox^-} + \underset{5.10\ mmol}{H_2O}$$

$$\underset{5.10\ mmol}{Hox^-} + \underset{1.50\ mmol}{OH^-} \rightarrow \underset{1.50\ mmol}{ox^{2-}} + \underset{1.50\ mmol}{H_2O}$$

In tabular form,

Solutions to Example 17.3.3

	H_2ox	OH^-	Hox^-	ox^{2-}
initial	5.10 mmol	6.60 mmol	0 mmol	0 mmol
change (step 1)	−5.10 mmol	−5.10 mmol	+5.10 mmol	0 mmol
final (step 1)	0 mmol	1.50 mmol	5.10 mmol	0 mmol
change (step 2)	—	−1.50 mmol	−1.50 mmol	+1.50 mmol
final	0 mmol	0 mmol	3.60 mmol	1.50 mmol

B The equilibrium between the weak acid (Hox^-) and its conjugate base (ox^{2-}) in the final solution is determined by the magnitude of the second ionization constant, $K_{a2} = 10^{-3.81} = 1.6 \times 10^{-4}$. To calculate the pH of the solution, we need to know $[H^+]$, which is determined using exactly the same method as in the acetic acid titration in Example 7.3.2:

$$\text{final volume of solution} = 100.0\,mL + 55.0\,mL = 155.0\,mL$$

Thus the concentrations of Hox^- and ox^{2-} are as follows:

$$\left[Hox^-\right] = \frac{3.60\ mmol\ Hox^-}{155.0\ mL} = 2.32 \times 10^{-2}\ M$$

$$\left[ox^{2-}\right] = \frac{1.50\ mmol\ ox^{2-}}{155.0\ mL} = 9.68 \times 10^{-3}\ M$$

We can now calculate [H+] at equilibrium using the following equation:

$$K_{a2} = \frac{\left[ox^{2-}\right]\left[H^+\right]}{\left[Hox^-\right]}$$

Rearranging this equation and substituting the values for the concentrations of Hox^- and ox^{2-},

$$\left[H^+\right] = \frac{K_{a2}\left[Hox^-\right]}{\left[ox^{2-}\right]} = \frac{\left(1.6 \times 10^{-4}\right)\left(2.32 \times 10^{-2}\right)}{\left(9.68 \times 10^{-3}\right)} = 3.7 \times 10^{-4}\ M$$

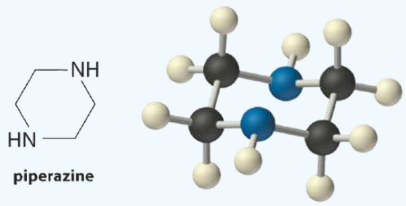
So

$$pH = -\log\left[H^+\right] = -\log\left(3.7 \times 10^{-4}\right) = 3.43$$

This answer makes chemical sense because the pH is between the first and second pK_a values of oxalic acid, as it must be. We added enough hydroxide ion to completely titrate the first, more acidic proton (which should give us a pH greater than pK_{a1}), but we added only enough to titrate less than half of the second, less acidic proton, with pK_{a2}. If we had added exactly enough hydroxide to completely titrate the first proton plus half of the second, we would be at the midpoint of the second step in the titration, and the pH would be 3.81, equal to pK_{a2}.

? Exercise 7.3.3: Piperazine

Piperazine is a diprotic base used to control intestinal parasites ("worms") in pets and humans. A dog is given 500 mg (5.80 mmol) of piperazine (pK_{b1} = 4.27, pK_{b2} = 8.67). If the dog's stomach initially contains 100 mL of 0.10 M HCl (pH = 1.00), calculate the pH of the stomach contents after ingestion of the piperazine.



Answer

pH=4.9

Indicators

In practice, most acid–base titrations are not monitored by recording the pH as a function of the amount of the strong acid or base solution used as the titrant. Instead, an acid–base indicator is often used that, if carefully selected, undergoes a dramatic color change at the pH corresponding to the equivalence point of the titration. Indicators are weak acids or bases that exhibit intense colors that vary with pH. The conjugate acid and conjugate base of a good indicator have very different colors so that they can be distinguished easily. Some indicators are colorless in the conjugate acid form but intensely colored when deprotonated (phenolphthalein, for example), which makes them particularly useful.

We can describe the chemistry of indicators by the following general equation:

$$\mathrm{HIn(aq)} \rightleftharpoons \mathrm{H^+(aq) + In^-(aq)}$$

where the protonated form is designated by HIn and the conjugate base by $\mathrm{In^-}$. The ionization constant for the deprotonation of indicator HIn is as follows:

$$K_{In} = \frac{[\mathrm{H^+}][\mathrm{In^-}]}{[\mathrm{HIn}]} \tag{7.3.6}$$

The pK_{in} (its pK_a) determines the pH at which the indicator changes color.

Many different substances can be used as indicators, depending on the particular reaction to be monitored. For example, red cabbage juice contains a mixture of colored substances that change from deep red at low pH to light blue at intermediate pH to yellow at high pH. Similarly, *Hydrangea macrophylla* flowers can be blue, red, pink, light purple, or dark purple depending on the soil pH (Figure 7.3.6). Acidic soils will produce blue flowers, whereas alkaline soils will produce pinkish flowers.

Irrespective of the origins, a good indicator must have the following properties:

- The color change must be easily detected.
- The color change must be rapid.
- The indicator molecule must not react with the substance being titrated.
- To minimize errors, the indicator should have a pK_{in} that is within one pH unit of the expected pH at the equivalence point of the titration.



Figure 7.3.6: Naturally occurring pH indicators can be found in red cabbage and Hydrangea macrophylla flowers. Red Cabbage image (CC BY-SA 3.0; KENPEI via Wikipedia) and Hydrangea macrophylla flowers (pixabay).

Synthetic indicators have been developed that meet these criteria and cover virtually the entire pH range. Figure 7.3.7 shows the approximate pH range over which some common indicators change color and their change in color. In addition, some indicators (such as thymol blue) are polyprotic acids or bases, which change color twice at widely separated pH values.

Indicator	pK_{in}	Color change
Alizarin yellow R	11.0	yellow to red
Thymolphthalein	9.9	colorless to blue
Phenolphthalein	9.5	colorless to pink
Thymol blue	9.2	yellow to blue
Phenol red	7.4	yellow to red
Bromothymol blue	7.3	yellow to blue
Bromocresol purple	6.4	yellow to purple
Ethyl red	5.4	colorless to red
Resorcin blue	5.3	red to blue
Resazurin	5.1	orange to violet
Methyl red	5.0	red to yellow
Bromophenol blue	4.1	yellow to blue
Thymol blue	1.7	red to yellow
Malachite green	1.3	yellow to turquoise
Methyl violet	0.8	yellow to blue

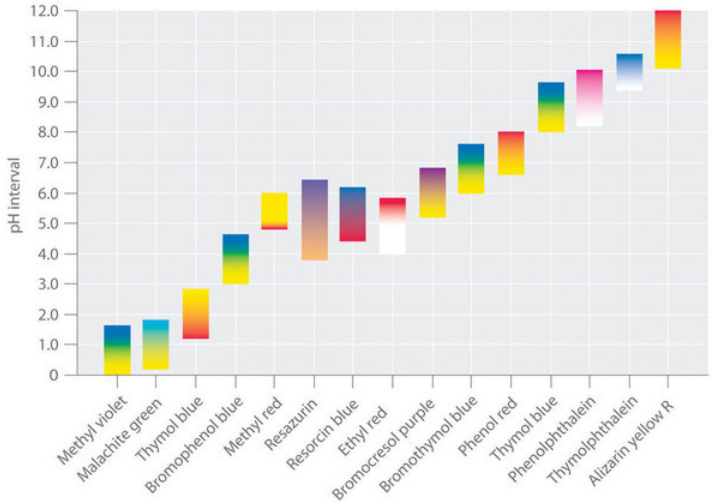


Figure 7.3.7: Some Common Acid–Base Indicators. Approximate colors are shown, along with pK_{in} values and the pH range over which the color changes. (CC BY-SA-NC; Anonymous by request)

It is important to be aware that an indicator does not change color abruptly at a particular pH value; instead, it actually undergoes a pH titration just like any other acid or base. As the concentration of HIn decreases and the concentration of In− increases, the color of the solution slowly changes from the characteristic color of HIn to that of In−. As we will see later, the [In−]/[HIn] ratio changes from 0.1 at a pH one unit below pKin to 10 at a pH one unit above pKin. Thus most indicators change color over a pH range of about two pH units.

We have stated that a good indicator should have a pKin value that is close to the expected pH at the equivalence point. For a strong acid–strong base titration, the choice of the indicator is not especially critical due to the very large change in pH that occurs around the equivalence point. In contrast, using the wrong indicator for a titration of a weak acid or a weak base can result in relatively large errors, as illustrated in Figure 7.3.8. This figure shows plots of pH versus volume of base added for the titration of 50.0 mL of a 0.100 M solution of a strong acid (HCl) and a weak acid (acetic acid) with 0.100 M $NaOH$. The pH ranges over which two common indicators (methyl red, $pK_{in} = 5.0$, and phenolphthalein, $pK_{in} = 9.5$) change color are also shown. The horizontal bars indicate the pH ranges over which both indicators change color cross the HCl titration curve, where it is almost vertical. Hence both indicators change color when essentially the same volume of NaOH has been added (about 50 mL), which corresponds to the equivalence point. In contrast, the titration of acetic acid will give very different results depending on whether methyl red or phenolphthalein is used as the indicator. Although the pH range over which phenolphthalein changes color is slightly greater than the pH at the equivalence point of the strong acid titration, the error will be negligible due to the slope of this portion of the titration curve. Just as with the HCl titration, the phenolphthalein indicator will turn pink when about 50 mL of NaOH has been added to the acetic acid solution. In contrast, methyl red begins to change from red to yellow around pH 5, which is near the

midpoint of the acetic acid titration, not the equivalence point. Adding only about 25–30 mL of NaOH will therefore cause the methyl red indicator to change color, resulting in a huge error.

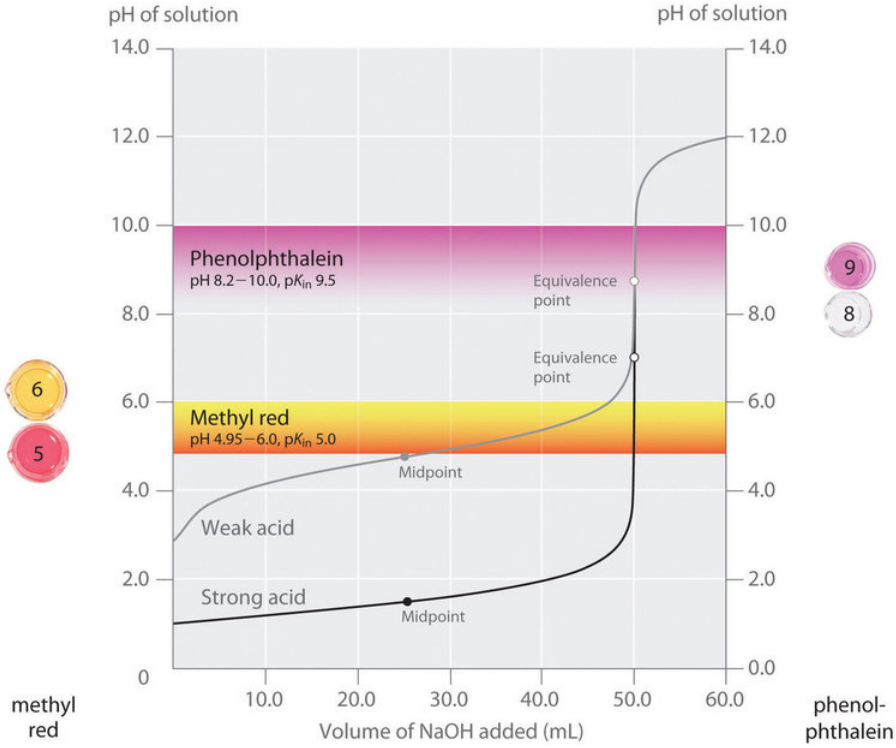


Figure 7.3.8: Choosing the Correct Indicator for an Acid–Base Titration. (CC BY-SA-NC; Anonymous by request)

If the pH of the solution is between 4.95 and 6 then methyl red should be used. If the pH is between 8,2 and 10 then phenolphthalein should be used.

The graph shows the results obtained using two indicators (methyl red and phenolphthalein) for the titration of 0.100 M solutions of a strong acid (HCl) and a weak acid (acetic acid) with 0.100 M $NaOH$. Due to the steepness of the titration curve of a strong acid around the equivalence point, either indicator will rapidly change color at the equivalence point for the titration of the strong acid. In contrast, the pKin for methyl red (5.0) is very close to the pK_a of acetic acid (4.76); the midpoint of the color change for methyl red occurs near the midpoint of the titration, rather than at the equivalence point.

In general, for titrations of strong acids with strong bases (and vice versa), any indicator with a pKin between about 4.0 and 10.0 will do. For the titration of a weak acid, however, the pH at the equivalence point is greater than 7.0, so an indicator such as phenolphthalein or thymol blue, with pKin > 7.0, should be used. Conversely, for the titration of a weak base, where the pH at the equivalence point is less than 7.0, an indicator such as methyl red or bromocresol blue, with pKin < 7.0, should be used.

The existence of many different indicators with different colors and pKin values also provides a convenient way to estimate the pH of a solution without using an expensive electronic pH meter and a fragile pH electrode. Paper or plastic strips impregnated with combinations of indicators are used as “pH paper,” which allows you to estimate the pH of a solution by simply dipping a piece of pH paper into it and comparing the resulting color with the standards printed on the container (Figure 7.3.9).

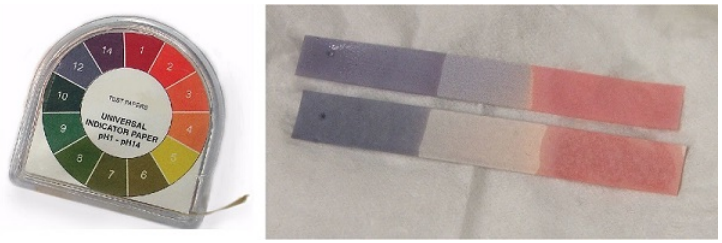


Figure 7.3.9: pH Paper. pH paper contains a set of indicators that change color at different pH values. The approximate pH of a solution can be determined by simply dipping a paper strip into the solution and comparing the color to the standards provided. (CC BY-SA-NC; Anonymous by request)



pH Indicators: pH Indicators(opens in new window) [youtu.be]

Summary and Takeaway

Plots of acid–base titrations generate titration curves that can be used to calculate the pH, the pOH, the pK_a, and the pK_b of the system. The shape of a titration curve, a plot of pH versus the amount of acid or base added, provides important information about what is occurring in solution during a titration. The shapes of titration curves for weak acids and bases depend dramatically on the identity of the compound. The equivalence point of an acid–base titration is the point at which exactly enough acid or base has been added to react completely with the other component. The equivalence point in the titration of a strong acid or a strong base occurs at pH 7.0. In titrations of weak acids or weak bases, however, the pH at the equivalence point is greater or less than 7.0, respectively. The pH tends to change more slowly before the equivalence point is reached in titrations of weak acids and weak bases than in titrations of strong acids and strong bases. The pH at the midpoint, the point halfway on the titration curve to the equivalence point, is equal to the pK_a of the weak acid or the pK_b of the weak base. Thus titration methods can be used to determine both the concentration and the pK_a (or the pK_b) of a weak acid (or a weak base). Acid–base indicators are compounds that change color at a particular pH. They are typically weak acids or bases whose changes in color correspond to deprotonation or protonation of the indicator itself.

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7.4: Solving Titration Problems

Skills to Develop

- Calculate the pH at any point in an acid–base titration.

In this section, we will see how to perform calculations to predict the pH at any point in a titration of a weak acid or base, using the techniques we already know for acid-base equilibria and buffers.

Consider Figure 7.4.1 from the previous section, showing the curves for the titrations of a weak acid or weak base. The pH at different points in each curve is determined by what species are present in the mixture at that point. Thus, we must use different techniques to solve for the pH depending on how far along the titration is. There are three scenarios we will consider, using the titration of 50.0 mL of 0.100 M acetic acid with 0.200 M NaOH (Figure 7.4.1*a*) as an example:

- The pH at the beginning of the titration, before any titrant is added
- The pH in the buffer region, before reaching the equivalence point
- The pH at the equivalence point

In the following examples, we will use a pK_a of 4.76 for acetic acid at 25°C ($K_a = 1.7 \times 10^{-5}$).

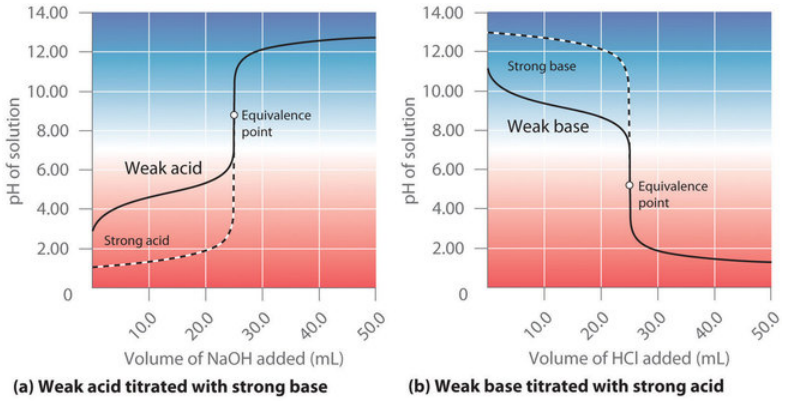


Figure 7.4.3: The Titration of (a) a Weak Acid with a Strong Base and (b) a Weak Base with a Strong Acid. (a) As 0.200 M $NaOH$ is slowly added to 50.0 mL of 0.100 M acetic acid, the pH increases slowly at first, then increases rapidly as the equivalence point is approached, and then again increases more slowly. The corresponding curve for the titration of 50.0 mL of 0.100 M HCl with 0.200 M $NaOH$ is shown as a dashed line. (b) As 0.200 M HCl is slowly added to 50.0 mL of 0.100 M NH_3, the pH decreases slowly at first, then decreases rapidly as the equivalence point is approached, and then again decreases more slowly. The corresponding curve for the titration of 50.0 mL of 0.100 M $NaOH$ with 0.200 M HCl is shown as a dashed line.

Calculating the pH of a Solution of a Weak Acid or a Weak Base

At the beginning of a titration, we simply have a solution of a weak acid or base of a certain concentration. As discussed in the previous chapter, if we know K_a or K_b and the initial concentration of a weak acid or a weak base, we can calculate the pH by setting up an ICE table (i.e, initial concentrations, changes in concentrations, and equilibrium concentrations). In this situation, the initial concentration of acetic acid is 0.100 M. If we define x as $[H^+]$ due to the dissociation of the acid, then the table of concentrations for the ionization of 0.100 M acetic acid is as follows:

$$CH_3CO_2H_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3CO_2^- \tag{7.4.1}$$

ICE	$[CH_3CO_2H]$	$[H^+]$	$[CH_3CO_2^-]$
initial	0.100	1.00×10^{-7}	0
change	−x	+x	+x
equilibrium	0.100 − x	x	x

In this and all subsequent examples, we will ignore $[H^+]$ and $[OH^-]$ due to the autoionization of water when calculating the final concentration. (However, you should check that this assumption is justified!)

Inserting the expressions for the final concentrations into the equilibrium equation (and using approximations),

$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]} = \frac{(x)(x)}{0.100 - x} \approx \frac{x^2}{0.100} = 1.74 \times 10^{-5} \tag{7.4.2}$$

Solving this equation gives $x = [H^+] = 1.32 \times 10^{-3}\ M$. Thus the pH of a 0.100 M solution of acetic acid is as follows:

$$pH = -\log(1.32 \times 10^{-3}) = 2.879 \tag{7.4.3}$$

Calculating the pH during the Titration of a Weak Acid or a Weak Base

Now consider what happens when we begin to add $NaOH$ to the CH_3CO_2H (Figure 7.4.1*a*). Because the neutralization reaction with strong base proceeds to completion, all of the OH^- ions added will react with the acetic acid to generate acetate ion and water:

$$CH_3CO_2H_{(aq)} + OH^-_{(aq)} \rightarrow CH_3CO^-_{2\ (aq)} + H_2O_{(l)} \tag{7.4.4}$$

All problems of this type must be solved in two steps: a stoichiometric calculation followed by an equilibrium calculation. In the first step, we use the stoichiometry of the neutralization reaction to calculate the amounts of acid and conjugate base present in solution after the neutralization reaction has occurred. In the second step, we use the equilibrium equation to determine $[\mathrm{H^+}]$ of the resulting solution.

Example 7.4.1: Calculating pH in the Buffer Region

What is the pH when 5.00 mL of 0.200 M $NaOH$ has been added to 50.00 mL of 0.100 M CH_3CO_2H (part (a) in Figure 7.4.1)?

Strategy

Step 1: Use stoichiometry of the neutralization to determine the amounts of acid and conjugate base present in solution

Step 2: Solve for equilibrium concentrations using ICE tables or Henderson-Hasselbalch approximation

Solution

Step 1

To determine the amount of acid and conjugate base in solution after the neutralization reaction, we calculate the amount of $\mathrm{CH_3CO_2H}$ in the original solution and the amount of $\mathrm{OH^-}$ in the NaOH solution that was added. The acetic acid solution contained

$$50.00\ \cancel{mL}(0.100\ mmol(\mathrm{CH_3CO_2H})/\ \cancel{mL}) = 5.00\ mmol(\mathrm{CH_3CO_2H}) \tag{7.4.5}$$

The NaOH solution contained

5.00 mL=1.00 mmol $NaOH$

Comparing the amounts shows that CH_3CO_2H is in excess. Because OH^- reacts with CH_3CO_2H in a 1:1 stoichiometry, the amount of excess CH_3CO_2H is as follows:

5.00 mmol CH_3CO_2H − 1.00 mmol OH^- = 4.00 mmol CH_3CO_2H

Each 1 mmol of OH^- reacts to produce 1 mmol of acetate ion, so the final amount of $CH_3CO_2^-$ is 1.00 mmol.

The stoichiometry of the reaction is summarized in the following table, which shows the numbers of moles of the various species, not their concentrations.

$$\mathrm{CH_3CO_2H(aq) + OH^-(aq) \rightleftharpoons CH_3CO_2^-(aq) + H_2O(l)} \tag{7.4.6}$$

ICE	$[\mathrm{CH_3CO_2H}]$	$[\mathrm{OH^-}]$	$[\mathrm{CH_3CO_2^-}]$
initial	5.00 mmol	1.00 mmol	0 mmol
change	−1.00 mmol	−1.00 mmol	+1.00 mmol
final	4.00 mmol	0 mmol	1.00 mmol

This ICE table gives the initial amount of acetate and the final amount of OH^- ions as 0. Because an aqueous solution of acetic acid always contains at least a small amount of acetate ion in equilibrium with acetic acid, the initial acetate concentration is not actually 0. The value can be ignored in this calculation, however, because the amount of $CH_3CO_2^-$ in equilibrium is insignificant compared to the amount of OH^- added. Moreover, due to the autoionization of water, no aqueous solution can contain 0 mmol of OH^-, but the amount of OH^- due to the autoionization of water is insignificant compared to the amount of OH^- added. We use the initial amounts of the reactants to determine the stoichiometry of the reaction and defer a consideration of the equilibrium until the second half of the problem.

Step 2

Now that we have determined that there is a mixture of $\mathrm{CH_3CO_2H}$ and $\mathrm{CH_3CO_2^-}$ present in solution, we know that this point in the titration is in the buffer region. Therefore, we can use the equilibrium method or the Henderson-Hasselbalch equation.

To calculate $[\mathrm{H^+}]$ using the acid ionization equilibrium, we must first calculate $[\mathrm{CH_3CO_2H}]$ and $[\mathrm{CH_3CO_2^-}]$ using the number of millimoles of each and the total volume of the solution at this point in the titration:

$$final\ volume = 50.00\ mL + 5.00\ mL = 55.00\ mL \tag{7.4.7}$$

$$[CH_3CO_2H] = \frac{4.00\ mmol\ CH_3CO_2H}{55.00\ mL} = 7.27 \times 10^{-2}\ M \tag{7.4.8}$$

$$\left[CH_3CO_2^-\right] = \frac{1.00\ mmol\ CH_3CO_2^-}{55.00\ mL} = 1.82 \times 10^{-2}\ M \tag{7.4.9}$$

Knowing the concentrations of acetic acid and acetate ion at equilibrium and K_a for acetic acid (1.74×10^{-5}), we can calculate $[H^+]$ at equilibrium:

$$K_a = \frac{\left[CH_3CO_2^-\right][H^+]}{[CH_3CO_2H]} \tag{7.4.10}$$

$$\left[H^+\right] = \frac{K_a\,[CH_3CO_2H]}{\left[CH_3CO_2^-\right]} = \frac{\left(1.72 \times 10^{-5}\right)\left(7.27 \times 10^{-2}\ M\right)}{\left(1.82 \times 10^{-2}\right)} = 6.95 \times 10^{-5}\ M \tag{7.4.11}$$

Calculating $-\log[\mathrm{H^+}]$ gives

$$pH = -\log(6.95 \times 10^{-5}) = 4.158. \tag{7.4.12}$$

Alternatively, since the concentrations of each component are large compared to K_a, we can use the Henderson-Hasselbalch approximation, treating the system as a buffer:

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \tag{7.4.13}$$

$$pH = 4.76 + \log\left(\frac{1.00mmol}{4.00mmol} = 4.76 + (-0.602) = 4.158\right) \tag{7.4.14}$$

This approach is mathematically equivalent to the first, but note that it is not necessary to convert millimoles into molar concentration to use the Henderson-Hasselbalch equation, which makes this method a little simpler.

Exercise 7.4.1

Calculate the pH of a solution prepared by adding 45.0 mL of a 0.213 M HCl solution to 125.0 mL of a 0.150 M solution of ammonia. The pK_b of ammonia is 4.75 at 25°C.

Answer

9.23 (Note that since the ammonia is approximately half-neutralized at this point, this pH is very close to the pK_a of ammonium, 9.25!)

Any pH point in a titration before the weak acid is fully neutralized can be solved by the above method. At the equivalence point, however, there is no longer a significant amount of the starting acid remaining, and the sample no longer constitutes a buffer.

Rather, the sample consists predominantly of the weak acid's conjugate base. The pH is determined by this base's concentration and pK_b, and can be solved for using a base dissociation equilibrium. In Example 7.4.2, we calculate the pH at the equivalence point of our titration curve of acetic acid.

Example 7.4.2: Calculating pH at the Equivalence Point

What is the pH of the solution after 25.00 mL of 0.200 M $NaOH$ is added to 50.00 mL of 0.100 M acetic acid?

Given: volume and molarity of base and acid

Asked for: pH

Strategy:

A. Write the balanced chemical equation for the reaction. Then calculate the initial numbers of millimoles of OH^- and CH_3CO_2H. Determine which species, if either, is present in excess.
B. Tabulate the results showing initial numbers, changes, and final numbers of millimoles.
C. If excess acetate is present after the reaction with $OH-$, write the equation for the reaction of acetate with water. Use a tabular format to obtain the concentrations of all the species present.
D. Calculate K_b using the relationship $K_w = K_aK_b$. Calculate [OH−] and use this to calculate the pH of the solution.

SOLUTION

A Ignoring the spectator ion (Na^+), the equation for this reaction is as follows:

$$CH_3CO_2H_{(aq)} + OH^-(aq) \rightarrow CH_3CO_2^-(aq) + H_2O(l) \tag{7.4.15}$$

The initial numbers of millimoles of OH^- and CH_3CO_2H are as follows:

$$25.00 \text{ mL}(0.200 \text{ mmol } OH-/\text{mL}) = 5.00 \text{ mmol } OH-$$

$$50.00\ mL(0.100 mmol CH_3CO_2H/mL) = 5.00 mmol\ CH_3CO_2H \tag{7.4.16}$$

The number of millimoles of OH^- equals the number of millimoles of CH_3CO_2H, so neither species is present in excess.

B Because the number of millimoles of OH^- added corresponds to the number of millimoles of acetic acid in solution, this is the equivalence point. The results of the neutralization reaction can be summarized in tabular form.

$$CH_3CO_2H_{(aq)} + OH^-_{(aq)} \rightleftharpoons CH_3CO_2^-(aq) + H_2O(l) \tag{7.4.17}$$

ICE	$[CH_3CO_2H]$	$[OH^-]$	$[CH_3CO_2^-]$
initial	5.00 mmol	5.00 mmol	0 mmol
change	−5.00 mmol	−5.00 mmol	+5.00 mmol
final	0 mmol	0 mmol	5.00 mmol

C Because the product of the neutralization reaction is a weak base, we must consider the reaction of the weak base with water to calculate [H+] at equilibrium and thus the final pH of the solution. The initial concentration of acetate is obtained from the neutralization reaction:

$$[\mathrm{CH_3CO_2}] = \frac{5.00\ mmol\ CH_3CO_2^-}{(50.00 + 25.00)\ mL} = 6.67 \times 10^{-2}\ M \tag{7.4.18}$$

The equilibrium reaction of acetate with water is as follows:

$$\mathrm{CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)} \tag{7.4.19}$$

The equilibrium constant for this reaction is

$$K_b = \frac{K_w}{K_a} \tag{7.4.20}$$

where K_a is the acid ionization constant of acetic acid. We therefore define x as $[OH^-]$ produced by the reaction of acetate with water. Here is the completed table of concentrations:

$$H_2O_{(l)} + CH_3CO_{2(aq)}^- \rightleftharpoons CH_3CO_2H_{(aq)} + OH_{(aq)}^- \tag{7.4.21}$$

	$[CH_3CO_2^-]$	$[CH_3CO_2H]$	$[OH^-]$
initial	0.0667	0	1.00 × 10−7
change	−x	+x	+x
equilibrium	(0.0667 − x)	x	x

D Substituting the expressions for the final values from this table into Equation 7.4.20,

$$K_b = \frac{K_w}{K_a} = \frac{1.01 \times 10^{-14}}{1.74 \times 10^{-5}} = 5.80 \times 10^{-10} = \frac{x^2}{0.0667} \tag{7.4.22}$$

We can obtain K_b by rearranging Equation 7.4.22 and substituting the known values:

$$K_b = K_w K_a = (1.01 \times 10^{-14})(1.74 \times 10^{-5}) = 5.80 \times 10^{-10} = x20.0667 \tag{7.4.23}$$

which we can solve to get $x = 6.22 \times 10^{-6}$. Thus $[OH^-] = 6.22 \times 10^{-6}\ M$, and the pH of the final solution is 8.794 (Figure $7.4.3a$). As expected for the titration of a weak acid, the pH at the equivalence point is greater than 7.00 because the product of the titration is a base, the acetate ion, which then reacts with water to produce OH^-.

Exercise 7.4.2

Calculate the pH of a solution prepared by adding 88.0 mL of a 0.213 M HCl solution to 125.0 mL of a 0.150 M solution of ammonia. The pK_b of ammonia is 4.75 at 25°C.

Answer

5.14

Titrations of Polyprotic Acids or Bases

When a strong base is added to a solution of a polyprotic acid, the neutralization reaction occurs in stages. The most acidic group is titrated first, followed by the next most acidic, and so forth. If the pK_a values are separated by at least three pK_a units, then the overall titration curve shows well-resolved “steps” corresponding to the titration of each proton. A titration of the triprotic acid H_3PO_4 with $NaOH$ is illustrated in Figure 7.4.2 and shows two well-defined steps: the first midpoint corresponds to pK_a1, and the second midpoint corresponds to pK_{a2}. Because HPO_4^{2-} is such a weak acid, pK_{a3} has such a high value that the third step cannot be resolved using 0.100 M $NaOH$ as the titrant.

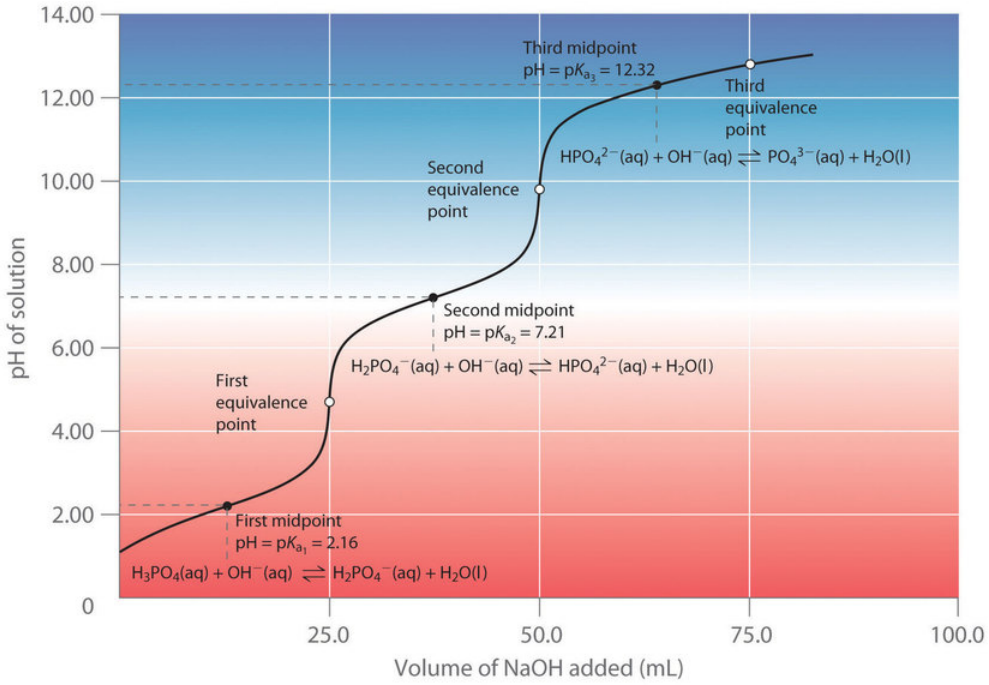


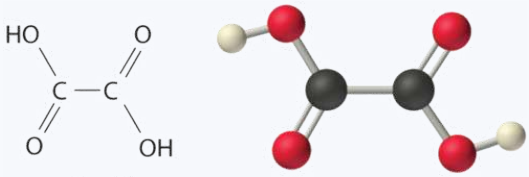
Figure 7.4.2: Titration Curve for Phosphoric Acid (H_3PO_4, a Typical Polyprotic Acid. The curve for the titration of 25.0 mL of a 0.100 M H_3PO_4 solution with 0.100 M $NaOH$ along with the species in solution at each Ka is shown. Note the two distinct equivalence points corresponding to deprotonation of H_3PO_4 at pH ≈ 4.6 and $H_2PO_4^{2-}$ at pH ≈ 9.8. Because HPO_4^{2-} is a very weak acid, the third equivalence point, at pH ≈ 13, is not well defined.

The titration curve for the reaction of a polyprotic base with a strong acid is the mirror image of the curve shown in Figure 7.4.2. The initial pH is high, but as acid is added, the pH decreases in steps if the successive pK_b values are well separated.

In calculating the pH in a titration of a polyprotic acid or base, it is important to know which pK_a or pK_b value to use, based on the reaction stoichiometry at the point of interest.

Example 7.4.3

Calculate the pH of a solution prepared by adding 55.0 mL of a 0.120 M $NaOH$ solution to 100.0 mL of a 0.0510 M solution of oxalic acid (HO_2CCO_2H), a diprotic acid (abbreviated as H2ox). Oxalic acid, the simplest dicarboxylic acid, is found in rhubarb and many other plants. Rhubarb leaves are toxic because they contain the calcium salt of the fully deprotonated form of oxalic acid, the oxalate ion ($-O_2CCO^{2-}$, abbreviated ox^{2-}). Oxalate salts are toxic for two reasons. First, oxalate salts of divalent cations such as Ca^{2+} are insoluble at neutral pH but soluble at low pH. As a result, calcium oxalate dissolves in the dilute acid of the stomach, allowing oxalate to be absorbed and transported into cells, where it can react with calcium to form tiny calcium oxalate crystals that damage tissues. Second, oxalate forms stable complexes with metal ions, which can alter the distribution of metal ions in biological fluids.



oxalic acid

Given: volume and concentration of acid and base

Asked for: pH

Strategy:

A. Calculate the initial millimoles of the acid and the base. Use a tabular format to determine the amounts of all the species in solution.
B. Calculate the concentrations of all the species in the final solution. Determine $[H+]$ and convert this value to pH.

Solution:

A Table E5 gives the pK_a values of oxalic acid as 1.25 and 3.81. Again we proceed by determining the millimoles of acid and base initially present:

$$100.00\ \cancel{mL}\left(\frac{0.510\ mmol\ H_2ox}{\cancel{mL}}\right) = 5.10\ mmol\ H_2ox \tag{7.4.24}$$

$$55.00\ \cancel{mL}\left(\frac{0.120\ mmol\ NaOH}{\cancel{mL}}\right) = 6.60\ mmol\ NaOH \tag{7.4.25}$$

The strongest acid (H_2ox) reacts with the base first. This leaves (6.60 − 5.10) = 1.50 mmol of OH^- to react with Hox−, forming ox^{2-} and H_2O. The reactions can be written as follows:

$$\underset{5.10\ mmol}{H_2ox} + \underset{6.60\ mmol}{OH^-} \rightarrow \underset{5.10\ mmol}{Hox^-} + \underset{5.10\ mmol}{H_2O} \tag{7.4.26}$$

$$\underset{5.10\ mmol}{Hox^-} + \underset{1.50\ mmol}{OH^-} \rightarrow \underset{1.50\ mmol}{ox^{2-}} + \underset{1.50\ mmol}{H_2O} \tag{7.4.27}$$

In tabular form,

	H_2ox	OH^-	Hox^-	ox^{2-}
initial	5.10 mmol	6.60 mmol	0 mmol	0 mmol
change (step 1)	−5.10 mmol	−5.10 mmol	+5.10 mmol	0 mmol
final (step 1)	0 mmol	1.50 mmol	5.10 mmol	0 mmol
change (step 2)	—	−1.50 mmol	−1.50 mmol	+1.50 mmol
final	0 mmol	0 mmol	3.60 mmol	1.50 mmol

B The equilibrium between the weak acid (Hox^-) and its conjugate base (ox^{2-}) in the final solution is determined by the magnitude of the second ionization constant, $K_{a2} = 10^{-3.81} = 1.6 \times 10^{-4}$. To calculate the pH of the solution, we need to know $[H^+]$, which is determined using exactly the same method as in the acetic acid titration in Example 7.4.2:

final volume of solution = 100.0 mL + 55.0 mL = 155.0 mL

Thus the concentrations of Hox^- and ox^{2-} are as follows:

$$\left[Hox^-\right] = \frac{3.60\ mmol\ Hox^-}{155.0\ mL} = 2.32 \times 10^{-2}\ M \tag{7.4.28}$$

$$\left[ox^{2-}\right] = \frac{1.50\ mmol\ ox^{2-}}{155.0\ mL} = 9.68 \times 10^{-3}\ M \tag{7.4.29}$$

We can now calculate [H+] at equilibrium using the following equation:

$$K_{a2} = \frac{\left[ox^{2-}\right]\left[H^+\right]}{\left[Hox^-\right]} \tag{7.4.30}$$

Rearranging this equation and substituting the values for the concentrations of Hox^- and ox^{2-},

$$\left[H^+\right] = \frac{K_{a2}\left[Hox^-\right]}{\left[ox^{2-}\right]} = \frac{\left(1.6 \times 10^{-4}\right)\left(2.32 \times 10^{-2}\right)}{\left(9.68 \times 10^{-3}\right)} = 3.7 \times 10^{-4}\ M \tag{7.4.31}$$

So

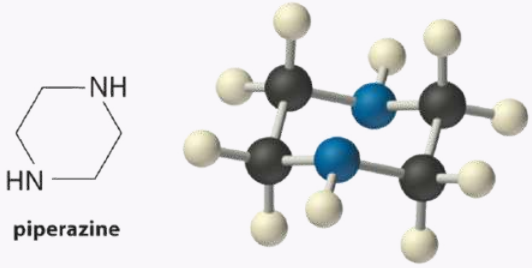
$$pH = -\log\left[H^+\right] = -\log\left(3.7 \times 10^{-4}\right) = 3.43 \tag{7.4.32}$$

This answer makes chemical sense because the pH is between the first and second pK_a values of oxalic acid, as it must be. We added enough hydroxide ion to completely titrate the first, more acidic proton (which should give us a pH greater than pK_{a1}),

but we added only enough to titrate less than half of the second, less acidic proton, with pK_{a2}. If we had added exactly enough hydroxide to completely titrate the first proton plus half of the second, we would be at the midpoint of the second step in the titration, and the pH would be 3.81, equal to pK_{a2}.

Exercise 7.4.3: Piperazine

Piperazine is a diprotic base used to control intestinal parasites (“worms”) in pets and humans. A dog is given 500 mg (5.80 mmol) of piperazine (pK_{b1} = 4.27, pK_{b2} = 8.67). If the dog’s stomach initially contains 100 mL of 0.10 M HCl (pH = 1.00), calculate the pH of the stomach contents after ingestion of the piperazine.



Answer

pH=4.9

Summary

Plots of acid–base titrations generate titration curves that can be used to calculate the pH, the pOH, the pK_a, and the pK_b of the system. To calculate pH at any point in a titration, the amounts of all species must first be determined using the stoichiometry of the neutralization reaction. Then, equilibrium methods can be used to determine the pH. In titrations of polyprotic acids or bases, the neutralization typically occurs in discrete steps that can be treated separately to calculate pH.

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7.5: Solubility Equilibria

Learning Objectives

- To calculate the solubility of an ionic compound from its K_{sp}

We begin our discussion of solubility and complexation equilibria—those associated with the formation of complex ions—by developing quantitative methods for describing dissolution and precipitation reactions of ionic compounds in aqueous solution. Just as with acid–base equilibria, we can describe the concentrations of ions in equilibrium with an ionic solid using an equilibrium constant expression.

The Solubility Product

When a slightly soluble ionic compound is added to water, some of it dissolves to form a solution, establishing an equilibrium between the pure solid and a solution of its ions. For the dissolution of calcium phosphate, one of the two main components of kidney stones, the equilibrium can be written as follows, with the solid salt on the left:

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO^{3-}_{4(aq)} \tag{7.5.1}$$

As you will discover in Section 17.4 and in more advanced chemistry courses, basic anions, such as S^{2-}, PO_4^{3-}, and CO_3^{2-}, react with water to produce OH^- and the corresponding protonated anion. Consequently, their calculated molarities, assuming no protonation in aqueous solution, are only approximate.

The equilibrium constant for the dissolution of a sparingly soluble salt is the **solubility product (K_{sp})** of the salt. Because the concentration of a pure solid such as $Ca_3(PO_4)_2$ is a constant, it does not appear explicitly in the equilibrium constant expression. The equilibrium constant expression for the dissolution of calcium phosphate is therefore

$$K = \frac{[\mathrm{Ca^{2+}}]^3[\mathrm{PO_4^{3-}}]^2}{[\mathrm{Ca_3(PO_4)_2}]} \tag{7.5.2}$$

$$[\mathrm{Ca_3(PO_4)_2}]K = K_{\mathrm{sp}} = [\mathrm{Ca^{2+}}]^3[\mathrm{PO_4^{3-}}]^2 \tag{7.5.3}$$

At 25°C and pH 7.00, Ksp for calcium phosphate is 2.07×10^{-33}, indicating that the concentrations of Ca^{2+} and PO_4^{3-} ions in solution that are in equilibrium with solid calcium phosphate are very low. The values of K_{sp} for some common salts are listed in Table 7.5.1, which shows that the magnitude of K_{sp} varies dramatically for different compounds. Although K_{sp} is not a function of pH in Equations 7.5.2 and 7.5.3, changes in pH can affect the solubility of a compound as discussed later.

> *As with any K, the concentration of a pure solid does not appear explicitly in K_{sp}.*

Table 7.5.1: Solubility Products for Selected Ionic Substances at 25°C

Solid	Color	K_{sp}		Solid	Color	K_{sp}
Acetates				**Iodides**		
$Ca(O_2CCH_3)_2{\cdot}3H_2O$	white	4×10^{-3}		Hg_2I_2*	yellow	5.2×10^{-29}
Bromides				PbI_2	yellow	9.8×10^{-9}
AgBr	off-white	5.35×10^{-13}		**Oxalates**		
Hg_2Br_2*	yellow	6.40×10^{-23}		$Ag_2C_2O_4$	white	5.40×10^{-12}
Carbonates				$MgC_2O_4{\cdot}2H_2O$	white	4.83×10^{-6}
$CaCO_3$	white	3.36×10^{-9}		PbC_2O_4	white	4.8×10^{-10}
$PbCO_3$	white	7.40×10^{-14}		**Phosphates**		

*These contain the Hg_2^{2+} ion.

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Solid	Color	K_{sp}		Solid	Color	K_{sp}
Chlorides				Ag_3PO_4	white	8.89×10^{-17}
AgCl	white	1.77×10^{-10}		$Sr_3(PO_4)_2$	white	4.0×10^{-28}
Hg_2Cl_2*	white	1.43×10^{-18}		$FePO_4 \cdot 2H_2O$	pink	9.91×10^{-16}
$PbCl_2$	white	1.70×10^{-5}		**Sulfates**		
Chromates				Ag_2SO_4	white	1.20×10^{-5}
$CaCrO_4$	yellow	7.1×10^{-4}		$BaSO_4$	white	1.08×10^{-10}
$PbCrO_4$	yellow	2.8×10^{-13}		$PbSO_4$	white	2.53×10^{-8}
Fluorides				**Sulfides**		
BaF_2	white	1.84×10^{-7}		Ag_2S	black	6.3×10^{-50}
PbF_2	white	3.3×10^{-8}		CdS	yellow	8.0×10^{-27}
Hydroxides				PbS	black	8.0×10^{-28}
$Ca(OH)_2$	white	5.02×10^{-6}		ZnS	white	1.6×10^{-24}
$Cu(OH)_2$	pale blue	1×10^{-14}				
$Mn(OH)_2$	light pink	1.9×10^{-13}				
$Cr(OH)_3$	gray-green	6.3×10^{-31}				
$Fe(OH)_3$	rust red	2.79×10^{-39}				

*These contain the Hg_2^{2+} ion.



Definition of a Solubility Product: Definition of a Solubility Product(opens in new window) [youtu.be]

Solubility products are determined experimentally by directly measuring either the concentration of one of the component ions or the solubility of the compound in a given amount of water. However, whereas solubility is usually expressed in terms of mass of solute per 100 mL of solvent, K_{sp}, like K, is defined in terms of the molar concentrations of the component ions.



A color photograph of a kidney stone, 8 mm in length. Kidney stones form from sparingly soluble calcium salts and are largely composed of $Ca(O_2CCO_2)\cdot H_2O$ and $Ca_3(PO_4)_2$. from Wikipedia.

Example 7.5.1

Calcium oxalate monohydrate [$Ca(O_2CCO_2)\cdot H_2O$, also written as $CaC_2O_4\cdot H_2O$] is a sparingly soluble salt that is the other major component of kidney stones [along with $Ca_3(PO_4)_2$]. Its solubility in water at 25°C is 7.36×10^{-4} g/100 mL. Calculate its K_{sp}.

Given: solubility in g/100 mL

Asked for: K_{sp}

Strategy:

A. Write the balanced dissolution equilibrium and the corresponding solubility product expression.

B. Convert the solubility of the salt to moles per liter. From the balanced dissolution equilibrium, determine the equilibrium concentrations of the dissolved solute ions. Substitute these values into the solubility product expression to calculate K_{sp}.

Solution

A We need to write the solubility product expression in terms of the concentrations of the component ions. For calcium oxalate monohydrate, the balanced dissolution equilibrium and the solubility product expression (abbreviating oxalate as ox^{2-}) are as follows:

$$Ca(O_2CCO_2)\cdot H_2O(s) \rightleftharpoons Ca^{2+}(aq) + {}^{-}O_2CCO_2^{-}(aq) + H_2O(l) \quad K_{sp} = [Ca^{2+}][ox^{2-}]$$

Neither solid calcium oxalate monohydrate nor water appears in the solubility product expression because their concentrations are essentially constant.

B Next we need to determine $[Ca^{2+}]$ and $[ox^{2-}]$ at equilibrium. We can use the mass of calcium oxalate monohydrate that dissolves in 100 mL of water to calculate the number of moles that dissolve in 100 mL of water. From this we can determine the number of moles that dissolve in 1.00 L of water. For dilute solutions, the density of the solution is nearly the same as that of water, so dissolving the salt in 1.00 L of water gives essentially 1.00 L of solution. Because each 1 mol of dissolved calcium oxalate monohydrate dissociates to produce 1 mol of calcium ions and 1 mol of oxalate ions, we can obtain the equilibrium concentrations that must be inserted into the solubility product expression. The number of moles of calcium oxalate monohydrate that dissolve in 100 mL of water is as follows:

$$\frac{7.36 \times 10^{-4}\ \text{g}}{146.1\ \text{g/mol}} = 5.04 \times 10^{-6}\ \text{mol}\ Ca(O_2CCO_2)\cdot H_2O$$

The number of moles of calcium oxalate monohydrate that dissolve in 1.00 L of the saturated solution is as follows:

$$\left(\frac{5.04\times10^{-6}\ \text{mol Ca}(\text{O}_2\text{CCO}_2\cdot)\text{H}_2\text{O}}{100\ \text{mL}}\right)\left(\frac{1000\ \text{mL}}{1.00\ \text{L}}\right)=5.04\times10^{-5}\ \text{mol/L}=5.04\times10^{-5}\ \text{M}$$

Because of the stoichiometry of the reaction, the concentration of Ca^{2+} and ox^{2-} ions are both 5.04×10^{-5} M. Inserting these values into the solubility product expression,

$$K_{sp}=[Ca^{2+}][ox^{2-}]=(5.04\times10^{-5})(5.04\times10^{-5})=2.54\times10^{-9}$$

In our calculation, we have ignored the reaction of the weakly basic anion with water, which tends to make the actual solubility of many salts greater than the calculated value.

Exercise 7.5.1: Calcite

One crystalline form of calcium carbonate ($CaCO_3$) is "calcite", found as both a mineral and a structural material in many organisms. Calcite is found in the teeth of sea urchins. The urchins create depressions in limestone that they can settle in by grinding the rock with their teeth. Limestone, however, also consists of calcite, so how can the urchins grind the rock without also grinding their teeth? Researchers have discovered that the teeth are shaped like needles and plates and contain magnesium. The concentration of magnesium increases toward the tip, which contributes to the hardness. Moreover, each tooth is composed of two blocks of the polycrystalline calcite matrix that are interleaved near the tip. This creates a corrugated surface that presumably increases grinding efficiency. Toolmakers are particularly interested in this approach to grinding.



A crystal of calcite ($CaCO_3$), illustrating the phenomenon of double refraction. When a transparent crystal of calcite is placed over a page, we see two images of the letters. from Wikipedia

The solubility of calcite in water is 0.67 mg/100 mL. Calculate its K_{sp}.

Answer

4.5×10^{-9}

> *The reaction of weakly basic anions with H_2O tends to make the actual solubility of many salts higher than predicted.*



Finding Ksp from Ion Concentrations: Finding Ksp from Ion Concentrations(opens in new window) [youtu.be]

Tabulated values of K_{sp} can also be used to estimate the solubility of a salt with a procedure that is essentially the reverse of the one used in Example 7.5.1. In this case, we treat the problem as a typical equilibrium problem and set up a table of initial

concentrations, changes in concentration, and final concentrations (ICE Tables), remembering that the concentration of the pure solid is essentially constant.

Example 7.5.2

We saw that the K_{sp} for $Ca_3(PO_4)_2$ is 2.07×10^{-33} at 25°C. Calculate the aqueous solubility of $Ca_3(PO_4)_2$ in terms of the following:

a. the molarity of ions produced in solution
b. the mass of salt that dissolves in 100 mL of water at 25°C

Given: K_{sp}

Asked for: molar concentration and mass of salt that dissolves in 100 mL of water

Strategy:

A. Write the balanced equilibrium equation for the dissolution reaction and construct a table showing the concentrations of the species produced in solution. Insert the appropriate values into the solubility product expression and calculate the molar solubility at 25°C.

B. Calculate the mass of solute in 100 mL of solution from the molar solubility of the salt. Assume that the volume of the solution is the same as the volume of the solvent.

Solution:

A. **A** The dissolution equilibrium for $Ca_3(PO_4)_2$ (Equation 7.5.2) is shown in the following ICE table. Because we are starting with distilled water, the initial concentration of both calcium and phosphate ions is zero. For every 1 mol of $Ca_3(PO_4)_2$ that dissolves, 3 mol of Ca^{2+} and 2 mol of PO_4^{3-} ions are produced in solution. If we let x equal the solubility of $Ca_3(PO_4)_2$ in moles per liter, then the change in $[Ca^{2+}]$ will be $+3x$, and the change in $[PO_4^{3-}]$ will be $+2x$. We can insert these values into the table.

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

Solutions to Example 17.4.2

	Ca3(PO4)2	[Ca2+]	$[PO_4^{3-}]$
initial	pure solid	0	0
change	—	+3*x*	+2*x*
final	pure solid	3*x*	2*x*

Although the amount of solid $Ca_3(PO_4)_2$ changes as some of it dissolves, its molar concentration does not change. We now insert the expressions for the equilibrium concentrations of the ions into the solubility product expression (Equation 17.2):

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (3x)^3(2x)^2 \quad (7.5.4)$$

$$2.07 \times 10^{-33} = 108x^5 \quad (7.5.5)$$

$$1.92 \times 10^{-35} = x^5 \quad (7.5.6)$$

$$1.14 \times 10^{-7}\ \text{M} = x \quad (7.5.7)$$

This is the molar solubility of calcium phosphate at 25°C. However, the molarity of the ions is $2x$ and $3x$, which means that $[PO_4^{3-}] = 2.28 \times 10^{-7}$ and $[Ca^{2+}] = 3.42 \times 10^{-7}$.

b. **B** To find the mass of solute in 100 mL of solution, we assume that the density of this dilute solution is the same as the density of water because of the low solubility of the salt, so that 100 mL of water gives 100 mL of solution. We can then determine the amount of salt that dissolves in 100 mL of water:

$$\left(\frac{1.14 \times 10^{-7}\ \text{mol}}{1\ \text{L}}\right) 100\ \text{mL} \left(\frac{1\ \text{L}}{1000\ \text{mL}}\right) \left(\frac{310.18\ \text{g}\ Ca_3(PO_4)_2}{1\ \text{mol}}\right) = 3.54 \times 10^{-6}\ \text{g}\ Ca_3(PO_4)_2$$

? Exercise 7.5.2

The solubility product of silver carbonate (Ag_2CO_3) is 8.46×10^{-12} at 25°C. Calculate the following:

a. the molarity of a saturated solution
b. the mass of silver carbonate that will dissolve in 100 mL of water at this temperature

Answer

a. 1.28×10^{-4} M
b. 3.54 mg



Finding the Solubility of a Salt: Finding the Solubility of a Salt (opens in new window) [youtu.be]

The Ion Product

The **ion product (*Q*)** of a salt is the product of the concentrations of the ions in solution raised to the same powers as in the solubility product expression. It is analogous to the reaction quotient (*Q*) discussed for gaseous equilibria. Whereas K_{sp} describes equilibrium concentrations, the ion product describes concentrations that are not necessarily equilibrium concentrations.

> *The ion product Q is analogous to the reaction quotient Q for gaseous equilibria.*

As summarized in Figure 7.5.1, there are three possible conditions for an aqueous solution of an ionic solid:

- $Q < K_{sp}$. The solution is unsaturated, and more of the ionic solid, if available, will dissolve.
- $Q = K_{sp}$. The solution is saturated and at equilibrium.
- $Q > K_{sp}$. The solution is supersaturated, and ionic solid will precipitate.

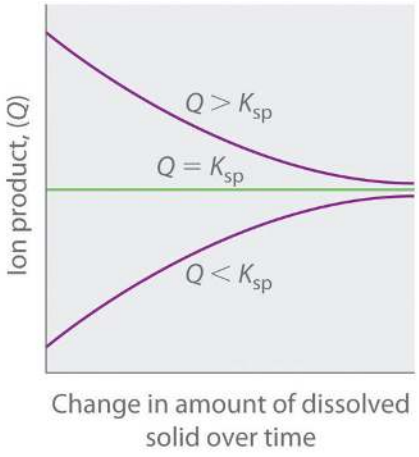


Figure 7.5.1: The Relationship between Q and K_{sp}. If Q is less than K_{sp}, the solution is unsaturated and more solid will dissolve until the system reaches equilibrium (Q = K_{sp}). If Q is greater than K_{sp}, the solution is supersaturated and solid will precipitate until Q = K_{sp}. If Q = K_{sp}, the rate of dissolution is equal to the rate of precipitation; the solution is saturated, and no net change in the amount of dissolved solid will occur.

Graph of ion product against change in amount of dissolved solid over time. The purple curves are when Q is greater or less than Ksp. The green line is when Q is equal to Ksp.

The process of calculating the value of the ion product and comparing it with the magnitude of the solubility product is a straightforward way to determine whether a solution is unsaturated, saturated, or supersaturated. More important, the ion product tells chemists whether a precipitate will form when solutions of two soluble salts are mixed.

Example 7.5.3

We mentioned that barium sulfate is used in medical imaging of the gastrointestinal tract. Its solubility product is 1.08×10^{-10} at 25°C, so it is ideally suited for this purpose because of its low solubility when a "barium milkshake" is consumed by a patient. The pathway of the sparingly soluble salt can be easily monitored by x-rays. Will barium sulfate precipitate if 10.0 mL of 0.0020 M Na_2SO_4 is added to 100 mL of 3.2×10^{-4} M $BaCl_2$? Recall that NaCl is highly soluble in water.

Given: K_{sp} and volumes and concentrations of reactants

Asked for: whether precipitate will form

Strategy:

A. Write the balanced equilibrium equation for the precipitation reaction and the expression for K_{sp}.
B. Determine the concentrations of all ions in solution when the solutions are mixed and use them to calculate the ion product (Q).
C. Compare the values of Q and K_{sp} to decide whether a precipitate will form.

Solution

A The only slightly soluble salt that can be formed when these two solutions are mixed is $BaSO_4$ because NaCl is highly soluble. The equation for the precipitation of $BaSO_4$ is as follows:

$$BaSO_{4(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

The solubility product expression is as follows:

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.08 \times 10^{-10}$$

B To solve this problem, we must first calculate the ion product—$Q = [Ba^{2+}][SO_4^{2-}]$—using the concentrations of the ions that are present after the solutions are mixed and before any reaction occurs. The concentration of Ba^{2+} when the solutions are mixed is the total number of moles of Ba^{2+} in the original 100 mL of $BaCl_2$ solution divided by the final volume (100 mL + 10.0 mL = 110 mL):

$$\text{moles } Ba^{2+} = 100 \text{ mL} \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) \left(\frac{3.2 \times 10^{-4} \text{ mol}}{1 \text{ L}} \right) = 3.2 \times 10^{-5} \text{ mol } Ba^{2+}$$

$$[Ba^{2+}] = \left(\frac{3.2 \times 10^{-5}\ \text{mol}\ Ba^{2+}}{110\ \text{mL}}\right)\left(\frac{1000\ \text{mL}}{1\ \text{L}}\right) = 2.9 \times 10^{-4}\ \text{M}\ Ba^{2+}$$

Similarly, the concentration of SO_4^{2-} after mixing is the total number of moles of SO_4^{2-} in the original 10.0 mL of Na_2SO_4 solution divided by the final volume (110 mL):

$$\text{moles}\ SO_4^{2-} = 10.0\ \text{mL}\left(\frac{1\ \text{L}}{1000\ \text{mL}}\right)\left(\frac{0.0020\ \text{mol}}{1\ \text{L}}\right) = 2.0 \times 10^{-5}\ \text{mol}\ SO_4^{2-}$$

$$[SO_4^{2-}] = \left(\frac{2.0 \times 10^{-5}\ \text{mol}\ SO_4^{2-}}{110\ \text{mL}}\right)\left(\frac{1000\ \text{mL}}{1\ \text{L}}\right) = 1.8 \times 10^{-4}\ \text{M}\ SO_4^{2-}$$

We can now calculate Q:

$$Q = [Ba^{2+}][SO_4^{2-}] = (2.9\times10^{-4})(1.8\times10^{-4}) = 5.2\times10^{-8}$$

C We now compare Q with the K_{sp}. If $Q > K_{sp}$, then $BaSO_4$ will precipitate, but if $Q < K_{sp}$, it will not. Because $Q > K_{sp}$, we predict that $BaSO_4$ will precipitate when the two solutions are mixed. In fact, $BaSO_4$ will continue to precipitate until the system reaches equilibrium, which occurs when $[Ba^{2+}][SO_4^{2-}] = K_{sp} = 1.08 \times 10^{-10}$.

? Exercise 7.5.3

The solubility product of calcium fluoride (CaF_2) is 3.45×10^{-11}. If 2.0 mL of a 0.10 M solution of NaF is added to 128 mL of a 2.0×10^{-5}M solution of $Ca(NO_3)_2$, will CaF_2 precipitate?

Answer

yes ($Q = 4.7 \times 10^{-11} > K_{sp}$)



Determining if a Precipitate forms (The Ion Product): Determining if a Precipitate forms (The Ion Product)(opens in new window) [youtu.be]

The Common Ion Effect and Solubility

The solubility product expression tells us that the equilibrium concentrations of the cation and the anion are inversely related. That is, as the concentration of the anion increases, the maximum concentration of the cation needed for precipitation to occur decreases—and vice versa—so that K_{sp} is constant. Consequently, the solubility of an ionic compound depends on the concentrations of other salts that contain the same ions. Adding a common cation or anion shifts a solubility equilibrium in the direction predicted by Le Chatelier's principle. As a result, the solubility of any sparingly soluble salt is almost always decreased by the presence of a soluble salt that contains a common ion. The exceptions generally involve the formation of complex ions, which is discussed later.

Consider, for example, the effect of adding a soluble salt, such as $CaCl_2$, to a saturated solution of calcium phosphate [$Ca_3(PO_4)_2$]. We have seen that the solubility of $Ca_3(PO_4)_2$ in water at 25°C is 1.14×10^{-7} M ($K_{sp} = 2.07 \times 10^{-33}$). Thus a saturated solution of $Ca_3(PO_4)_2$ in water contains $3 \times (1.14 \times 10^{-7}\ \text{M}) = 3.42 \times 10^{-7}$ M Ca^{2+} and $2 \times (1.14 \times 10^{-7}\ \text{M}) = 2.28 \times 10^{-7}$ M PO_4^{3-}, according

to the stoichiometry shown in Equation 7.5.1 (neglecting hydrolysis to form HPO_4^{2-} as described in Chapter 16). If $CaCl_2$ is added to a saturated solution of $Ca_3(PO_4)_2$, the Ca^{2+} ion concentration will increase such that $[Ca^{2+}] > 3.42 \times 10^{-7}$ M, making $Q > K_{sp}$. The only way the system can return to equilibrium is for the reaction in Equation 7.5.1 to proceed to the left, resulting in precipitation of $Ca_3(PO_4)_2$. This will decrease the concentration of both Ca^{2+} and PO_4^{3-} until $Q = K_{sp}$.

> *The common ion effect usually **decreases** the solubility of a sparingly soluble salt.*

Example 7.5.4

Calculate the solubility of calcium phosphate [$Ca_3(PO_4)_2$] in 0.20 M $CaCl_2$.

Given: concentration of $CaCl_2$ solution

Asked for: solubility of $Ca_3(PO_4)_2$ in $CaCl_2$ solution

Strategy:

A. Write the balanced equilibrium equation for the dissolution of $Ca_3(PO_4)_2$. Tabulate the concentrations of all species produced in solution.

B. Substitute the appropriate values into the expression for the solubility product and calculate the solubility of $Ca_3(PO_4)_2$.

Solution

A The balanced equilibrium equation is given in the following table. If we let x equal the solubility of $Ca_3(PO_4)_2$ in moles per liter, then the change in $[Ca^{2+}]$ is once again $+3x$, and the change in $[PO_4^{3-}]$ is $+2x$. We can insert these values into the ICE table.

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO^{3-}_{4(aq)}$$

Solutions to Example 17.4.4

	Ca3(PO4)2	$[Ca^{2+}]$	$[PO_4^{3-}]$
initial	pure solid	0.20	0
change	—	$+3x$	$+2x$
final	pure solid	$0.20 + 3x$	$2x$

B The K_{sp} expression is as follows:

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (0.20 + 3x)^3(2x)^2 = 2.07\times10^{-33}$$

Because $Ca_3(PO_4)_2$ is a sparingly soluble salt, we can reasonably expect that $x << 0.20$. Thus $(0.20 + 3x)$ M is approximately 0.20 M, which simplifies the K_{sp} expression as follows:

$$\begin{aligned} K_{sp} = (0.20)^3(2x)^2 &= 2.07 \times 10^{-33} \\ x^2 &= 6.5 \times 10^{-32} \\ x &= 2.5 \times 10^{-16}\ \text{M} \end{aligned}$$

This value is the solubility of $Ca_3(PO_4)_2$ in 0.20 M $CaCl_2$ at 25°C. It is approximately nine orders of magnitude less than its solubility in pure water, as we would expect based on Le Chatelier's principle. With one exception, this example is identical to Example 7.5.2—here the initial $[Ca^{2+}]$ was 0.20 M rather than 0.

Exercise 7.5.4

Calculate the solubility of silver carbonate in a 0.25 M solution of sodium carbonate. The solubility of silver carbonate in pure water is 8.45×10^{-12} at 25°C.

Answer

2.9×10^{-6} M (versus 1.3×10^{-4} M in pure water)



The Common Ion Effect in Solubility Products: The Common Ion Effect in Solubility Products(opens in new window) [youtu.be]

Summary

The solubility product (K_{sp}) is used to calculate equilibrium concentrations of the ions in solution, whereas the ion product (Q) describes concentrations that are not necessarily at equilibrium. The equilibrium constant for a dissolution reaction, called the solubility product (K_{sp}), is a measure of the solubility of a compound. Whereas solubility is usually expressed in terms of mass of solute per 100 mL of solvent, K_{sp} is defined in terms of the molar concentrations of the component ions. In contrast, the ion product (Q) describes concentrations that are not necessarily equilibrium concentrations. Comparing Q and K_{sp} enables us to determine whether a precipitate will form when solutions of two soluble salts are mixed. Adding a common cation or common anion to a solution of a sparingly soluble salt shifts the solubility equilibrium in the direction predicted by Le Chatelier's principle. The solubility of the salt is almost always decreased by the presence of a common ion.

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7.E: Buffers, Titrations and Solubility Equilibria (Exercises)

7.1: Acid-Base Buffers

Exercise 7.E.1

What is the role of a buffer in chemistry and biology?

Answer

The role of a buffer in chemistry and biology is to resist pH changes upon the addition of an acid or base.

Exercise 7.E.2

Explain why the most effective buffers are those that contain approximately equal amounts of the weak acid and its conjugate base.

Answer

The most effective buffers are those that contain approximately equal amounts of the weak acid and its conjugate base because when placed in the Henderson-Hasselbalch equation the pH approximately equals the pK_a. This is the goal because the more the ratio needs to differ to achieve the desired pH, the less effective the buffer and it should not differ by more than tenfold.

Exercise 7.E.3

If you were given a solution of sodium acetate, describe a way you could convert the solution to a buffer.

Answer

Sodium acetate is a salt, therefore it can't be regarded as an acid or a base. One way to convert the solution to a buffer is to combine sodium acetate with a weak acid such as acetic acid. The sodium acetate would react with the hydronium ions and the acetic acid would react with hydroxide ions to prevent drastic changes in pH.

Exercise 7.E.4

Benzenesulfonic acid ($pKa = 0.70$) is synthesized by treating benzene with concentrated sulfuric acid. Calculate the following:

a. the pH of a 0.286 M solution of benzenesulfonic acid
b. the pH after adding enough sodium benzenesulfonate to give a final benzenesulfonate concentration of 0.100 M

Answer

a. $pH = -log([H^+]) = -log(0.2388) = 0.62$

$$K_a = \frac{[H^+][A^-]}{[HA]} \rightarrow K_a = \frac{[H^+]^2}{[HA]} \rightarrow [H^+] = \sqrt{K_a \times [HA]} = \sqrt{10^{-0.70} \times 0.286\ M} = 0.2388$$

b. $pH = -log([H^+]) = -log(0.14125) = 0.850$

$$K_a = \frac{[H^+][A^-]}{[HA]} \rightarrow K_a = \frac{[H^+]^2}{[HA]} \rightarrow [H^+] = \sqrt{K_a \times [HA]} = \sqrt{10^{-0.70} \times 0.100\ M} = 0.14125$$

Exercise 7.E.5

Which of the following will produce a buffer solution? Explain your reasoning in each case.

a. mixing 100 mL of 0.1 M HCl and 100 mL of 0.1 M sodium fluoride

b. mixing 50 mL of 0.1 M HCl and 100 mL of 0.1 M sodium fluoride
c. mixing 100 mL of 0.1 M hydrofluoric acid and 100 mL of 0.1 M HCl
d. mixing 100 mL of 0.1 M hydrofluoric acid and 50 mL of 0.1 M $NaOH$
e. mixing 100 mL of 0.1 M sodium fluoride and 50 mL of 0.1 M $NaOH$.

Answer

a. This will not produce a buffer solution because the hydrochloric acid completely neutralizes the sodium fluoride to give sodium chloride.

b. This will produce a buffer solution because the hydrochloric acid neutralizes only half of the acetic acid to give a solution containing equal amounts of hydrofluoric acid and sodium chloride.

c. This will not produce a buffer solution because hydrofluoric acid is a weak acid and hydrochloric acid is a strong acid.

d. This will produce a buffer solution because the solution will contain a 2:1 ratio of hydrofluoric acid and sodium hydroxide.

e. This will not produce a buffer solution solution because sodium fluoride is a weak base and sodium hydroxide is a strong base.

Exercise $7.E.6$

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?

Answer

pH = 8.95

Exercise $7.E.7$

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?

Answer

(a) pH = 5.222; (b) The solution is acidic. (c) pH = 5.220

7.2: Practical Aspects of Buffers

Exercise $7.E.8$

Why are buffers usually used only within approximately one pH unit of the pK_a or pK_b of the parent weak acid or base?

Answer

Buffers are usually used only within approximately one pH unit of the pK_a or pK_b of the parent weak acid or base because the ability of a buffer solution to maintain a nearly constant pH due to a small amount of acid or base is greatest at the pK_a and decreases as the pH of the solution goes above or below the pK_a.

$$pH = pK_a + log(\frac{[B]}{[A]})$$

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When $\frac{[B]}{[A]} = 10$: $pH = pK_a + 1$

When $\frac{[B]}{[A]} = \frac{1}{10}$: $pH = pK_a - 1$

Exercise 7.E.9

How much solid $NaCH_3CO_2 \cdot 3H_2O$ must be added to 0.300 L of a 0.50-*M* acetic acid solution to give a buffer with a pH of 5.00? (Hint: Assume a negligible change in volume as the solid is added.)

Answer

37 g (0.27 mol)

7.3: Acid-Base Titrations

Exercise 7.E.10

The titration curve for a monoprotic acid can be divided into four regions: the starting point, the region around the midpoint of the titration, the equivalence point, and the region after the equivalence point. For which region would you use each approach to describe the behavior of the solution?

a. a buffer
b. a solution of a salt of a weak base
c. a solution of a weak acid
d. diluting a strong base

Answer

a. I would use the region around the midpoint of the titration to describe the behavior of a buffer because the midpoint of the titration is defined as the point at which exactly enough acid or base has been added to neutralize one-half of the acid or the base originally present while maintaining a relatively constant pH.

b. I would use the equivalence point region to describe the behavior of a solution of a salt of a weak base because at this point the amount of titrant added is enough to completely neutralize the solution.

c. I would use the starting point region of the titration curve to describe the behavior of the solution of a weak acid because it is expected to be at a higher pH than a strong acid but lower than pH 7.

d. I would use the region after the equivalence point to describe the dilution of a strong base because in this region one can predict the pH by simply taking into account the amount of excess base.

Exercise 7.E.11

Why is the portion of the titration curve that lies below the equivalence point of a solution of a weak acid displaced upward relative to the titration curve of a strong acid? How are the slopes of the curves different at the equivalence point? Why?

Answer

The portion of the titration curve that lies below the equivalence point of a solution of a weak acid is displaced upward relative to the titration curve of a strong acid because the starting point of a weak acid is at a higher pH compared to that of a strong acid. The slope for a strong acid is greater compared to that of a weak acid because when a weak acid is neutralized, the solution that remains is basic because the acid's conjugate base remains in solution.

Exercise 7.E.12

Predict whether each solution will be neutral, basic, or acidic at the equivalence point of each titration.

a. An aqueous solution of $NaOH$ is titrated with 0.100 M HCl.
b. An aqueous solution of ethylamine ($CH_3CH_2NH_2$) is titrated with 0.150 M HNO_3
c. An aqueous solution of aniline hydrochloride ($C_6H_5NH_3^+Cl^-$) is titrated with 0.050 M KOH.

Answer

a. The solution will be neutral at the equivalence point because sodium hydroxide is a strong base and hydrochloric acid is a strong acid.

b. The solution will be acidic at the equivalence point because ethylamine is a weak base and nitric acid is a strong acid.

c. The solution will be basic at the equivalence point because aniline hydrochloride is a weak acid and potassium hydroxide is a strong base.

Exercise 7.E.13

The pKa values of phenol red, bromophenol blue, and phenolphthalein are 7.4, 4.1, and 9.5, respectively. Which indicator is best suited for each acid–base titration?

a. titrating a solution of $Ba(OH)_2$ with 0.100 M HCl
b. titrating a solution of trimethylamine (Me_3N) with 0.150 M HNO_3
c. titrating a solution of aniline hydrochloride ($C_6H_5NH_3^+Cl^-$) with 0.050 M KOH

Answer

a. Barium hydroxide is a strong base and hydrochloric acid is a strong acid thus phenol red with the $pK_a = 7.4$ is best suited for the reaction.

b. Trimethylamine is a weak base and nitric acid is a strong acid thus bromophenol blue with the $pK_a = 4.1$ is best suited for the reaction.

c. Aniline hydrochloride is a weak acid and potassium hydroxide is a strong base thus phenolphthalein with $pK_a = 9.5$ is best suited for the reaction.

Exercise 7.E.14

a. For the titration of any strong acid with any strong base, the pH at the equivalence point is 7.0. Why is this not usually the case in titrations of weak acids or weak bases?

b. Why are the titration curves for a strong acid with a strong base and a weak acid with a strong base identical in shape above the equivalence points but not below?

Answer

a. This is not usually the case in the titration of weak acids and weak bases because weak acids and weak bases would only ionize partially, thus complete neutralization does not occur.

b. The titration curve for a strong acid with a strong base is identical in shape above the equivalence point of the titration curve with a weak acid and strong base because both cases involve the addition of strong base. Not only does the strong base completely neutralize the acid but there is an excess of a strong base that makes the solution basic.

Exercise 7.E.15

Describe what is occurring on a molecular level during the titration of a weak acid, such as acetic acid, with a strong base, such as $NaOH$, at the following points along the titration curve. Which of these points corresponds to $pH = pK_a$?

a. at the beginning of the titration
b. at the midpoint of the titration
c. at the equivalence point
d. when excess titrant has been added

Answer

a. The titration begins with a pH is higher than the titration of a strong acid. At the beginning of the titration, there is a sharp increase in pH because the anion of the weak acid becomes a common ion that reduces the ionization of the acid.

b. There is a sharp increase at the beginning of the titration that changes gradually due to the solution becoming a buffer. This continues until the strong base has overcome the buffer capacity. At the midpoint of the titration, the concentration of the weak acid is equal to the concentration of its conjugate base. This point is also known as half-neutralization because half the acid has been neutralized by the strong base.

c. At the equivalence point the pH is greater than 7 because the acid (HA) has been converted to its conjugate base (A^-) by sodium hydroxide and equilibrium moves backward toward the acid and produces hydroxide:

$$A^- + H_2O \rightleftharpoons AH + OH^-$$

d. When the excess titrant has been added the solution becomes basic because sodium hydroxide completely neutralized the weak acid.

Exercise $7.E.16$

On a molecular level, describe what is happening during the titration of a weak base, such as ammonia, with a strong acid, such as HCl, at the following points along the titration curve. Which of these points corresponds to $pOH = pK_b$?

a. at the beginning of the titration
b. at the midpoint of the titration
c. at the equivalence point
d. when excess titrant has been added

Answer

a. The titration begins with a pH that is lower than the titration of a strong base but higher than the $pH = 7$. At the beginning of the titration, there is a sharp decrease in pH because the cation of the weak base becomes a common ion that reduces the ionization of the base.

b. The sharp decrease at the beginning of the titration changes gradually due to the solution becoming a buffer. This continues until the strong acid has overcome the buffer capacity. At the midpoint of the titration, the concentration of the weak base is equal to the concentration of its conjugate acid $pH = pK_a$. This point is also known as half-neutralization because half the base has been neutralized by the strong acid.

c. At the equivalence point the pH is less than 7 because the base NH_3 has been converted to its conjugate acid NH_4^+ by hydrochloric acid and equilibrium moves forwards toward the base and produces NH_4Cl^-:

$$NH_3 + HCl \rightleftharpoons NH_4Cl$$

d. When excess titrant has been added the solution becomes acidic because hydrochloric acid completely neutralized the weak base.

7.4: Solving Titration Problems

Exercise $7.E.17$

Calculate the pH at the following points in a titration of 40 mL (0.040 L) of 0.100 *M* barbituric acid (K_a = 9.8 × 10^{-5}) with 0.100 *M* KOH.

(a) no KOH added

(b) 20 mL of KOH solution added

(c) 39 mL of KOH solution added

(d) 40 mL of KOH solution added

(e) 41 mL of KOH solution added

Answer

(a) pH = 2.50; (b) pH = 4.01; (c) pH = 5.60; (d) pH = 8.35; (e) pH = 11.08

Exercise 7.E. 18

Calcium carbonate is a major contributor to the “hardness” of water. The amount of CaCO3 in a water sample can be determined by titrating the sample with an acid, such as HCl, which produces water and CO2. Write a balanced chemical equation for this reaction. Generate a plot of solution pH versus volume of 0.100 M HCl added for the titration of a solution of 250 mg of CaCO3 in 200.0 mL of water with 0.100 M HCl; assume that the HCl solution is added in 5.00 mL increments. What volume of HCl corresponds to the equivalence point?

Answer

$CaCO_3\,(aq) + 2\,HCl\,(aq) \rightarrow CaCl_2\,(aq) + H_2O\,(l) + CO_2\,(g)$

$CO_3^{2-}\,(aq) + H^+\,(aq) \rightleftharpoons HCO_3^-\,(aq)$

$HCO_3^{2-}\,(aq) + H^+\,(aq) \rightleftharpoons H_2CO_3\,(aq)$

$K_{a1} = 4.3 \times 10^{-7}$

$K_{a2} = 5.0 \times 10^{-11}$

At 0 mL addition of HCl: $pH = 14 - pOH = 14 - (-log(\sqrt{0.0125 \times \frac{10^{-14}}{5.0 \times 10^{-11}}}) = 11.20$

$CaCO_3 : 250\,mg \times \frac{1\,g}{1{,}000\,mg} \times \frac{1\,mol}{100.0869\,g} \times \frac{1}{200\,mL \times \frac{1\,L}{1{,}000\,mL}} = 0.0125\,M$

At 5 mL addition of HCl: $pH = -log(5 \times 10^{-11}) + log(\frac{0.002}{0.0005}) = 10.9$

$CaCO_3 : 0.2\,L \times 0.0125\,M = 0.0025\,mol$

$HCl : 0.005\,L \times 0.1\,M = 0.0005\,mol$

	CO_3^{2-}	H^+	HCO_3^-
I	0.0025	0.0005	0
C	-0.0005	-0.0005	0.0005
E	0.002	0	0.0005

At 10 mL addition of HCl: $pH = -log(5 \times 10^{-11}) + log(\frac{0.001}{0.0015}) = 10.5$

$CaCO_3 : 0.2\,L \times 0.0125\,M = 0.0025\,mol$

$HCl : 0.01\,L \times 0.1\,M = 0.001\,mol$

	CO_3^{2-}	H^+	HCO_3^-
I	0.0025	0.001	0
C	-0.001	-0.001	0.001
E	0.0015	0	0.001

At 15 mL addition of HCl:$pH = -log(5 \times 10^{-11}) + log(\frac{0.001}{0.0015}) = 10.1$

$CaCO_3$: $0.2\ L \times 0.0125\ M = 0.0025\ mol$

HCl : $0.015\ L \times 0.1\ M = 0.0015\ mol$

	CO_3^{2-}	H^+	HCO_3^-
I	0.0025	0.0015	0
C	-0.0015	-0.0015	0.0015
E	0.001	0	0.0015

At 20 mL addition of HCl:$pH = -log(5 \times 10^{-11}) + log(\frac{5 \times 10^{-4}}{0.002}) = 9.7$

$CaCO_3$: $0.2\ L \times 0.0125\ M = 0.0025\ mol$

HCl : $0.02\ L \times 0.1\ M = 0.002\ mol$

	CO_3^{2-}	H^+	HCO_3^-
I	0.0025	0.002	0
C	-0.002	-0.002	0.002
E	5×10^{-4}	0	0.002

At 25 mL addition of HCl: first equivalence point: $pH = \frac{-log(K_{a1}) - log(K_{a2})}{2} = \frac{-log(4.3 \times 10^{-7}) - log(5.0 \times 10^{-11})}{2} = 8.33$

HCO_3^- : $0.2\ L \times 0.0125\ M = 0.0025\ mol$

HCl : $0.025\ L \times 0.1\ M = 0.0025\ mol$

	HCO_3^-	H^+	H_2CO_3
I	0.0025	0.0025	0
C	-0.0025	-0.0025	0.0025
E	0	0	0.0025

At 30 mL addition of HCl: $pH = -log(4.3 \times 10^{-7}) + log(\frac{0.0025}{0.0005}) = 7.07$

HCO_3^- : $0.2\ L \times 0.0125\ M = 0.0025\ mol$

HCl : $0.03\ L \times 0.1\ M = 0.003$

	HCO_3^-	H^+	H_2CO_3
I	0.0025	0.003	0
C	-0.0025	-0.0025	0.0025
E	0	5×10^{-4}	0.0025

At 35 mL addition of HCl: $pH = -log(4.3 \times 10^{-7}) + log(\frac{0.0025}{0.001}) = 6.76$

HCO_3^- : $0.2\ L \times 0.0125\ M = 0.0025\ mol$

HCl : $0.035\ L \times 0.1\ M = 0.0035$

	HCO_3^-	H^+	H_2CO_3
I	0.0025	0.0035	0

C	-0.0025	-0.0025	0.0025
E	0	0.001	0.0025

At 40 mL addition of HCl: $pH = -log(4.3 \times 10^{-7}) + log(\frac{0.0025}{0.003}) = 6.59$

HCO_3^- : $0.2\ L \times 0.0125\ M = 0.0025\ mol$

HCl : $0.040\ L \times 0.1\ M = 0.004$

	HCO_3^-	H^+	H_2CO_3
I	0.0025	0.004	0
C	-0.0025	-0.0025	0.0025
E	0	0.0015	0.0025

At 45 mL addition of HCl: $pH = -log(4.3 \times 10^{-7}) + log(\frac{0.0025}{0.002}) = 6.46$

HCO_3^- : $0.2\ L \times 0.0125\ M = 0.0025\ mol$

HCl : $0.045\ L \times 0.1\ M = 0.0045$

	HCO_3^-	H^+	H_2CO_3
I	0.0025	0.0045	0
C	-0.0025	-0.0025	0.0025
E	0	0.002	0.0025

At 50 mL addition of HCl: second equivalence point: $pH = 3.86$

HCO_3^- : $0.2\ L \times 0.0125\ M = 0.0025\ mol$

HCl : $0.05\ L \times 0.1\ M = 0.005$

	HCO_3^-	H^+	H_2CO_3
I	0.0025	0.005	0
C	-0.0025	-0.0025	0.0025
E	0	0.0025	0.0025

At 55 mL addition of HCl: $pH = -log(\frac{0.003}{0.055}) = 1.26$

HCO_3^- : $0.2\ L \times 0.0125\ M = 0.0025\ mol$

HCl : $0.055\ L \times 0.1\ M = 0.0055$

	HCO_3^-	H^+	H_2CO_3
I	0.0025	0.0055	0
C	-0.0025	-0.0025	0.0025
E	0	0.003	0.0025

At 60 mL addition of HCl: $pH = -log(\frac{0.0035}{0.06}) = 1.23$

HCO_3^- : $0.2\ L \times 0.0125\ M = 0.0025\ mol$

HCl : $0.06\ L \times 0.1\ M = 0.006$

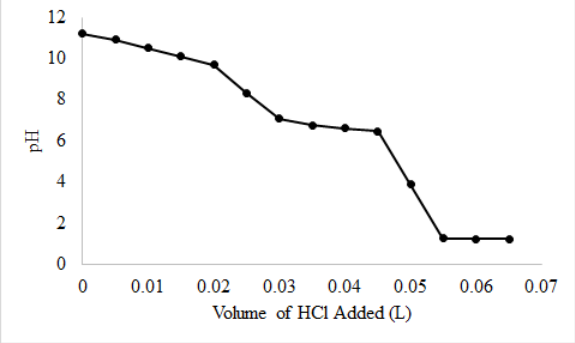
	HCO_3^-	H^+	H_2CO_3
I	0.0025	0.006	0
C	-0.0025	-0.0025	0.0025
E	0	0.0035	0.0025

At 65 mL addition of HCl: $pH = -log(\frac{0.0040}{0.065}) = 1.21$

HCO_3^- : $0.2\,L \times 0.0125\,M = 0.0025\,mol$

HCl : $0.06\,L \times 0.1\,M = 0.006$

	HCO_3^-	H^+	H_2CO_3
I	0.0025	0.0065	0
C	-0.0025	-0.0025	0.0025
E	0	0.0040	0.0025



7.5: Solubility Equilibria

Exercise 7.E.19

1. Write an expression for K_{sp} for each salt.

a. AgI
b. CaF_2
c. $PbCl_2$
d. Ag_2CrO_4

Answer

a. $K_{sp} = [Ag^+][I^-]$
b. $K_{sp} = [Ca^{2+}][F^-]^2$
c. $K_{sp} = [Pb^{2+}][Cl^-]^2$
d. $K_{sp} = [Ag^+]^2[CrO_4^{2-}]$

Exercise 7.E.20

Some species are not represented in a solubility product expression. Why?

Answer

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The solubility constant expression, K_{sp} is an equilibrium constant for a solid substance dissolving in a an aqueous solution. Thus, it is a measure of solubility and species that do not dissolve are not represented in the solubility product expression.

Exercise 7.E.21

How can an ion product be used to determine whether a solution is saturated?

Answer

An ion product can be used to determine whether a solution is saturated as it is compared to K_{sp} where there are three possible conditions for an aqueous solution of an ionic solid:

$Q < K_{sp}$. The solution is unsaturated, and mroe solid can dissolve.

$Q = K_{sp}$. The solution is saturated and at equilibrium.

$Q > K_{sp}$. The solution is supersaturated, and ionic solid will precipitate.

Exercise 7.E.22

Predict the molar solubility of each compound using the K_{sp} values given.

a. Li_3PO_4: 2.37×10^{-11}
b. $Ca(IO_3)_2$: 6.47×10^{-6}
c. $Y(IO_3)_3$: 1.12×10^{-10}

Answer

a. $K_{sp} = [Li^+]^3[PO_4^{3-}] \rightarrow 2.37 \times 10^{-11} = (3x)^3(x) \rightarrow x = 9.68 \times 10^{-4}$

b. $K_{sp} = [Ca^{2+}][IO_3^-]^2 \rightarrow 6.47 \times 10^{-6} = (x)(2x)^2 \rightarrow 1.17 \times 10^{-2}$

c. $K_{sp} = [Y^{3+}][IO_3]^-]^3 \rightarrow 1.12 \times 10^{-10} = (x)(3x)^3 \rightarrow x = 1.42 \times 10^{-3}$

3. $0.750\ L \times \frac{0.0144\ mol}{1\ L} \times \frac{311.199\ g}{1\ mol} = 3.37\ g$

$K_{sp} = [Ag^+]^2[SO_4^{2-}] \rightarrow 1.20 \times 10^{-5} = (2x)^2(x) \rightarrow x = 0.0144$

Exercise 7.E.23

A student prepared 750 mL of a saturated solution of silver sulfate (Ag_2SO_4). How many grams of Ag_2SO_4 does the solution contain? $K_{sp} = 1.20 \times 10^{-5}$.

Answer

$0.750\ L \times \frac{0.0144\ mol}{1\ L} \times \frac{311.199\ g}{1\ mol} = 3.37\ g$

$K_{sp} = [Ag^+]^2[SO_4^{2-}] \rightarrow 1.20 \times 10^{-5} = (2x)^2(x) \rightarrow x = 0.0144$

Exercise 7.E.24

Predict the molar concentration of each species in a saturated aqueous solution.

a. silver(I) bromide, AgBr, $K_{sp} = 5.35 \times 10^{-13}$
b. lead(I) oxalate, PbC_2O_4, $K_{sp} = 8.5 \times 10^{-9}$
c. iron(II) carbonate, $FeCO_3$, $K_{sp} = 3.13 \times 10^{-11}$
d. silver(I) phosphate, Ag_3PO_4, $K_{sp} = 8.89 \times 10^{-17}$
e. copper(I) cyanide, CuCN, $K_{sp} = 3.47 \times 10^{-20}$

Answer

a. $K_{sp} = [Ag^+][Br^-] \rightarrow 5.35 \times 10^{-13} = (x)(x) \rightarrow x = 7.31 \times 10^{-7}$

b. $K_{sp} = [PB^{2+}][C_2O_4] \rightarrow 8.5 \times 10^{-9} = (x)(x) \rightarrow x = 9.2 \times 10^{-5}$

c. $K_{sp} = [Fe^{2+}][CO_3^{2-}] \rightarrow 3.13 \times 10^{-11} = (x)(x) \rightarrow x = 5.60 \times 10^{-6}$

d. $K_{sp} = [Ag^+]^3[PO_4^{3-}] \rightarrow 8.89 \times 10^{-17} = (3x)^3(x) \rightarrow x = 4.26 \times 10^{-5}$

e. $K_{sp} = [Cu][CN] \rightarrow 3.47 \times 10^{-20} = (x)(x) \rightarrow x = 1.86 \times 10^{-10}$

Exercise 7.E.25

From the solubility data given, calculate K_{sp} for each compound.

a. AgI: 2.89 × 10^{-7} g/100 mL
b. SrF_2: 1.22 × 10^{-2} g/100 mL
c. $Pb(OH)_2$: 78 mg/500 mL
d. $BiAsO_4$: 14.4 mg/2.0 L

Answer

a. $K_{sp} = [Ag^+][I^-] = x^2 = (1.23 \times 10^{-8})^2) = 1.52 \times 10^{-16}$

$AgI : (2.89 \times 10^{-7}\ g \times \frac{1\ mol}{234.77\ g} \times \frac{1}{0.1\ L} = 1.23 \times 10^{-8}$

b. $K_{sp} = [Sr^{2+}][F^-]^2] = (x)(2x)^2 = 4x^3 = 4(9.72 \times 10^{-4})^3 = 3.66 \times 10^{-9}$

$SrF_2 = 1.22 \times 10^{-2}\ g \times \frac{1\ mol}{125.62\ g} \times \frac{1}{0.1\ L} = 9.72 \times 10^{-4}$

c. $K_{sp} = [Pb^{2+}][OH^-]^2 = 4x^3 = 4(6.47 \times 10^{-4})^3 = 1.08 \times 10^{-9}$

$Pb(OH)_2 = 0.078\ g \times \frac{1\ mol}{241.21\ g} \times \frac{1}{0.1\ L} = 6.47 \times 10^{-4}$

d. $K_{sp} = [Bi^{3+}][AsO_4^{3-}] = x^2 = (2.05 \times 10^{-5})^2 = 4.21 \times 10^{-10}$

$BiAsO_4 = 0.0144\ g \times \frac{1\ mol}{350.924\ g} \times \frac{1}{2\ L} = 2.05 \times 10^{-5}$

Exercise 7.E.26

You have calculated that 24.6 mg of $BaSO_4$ will dissolve in 1.0 L of water at 25°C. After adding your calculated amount to 1.0 L of water and stirring for several hours, you notice that the solution contains undissolved solid. After carefully filtering the solution and drying the solid, you find that 22.1 mg did not dissolve. According to your measurements, what is the K_{sp} of barium sulfate?

Answer

$K_{sp} = [Ba^{2+}][SO_4^{2-}] = (x)(x) = x^2 = (1.07 \times 10^{-5}\ M)^2 = 1.15 \times 10^{-10}$

$BaSO_4 : (24.6 - 22.1\ mg) \times \frac{1\ g}{1{,}000\ mg} \times \frac{1\ mol}{233.38\ g} \times \frac{1}{1.0\ L} = 1.07 \times 10^{-5}\ M$

Exercise 7.E.27

Explain why the presence of $MgCl_2$ decreases the molar solubility of the sparingly soluble salt $MgCO_3$.

Answer

Because of the common ion effect. Adding a soluble Mg^{2+} salt increases [Mg2+] in solution, and Le Chatelier's principle predicts that this will shift the solubility equilibrium of $MgCO_3$ to the left, decreasing its solubility.

Exercise 7.E.28

The K_{sp} of the phosphate fertilizer $CaHPO_4 \cdot 2H_2O$ is 2.7×10^{-7} at 25°C. What is the molar concentration of a saturated solution? What mass of this compound will dissolve in 3.0 L of water at this temperature?

Answer

$$K_{sp} = [Ca^{2+}][HPO_4^{2-}] \rightarrow 2.7 \times 10^{-7} = x^2 \rightarrow x = 5.2 \times 10^{-4}$$

$$CaHPO4 \cdot 2H2O : 3.0\ L \times \frac{2.7 \times 10^{-7}\ mol}{1\ L} \times \frac{290.1299\ g}{1\ mol} = 2.35 \times 10^{-4}\ g$$

Exercise 7.E.29

Use the data in Reference Table E3 to predict whether precipitation will occur when each pair of solutions is mixed.

a. 150 mL of 0.142 M $Ba(NO_3)_2$ with 200 mL of 0.089 M NaF
b. 250 mL of 0.079 M K_2CrO_4 with 175 mL of 0.087 M $CaCl_2$
c. 300 mL of 0.109 M $MgCl_2$ with 230 mL of 0.073 M $Na_2(C_2O_4)$

Answer

a. $Q = [Ba^{2+}][F^-]^2 = (0.060857)(0.05643)^2 = 1.94 \times 10^{-4} > 1.84 \times 10^{-7}$Therefore, precipitate will form.

$$Ba^{2+} : \frac{(0.150)(0.142)}{0.35} = 0.060857$$

$$F^- : \frac{(0.25)(0.079)}{0.35} = 0.05643$$

b. \(Q=[K^{+}][Cl^{-}]=(0.0465)(0.0358)=1.66 \times 10^{-3}<21.7. Therefore, precipitate will not form.

$$K^+ : \frac{(0.25)(0.079)}{0.425} = 0.0465$$

$$Cl^- : \frac{(0.175)(0.087)}{0.425} = 0.0358$$

c. $Q = [Mg^{2+}][C_2O_4^{2-}] = (0.0617)(0.0317) = 1.95 \times 10^{-3} > 8.5 \times 10^{-5}$ Therefore, precipitate will form.

$$Mg^{2+} : \frac{(0.3)(0.109)}{0.53} = 0.0617$$

$$C_2O_4 : \frac{(0.23)(0.073)}{0.53} = 0.0317$$

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7.S: Buffers, Titrations and Solubility Equilibria (Study Guide)

7.1: Acid-Base Buffers

- The common-ion effect argues that the dissociation of a weak electrolyte is decreased by adding a strong electrolyte to the solution that has a **common ion** with the weak electrolyte.
- Buffers are solutions that resist a change in pH

- Buffers have both acidic and basic species to neutralize H^+ and OH^- ions
- Acid dissociation equilibrium in buffered solution

$$HX(aq) \rightleftharpoons H^+(aq) + X^-(aq)$$

with

$$K_a = \frac{[H^+][X^-]}{[HX]}$$

or

$$[H^+] = K_a \frac{[HX]}{[X^-]}$$

  - pH determined by: value of K_a and the ratio of $[HX]/[X^-]$
  - if OH^- added:
    - $$OH^-(aq) + HX(aq) \rightleftharpoons H_2O(l) + X^-(aq)$$
      - Therefore [HX] decreases and $[X^-]$ increases
      - if amounts of HX and X^- present are very much larger than the amount of OH^- added, then the ratio of $[HX]/[X^-]$ will not change much, and so the increase in pH due to the added hydroxide ion is rather small
  - when [HX] and $[X^-]$ are about the same, buffers are most effective: i.e., when $[H^+] = K_a$

7.2 Practical Aspects of Buffers

- buffer capacity – amount of acid or base buffer can neutralize before the pH changes considerably
- capacity depends on amount of acid or base in buffer
- pH depends on K_a for acid and relative concentrations of the acid and base
- Henderson-Hasselbalch Approximation:

$$pH = pK_a + \log_{10} \frac{[base]}{[acid]}$$

- [base] and [acid] = concentrations of conjugate acid-base pair
- when [base]=[acid], pH = pK_a
- can use initial concentrations of acid and base components of buffer directly into equation

7.3: Acid-Base Titrations

- solution containing a known [base] added to an acid or acid solution added to base
- acid-base indicators used to signal equivalence point, choose indicator that changes colour as close to equivalence point as possible
- titration curve – pH vs Volume

Strong Acid – Strong base Titrations

- pH starts out low ends high
- pH before equivalence point is pH of acid not neutralized by base
- pH at equivalence point is pH of solution
- pH equals 7.00
- for strong base titrations, the pH starts high ends low

The Addition of a Strong Base to a Weak Acid

- Reactions between weak acid and strong base goes to completion
- calculating pH before equivalence point
  - stoichiometric calculations: allow strong base to react to completion producing a solution containing a weak acid and its conjugate base
- equilibrium calculation: use K_a and equilibrium expression to find equilibrium concentrations of the weak acid and its conjugate base, and H^+

Titration Curves for Weak Acids or Weak Bases

- Differences between strong acid-strong base titrations

1. solution of weak acid as higher initial pH than solution of a strong acid with same concentration
2. solution of weak acid rises more rapidly in early part of titration and more slowly as it reached the equivalence point
3. pH is not 7.00 at equivalence point

- before equivalence point solution has mixture of weak acid and its salt
- also called the buffer region of curve
- at equivalence point solution contains only salt
- weakly basic due to hydrolysis of anion
- after equivalence point solution has mixture of salt and excess strong base
- pH determined by [base]

- Titrations of Polyprotic Acids
  - reaction occurs in series of steps
  - titration curve shows multiple equivalence points

7.4: **Solving Titration Problems**

- Solving weak acid or base titration problems, look at where you are on the titration curve
  - initial pH before titrant added, acid or base equilibrium calculation
  - buffer region, use H-H
  - pH at equivalence point look at salt solution
  - pH after equivalence point, excess of titrant added
  - make sure to remember volume changes

7.5: Solubility Equilibria

- The Solubility-Product Constant, K_{sp}
- saturated solution – dissolved and undissolved solute are at equilibrium
- expressed by g/L
- molar solubility – moles of solute dissolved to form a liter of saturated solution (mol/L)
- K_{sp} equilibrium constant for the equilibrium between an ionic solid and its saturated solution
- Solubility of compound (g/L) à molar solubility of compound (mol/L) à [molar] of ions à K_{sp} of ions
- solubility affected by temperature and presence of other solutes. The solubility of ionic compound affected by:
- the presence of common ions
- pH of solution
- presence of complexing agent

- solubility of slightly soluble salt decreases when a second solute has a common ion

- solubility of any ionic compound affected if solution is acidic or basic
- change only noticeable if both ions are moderately acidic or basic
- solubility of slightly soluble salts containing basic anions increase as $[H^+]$ increases (as pH is lowered)
- the more basic an anion is, the greater the solubility will be affected by pH

- Q = ion product

- If Q > K_{sp}, precipitation occurs until Q = K_{sp}
- If Q = K_{sp}, equilibrium exists, have a saturated solution
- If Q < K_{sp}, solid dissolves until Q = K_{sp}

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CHAPTER OVERVIEW

8: Entropy and Free Energy

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General Chemistry

Among the many capabilities of chemistry is its ability to predict if a process will occur under specified conditions. Thermodynamics, the study of relationships between the energy and work associated with chemical and physical processes, provides this predictive ability. Previous chapters in this text have described various applications of thermochemistry, an important aspect of thermodynamics concerned with the heat flow accompanying chemical reactions and phase transitions. This chapter will introduce additional thermodynamic concepts, including those that enable the prediction of any chemical or physical changes under a given set of conditions.

8.1: Spontaneity
8.2: Entropy
8.3: The Second and Third Laws of Thermodynamics
8.4: Gibbs Free Energy
8.E: Entropy and Free Energy (Exercises)
8.S: Entropy and Free Energy (Study Guide)

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8.1: Spontaneity

Learning Objectives

- Distinguish between spontaneous and nonspontaneous processes
- Describe the dispersal of matter and energy that accompanies certain spontaneous processes

In this section, consider the differences between two types of changes in a system: Those that occur spontaneously and those that occur only with the continuous input of energy. In doing so, we'll gain an understanding as to why some systems are naturally inclined to change in one direction under certain conditions. We'll also gain insight into how the spontaneity of a process affects the distribution of energy and matter within the system.

8.1.1: Spontaneous and Nonspontaneous Processes

Processes have a natural tendency to occur in one direction under a given set of conditions. Water will naturally flow downhill, but uphill flow requires outside intervention such as the use of a pump. A spontaneous process is one that occurs naturally under certain conditions. A nonspontaneous process, on the other hand, will not take place unless it is "driven" by the continual input of energy from an external source. A process that is spontaneous in one direction under a particular set of conditions is nonspontaneous in the reverse direction. At room temperature and typical atmospheric pressure, for example, ice will spontaneously melt, but water will not spontaneously freeze.

The spontaneity of a process is *not* correlated to the speed of the process. A spontaneous change may be so rapid that it is essentially instantaneous or so slow that it cannot be observed over any practical period of time. To illustrate this concept, consider the decay of radioactive isotopes, a topic more thoroughly treated in the chapter on nuclear chemistry. Radioactive decay is by definition a spontaneous process in which the nuclei of unstable isotopes emit radiation as they are converted to more stable nuclei. All the decay processes occur spontaneously, but the rates at which different isotopes decay vary widely. Technetium-99m is a popular radioisotope for medical imaging studies that undergoes relatively rapid decay and exhibits a half-life of about six hours. Uranium-238 is the most abundant isotope of uranium, and its decay occurs much more slowly, exhibiting a half-life of more than four billion years (Figure 8.1.1).

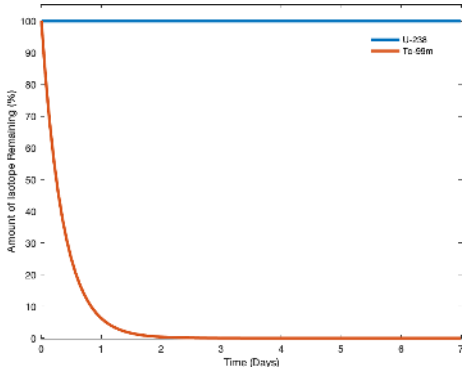


Figure 8.1.1: Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed. (CC by 4.0; Morgan Johnson via LibreTexts)

Two curves are shown to represent U-238 and Tc-99m respectively. The vertical axes represents the percentage of isotope remaining and the horizontal axes is the time that has elapsed in days.

As another example, consider the conversion of diamond into graphite (Figure 8.1.2).

$$\mathrm{C(s,\,diamond)} \longrightarrow \mathrm{C(s,\,graphite)} \tag{8.1.1}$$

The phase diagram for carbon indicates that graphite is the stable form of this element under ambient atmospheric pressure, while diamond is the stable allotrope at very high pressures, such as those present during its geologic formation. Thermodynamic calculations of the sort described in the last section of this chapter indicate that the conversion of diamond to graphite at ambient pressure occurs spontaneously, yet diamonds are observed to exist, and persist, under these conditions. Though the process is spontaneous under typical ambient conditions, its rate is extremely slow, and so for all practical purposes diamonds are indeed "forever." Situations such as these emphasize the important distinction between the thermodynamic and the kinetic aspects of a process. In this particular case, diamonds are said to be *thermodynamically unstable* but *kinetically stable* under ambient conditions.

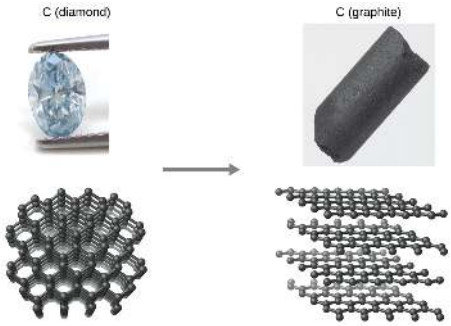


Figure 8.1.2: The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as graphitization, and its rate can be increased to easily measurable values at temperatures in the 1000–2000 K range. (credit "diamond" photo: modification of work by "Fancy Diamonds"/Flickr; credit "graphite" photo: modification of work by images-of-elements.com/carbon.php)

Comparison of diamond and graphite shown in its physical form as well as its molecular arrangement respectively.

8.1.2: Dispersal of Matter and Energy

As we extend our discussion of thermodynamic concepts toward the objective of predicting spontaneity, consider now an isolated system consisting of two flasks connected with a closed valve. Initially there is an ideal gas on the left and a vacuum on the right (Figure 8.1.3). When the valve is opened, the gas spontaneously expands to fill both flasks. Recalling the definition of pressure-volume work from the chapter on thermochemistry, note that no work has been done because the pressure in a vacuum is zero.

$$w = -P\Delta V \tag{8.1.2}$$

$$= 0 \;\; (\mathrm{P} = 0 \text{ in a vaccum}) \tag{8.1.3}$$

Note as well that since the system is isolated, no heat has been exchanged with the surroundings (q = 0). The first law of thermodynamics confirms that there has been no change in the system's internal energy as a result of this process.

$$\Delta U = q + w \qquad \text{(First Law of Thermodynamics)}$$
$$= 0 + 0 = 0 \qquad (8.1.4)$$

The spontaneity of this process is therefore not a consequence of any change in energy that accompanies the process. Instead, the movement of the gas appears to be related to the greater, more *uniform dispersal of matter* that results when the gas is allowed to expand. Initially, the system was comprised of one flask containing matter and another flask containing nothing. After the spontaneous process took place, the matter was distributed both more widely (occupying twice its original volume) and more uniformly (present in equal amounts in each flask).

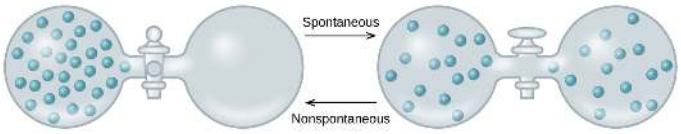


Figure 8.1.3: An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.
When the valve is closed, all of the gas molecules accumlating only in one side of the flask. The diagram with the open valve shows gas being equally distributed among the two flasks. The dispersion of the gas is labeled as spontaneous while the reverse is labeled as non spontaneous.

Now consider two objects at different temperatures: object X at temperature T_X and object Y at temperature T_Y, with $T_X > T_Y$ (Figure 8.1.4). When these objects come into contact, heat spontaneously flows from the hotter object (X) to the colder one (Y). This corresponds to a loss of thermal energy by X and a gain of thermal energy by Y.

$$q_X < 0 \quad \text{and} \quad q_Y = -q_X > 0 \qquad (8.1.5)$$

From the perspective of this two-object system, there was no net gain or loss of thermal energy, rather the available thermal energy was redistributed among the two objects. This spontaneous process resulted in a *more uniform dispersal of energy*.



Figure 8.1.4:When two objects at different temperatures come in contact, heat spontaneously flows from the hotter to the colder object.
Two separated blocks. One is labeled X and the other labeled Y. The diagram next to it shows the two blocks in contact with one another.

As illustrated by the two processes described, an important factor in determining the spontaneity of a process is the extent to which it changes the dispersal or distribution of matter and/or energy. In each case, a spontaneous process took place that resulted in a more uniform distribution of matter or energy.

Example 8.1.1: Redistribution of Matter during a Spontaneous Process

Describe how matter and energy are redistributed when the following spontaneous processes take place:

a. A solid sublimes.
b. A gas condenses.
c. A drop of food coloring added to a glass of water forms a solution with uniform color.

Solution



Figure 8.1.5:(credit a: modification of work by Jenny Downing; credit b: modification of work by “Fuzzy Gerdes”/Flickr; credit c: modification of work by Sahar Atwa)
This figure has three photos labeled, “a,” “b,” and “c.” Photo a shows a glass with dry ice in water. There is a thick vapor coming from the top of the glass. Photo b shows water forming outside of a glass containing cold beverage. Photo c shows a sealed container that holds a red liquid.

a. *Sublimation* is the conversion of a solid (relatively high density) to a gas (much lesser density). This process yields a much greater dispersal of matter, since the molecules will occupy a much greater volume after the solid-to-gas transition. However, an input of energy from the surroundings ss required for the molecules to leave the solid phase and enter the gas phase.
b. *Condensation* is the conversion of a gas (relatively low density) to a liquid (much greater density). This process yields a much lesser dispersal of matter, since the molecules will occupy a much lesser volume after the gas-to-liquid transition. As the gas molecules move together to form the droplets of liquid, they form intermolecular forces and thus release energy to the surroundings.
c. The process in question is *dilution*. The food dye molecules initially occupy a much smaller volume (the drop of dye solution) than they occupy once the process is complete (in the full glass of water). The process therefore entails a greater dispersal of matter. The process may also yield a more uniform dispersal of matter, since the initial state of the system involves two regions of different dye concentrations (high in the drop, zero in the water), and the final state of the system contains a single dye concentration throughout. This process can occur with out a change in energy because the molecules have kinetic energy relative to the temperature of the water, and so will be constantly in motion.

Exercise 8.1.1

Describe how matter and energy are redistributed when you empty a canister of compressed air into a room.

Answer

This process entails both a greater and more uniform dispersal of matter as the compressed air in the canister is permitted to expand into the lower-pressure air of the room. The process also requires an input of energy to disrupt the intermolecular forces between the closely-spaced gas molecules that are originally compressed into the container. If you were to touch the nozzle of the canister, you would notice that it is cold because the exiting molecules are taking energy away from their surroundings, and the canister is part of the surroundings.

Summary

Chemical and physical processes have a natural tendency to occur in one direction under certain conditions. A spontaneous process occurs without the need for a continual input of energy from some external source, while a nonspontaneous process requires such. Systems undergoing a spontaneous process may or may not experience a gain or loss of energy, but they will experience a change in the way matter and/or energy is distributed within the system. In this section we have only discussed nuclear decay, physical changes of pure substances, and macroscopic events such as water flowing downhill. In the following sections we will discuss mixtures and chemical reactions, situations in which the description of sponteneity becomes more challenging.

Glossary

nonspontaneous process
process that requires continual input of energy from an external source

spontaneous change
process that takes place without a continuous input of energy from an external source

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8.2: Entropy

Learning Objectives

- Define entropy
- Explain the relationship between entropy and the number of microstates
- Predict the sign of the entropy change for chemical and physical processes

In 1824, at the age of 28, Nicolas Léonard Sadi Carnot (Figure 8.2.2) published the results of an extensive study regarding the efficiency of steam heat engines. In a later review of Carnot's findings, Rudolf Clausius introduced a new thermodynamic property that relates the spontaneous heat flow accompanying a process to the temperature at which the process takes place. This new property was expressed as the ratio of the *reversible* heat (q_{rev}) and the kelvin temperature (T). The term reversible process refers to a process that takes place at such a slow rate that it is always at equilibrium and its direction can be changed (it can be "reversed") by an infinitesimally small change is some condition. Note that the idea of a reversible process is a formalism required to support the development of various thermodynamic concepts; no real processes are truly reversible, rather they are classified as *irreversible*.

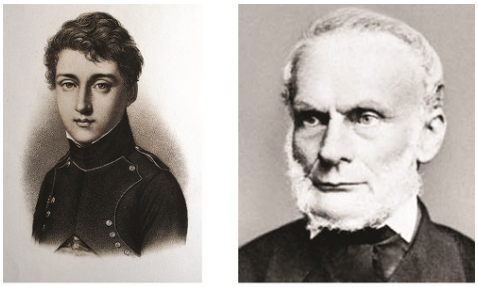


Figure 8.2.1: (a) Nicholas Léonard Sadi Carnot's research into steam-powered machinery and (b) Rudolf Clausius's later study of those findings led to groundbreaking discoveries about spontaneous heat flow processes.

Similar to other thermodynamic properties, this new quantity is a state function, and so its change depends only upon the initial and final states of a system. In 1865, Clausius named this property entropy (S) and defined its change for any process as the following:

$$\Delta S = \frac{q_{\text{rev}}}{T} \tag{8.2.1}$$

The entropy change for a real, irreversible process is then equal to that for the theoretical reversible process that involves the same initial and final states.

8.2.1: Entropy and Microstates

Following the work of Carnot and Clausius, Ludwig Boltzmann developed a molecular-scale statistical model that related the entropy of a system to the number of *microstates* possible for the system. A microstate (Ω) is a specific configuration of the locations and energies of the atoms or molecules that comprise a system like the following:

$$S = k \ln \Omega \tag{8.2.2}$$

Here k is the Boltzmann constant and has a value of $1.38 \times 10^{-23}\ J/K$.

As for other state functions, the change in entropy for a process is the difference between its final (S_f) and initial (S_i) values:

$$\begin{aligned} \Delta S &= S_{\text{f}} - S_{\text{i}} \\ &= k \ln \Omega_{\text{f}} - k \ln \Omega_{\text{i}} \\ &= k \ln \frac{\Omega_{\text{f}}}{\Omega_{\text{i}}} \end{aligned} \tag{8.2.3}$$

For processes involving an increase in the number of microstates of the system, $\Omega_f > \Omega_i$, the entropy of the system increases, $\Delta S > 0$. Conversely, processes that reduce the number of microstates in the system, $\Omega_f < \Omega_i$, yield a decrease in system entropy,

$\Delta S < 0$. This molecular-scale interpretation of entropy provides a link to the probability that a process will occur as illustrated in the next paragraphs.

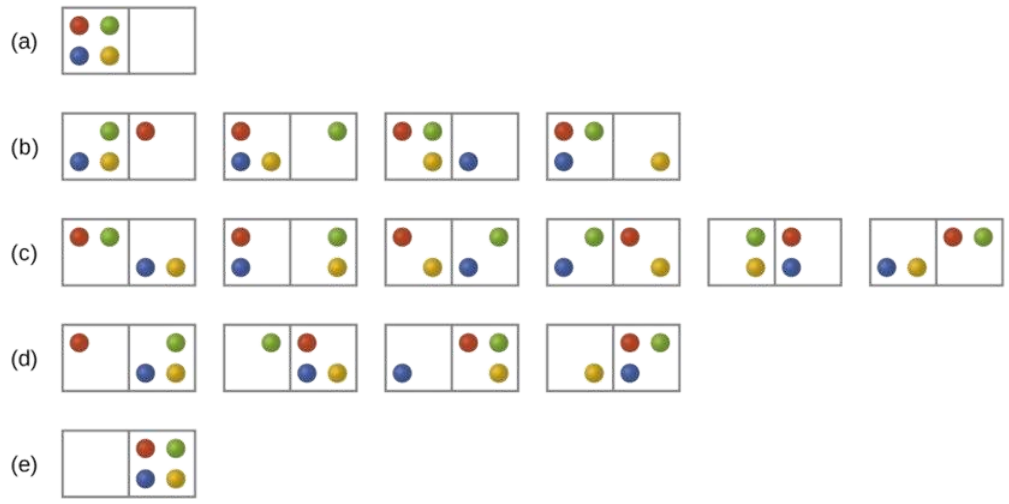


Figure 8.2.2: The sixteen microstates associated with placing four particles in two boxes are shown. The microstates are collected into five distributions—(a), (b), (c), (d), and (e)—based on the numbers of particles in each box.

Consider the general case of a system comprised of *N* particles distributed among *n* boxes. The number of microstates possible for such a system is n^N. For example, distributing four particles among two boxes will result in 2^4 = 16 different microstates as illustrated in Figure 8.2.2. Microstates with equivalent particle arrangements (not considering individual particle identities) are grouped together and are called *distributions* (sometimes called macrostates or configurations). The probability that a system will exist with its components in a given distribution is proportional to the number of microstates within the distribution. Since entropy increases logarithmically with the number of microstates, *the most probable distribution is therefore the one of greatest entropy*.

For this system, the most probable configuration is one of the six microstates associated with distribution (c) where the particles are evenly distributed between the boxes, that is, a configuration of two particles in each box. The probability of finding the system in this configuration is

$$\frac{6}{16} = \frac{3}{8}$$

The least probable configuration of the system is one in which all four particles are in one box, corresponding to distributions (a) and (e), each with a probability of

$$\frac{1}{16}$$

The probability of finding all particles in only one box (either the left box or right box) is then

$$\left(\frac{1}{16} + \frac{1}{16}\right) = \frac{2}{16} = \frac{1}{8}$$

As you add more particles to the system, the number of possible microstates increases exponentially (2^N). A macroscopic (laboratory-sized) system would typically consist of moles of particles ($N \sim 10^{23}$), and the corresponding number of microstates would be staggeringly huge. Regardless of the number of particles in the system, however, the distributions in which roughly equal numbers of particles are found in each box are always the most probable configurations.

> *The most probable distribution is therefore the one of greatest entropy.*

The previous description of an ideal gas expanding into a vacuum is a macroscopic example of this particle-in-a-box model. For this system, the most probable distribution is confirmed to be the one in which the matter is most uniformly dispersed or distributed between the two flasks. The spontaneous process whereby the gas contained initially in one flask expands to fill both flasks equally therefore yields an increase in entropy for the system.

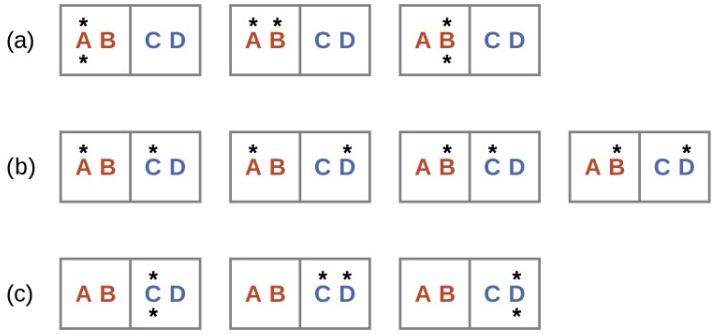
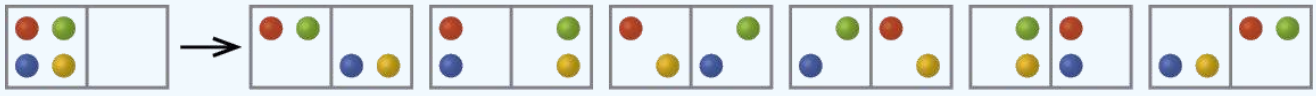


Figure 8.2.3: This shows a microstate model describing the flow of heat from a hot object to a cold object. (a) Before the heat flow occurs, the object comprised of particles **A** and **B** contains both units of energy and as represented by a distribution of three microstates. (b) If the heat flow results in an even dispersal of energy (one energy unit transferred), a distribution of four microstates results. (c) If both energy units are transferred, the resulting distribution has three microstates.

A similar approach may be used to describe the spontaneous flow of heat. Consider a system consisting of two objects, each containing two particles, and two units of energy (represented as "*") in Figure 8.2.3. The hot object is comprised of particles **A** and **B** and initially contains both energy units. The cold object is comprised of particles **C** and **D**, which initially has no energy units. Distribution (a) shows the three microstates possible for the initial state of the system, with both units of energy contained within the hot object. If one of the two energy units is transferred, the result is distribution (b) consisting of four microstates. If both energy units are transferred, the result is distribution (c) consisting of three microstates. And so, we may describe this system by a total of ten microstates. The probability that the heat does not flow when the two objects are brought into contact, that is, that the system remains in distribution (a), is $\frac{3}{10}$. More likely is the flow of heat to yield one of the other two distribution, the combined probability being $\frac{7}{10}$. The most likely result is the flow of heat to yield the uniform dispersal of energy represented by distribution (b), the probability of this configuration being $\frac{4}{10}$. As for the previous example of matter dispersal, extrapolating this treatment to macroscopic collections of particles dramatically increases the probability of the uniform distribution relative to the other distributions. This supports the common observation that placing hot and cold objects in contact results in spontaneous heat flow that ultimately equalizes the objects' temperatures. And, again, this spontaneous process is also characterized by an increase in system entropy.

✔ Example 8.2.1: Determination of ΔS

Consider the system shown here. What is the change in entropy for a process that converts the system from distribution (a) to (c)?



Solution

We are interested in the following change:

The initial number of microstates is one, the final six:

$$\Delta S = k \ln \frac{\Omega_c}{\Omega_a}$$

$$= 1.38 \times 10^{-23}\ J/K \times \ln \frac{6}{1}$$

$$= 2.47 \times 10^{-23}\ J/K$$

The sign of this result is consistent with expectation; since there are more microstates possible for the final state than for the initial state, the change in entropy should be positive.

Exercise 8.2.1

Consider the system shown in Figure 8.2.3. What is the change in entropy for the process where *all* the energy is transferred from the hot object (**AB**) to the cold object (**CD**)?

Answer

0 J/K

8.2.2: Predicting the Sign of ΔS

The relationships between entropy, microstates, and matter/energy dispersal described previously allow us to make generalizations regarding the relative entropies of substances and to predict the sign of entropy changes for chemical and physical processes. Consider the phase changes illustrated in Figure 8.2.4. In the solid phase, the atoms or molecules are restricted to nearly fixed positions with respect to each other and are capable of only modest oscillations about these positions. With essentially fixed locations for the system's component particles, the number of microstates is relatively small. In the liquid phase, the atoms or molecules are free to move over and around each other, though they remain in relatively close proximity to one another. This increased freedom of motion results in a greater variation in possible particle locations, so the number of microstates is correspondingly greater than for the solid. As a result, $S_{liquid} > S_{solid}$ and the process of converting a substance from solid to liquid (melting) is characterized by an increase in entropy, $\Delta S > 0$. By the same logic, the reciprocal process (freezing) exhibits a decrease in entropy, $\Delta S < 0$.

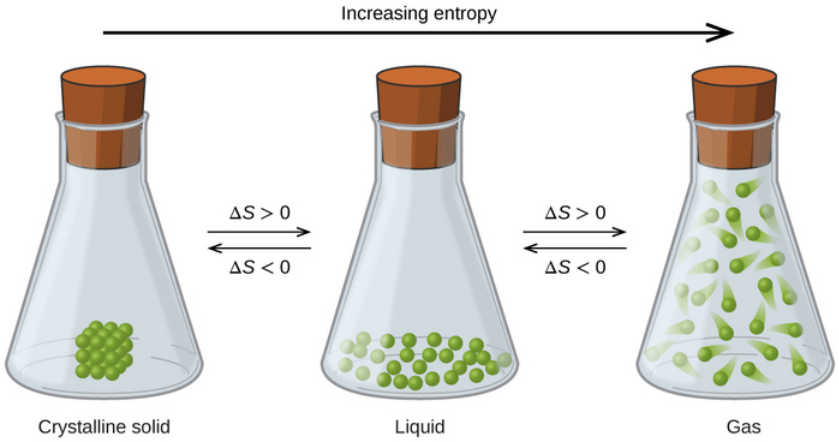


Figure 8.2.4: The entropy of a substance increases (ΔS > 0) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. The entropy decreases (ΔS < 0) as the substance transforms from a gas to a liquid and then to a solid.

Now consider the vapor or gas phase. The atoms or molecules occupy a *much* greater volume than in the liquid phase; therefore each atom or molecule can be found in many more locations than in the liquid (or solid) phase. Consequently, for any substance, $S_{gas} > S_{liquid} > S_{solid}$, and the processes of vaporization and sublimation likewise involve increases in entropy, $\Delta S > 0$. Likewise, the reciprocal phase transitions, condensation and deposition, involve decreases in entropy, $\Delta S < 0$.

According to kinetic-molecular theory, the temperature of a substance is proportional to the average kinetic energy of its particles. Raising the temperature of a substance will result in more extensive vibrations of the particles in solids and more rapid translations of the particles in liquids and gases. At higher temperatures, the distribution of kinetic energies among the atoms or molecules of the substance is also broader (more dispersed) than at lower temperatures. Thus, the entropy for any substance increases with temperature (Figure 8.2.5).

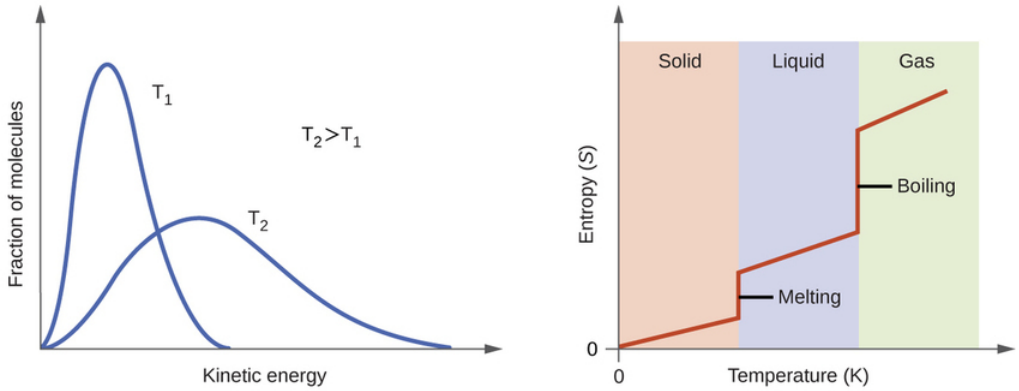


Figure 8.2.5: Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance melts or vaporizes, it experiences a significant increase in entropy.

The entropy of a substance is influenced by structure of the particles (atoms or molecules) that comprise the substance. With regard to atomic substances, heavier atoms possess greater entropy at a given temperature than lighter atoms, which is a consequence of the relation between a particle's mass and the spacing of quantized translational energy levels (which is a topic beyond the scope of our treatment). For molecules, greater numbers of atoms (regardless of their masses) increase the ways in which the molecules can vibrate and thus the number of possible microstates and the system entropy.

Finally, variations in the types of particles affects the entropy of a system. Compared to a pure substance, in which all particles are identical, the entropy of a mixture of two or more different particle types is greater. This is because of the additional orientations and interactions that are possible in a system comprised of nonidentical components. For example, when a solid dissolves in a liquid, the particles of the solid experience both a greater freedom of motion and additional interactions with the solvent particles. This corresponds to a more uniform dispersal of matter and energy and a greater number of microstates. The process of dissolution therefore involves an increase in entropy, $\Delta S > 0$.

Considering the various factors that affect entropy allows us to make informed predictions of the sign of ΔS for various chemical and physical processes as illustrated in Example .

✔ Example 8.2.2: Predicting the Sign of ΔS

Predict the sign of the entropy change for the following processes. Indicate the reason for each of your predictions.

a. One mole liquid water at room temperature $\longrightarrow$ one mole liquid water at 50 °C
b. $\mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq) \longrightarrow \mathrm{AgCl}(s)$
c. $\mathrm{C_6H_6}(l) + \dfrac{15}{2}\mathrm{O_2}(g) \longrightarrow 6\,\mathrm{CO_2}(g) + 3\,\mathrm{H_2O}(l)$
d. $\mathrm{NH_3}(s) \longrightarrow \mathrm{NH_3}(l)$

Solution

a. positive, temperature increases
b. negative, reduction in the number of ions (particles) in solution, decreased dispersal of matter
c. negative, net decrease in the amount of gaseous species
d. positive, phase transition from solid to liquid, net increase in dispersal of matter

? Exercise 8.2.2

Predict the sign of the enthalpy change for the following processes. Give a reason for your prediction.

a. $\mathrm{NaNO_3}(s) \longrightarrow \mathrm{Na^+}(aq) + \mathrm{NO_3^-}(aq)$
b. the freezing of liquid water
c. $\mathrm{CO_2}(s) \longrightarrow \mathrm{CO_2}(g)$
d. $\mathrm{CaCO}(s) \longrightarrow \mathrm{CaO}(s) + \mathrm{CO_2}(g)$

Answer a

Positive; The solid dissolves to give an increase of mobile ions in solution.

Answer b

Negative; The liquid becomes a more ordered solid.

Answer c

Positive; The relatively ordered solid becomes a gas

Answer d

Positive; There is a net production of one mole of gas.

Summary

Entropy (\(S\)) is a state function that can be related to the number of microstates for a system (the number of ways the system can be arranged) and to the ratio of reversible heat to kelvin temperature. It may be interpreted as a measure of the dispersal or distribution of matter and/or energy in a system, and it is often described as representing the “disorder” of the system. For a given substance, $S_{solid} < S_{liquid} \ll S_{gas}$ in a given physical state at a given temperature, entropy is typically greater for heavier atoms or more complex molecules. Entropy increases when a system is heated and when solutions form. Using these guidelines, the sign of entropy changes for some chemical reactions may be reliably predicted.

8.2.3: Key Equations

- $\Delta S = \frac{q_{\text{rev}}}{T}$
- $S = k \ln W$
- $\Delta S = k \ln \frac{W_{\text{f}}}{W_{\text{i}}}$

Glossary

entropy (*S*)

state function that is a measure of the matter and/or energy dispersal within a system, determined by the number of system microstates often described as a measure of the disorder of the system

microstate (*W*)

possible configuration or arrangement of matter and energy within a system

reversible process

process that takes place so slowly as to be capable of reversing direction in response to an infinitesimally small change in conditions; hypothetical construct that can only be approximated by real processes removed

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8.3: The Second and Third Laws of Thermodynamics

Learning Objectives

- State and explain the second and third laws of thermodynamics
- Calculate entropy changes for phase transitions and chemical reactions under standard conditions

8.3.1: The Second Law of Thermodynamics

In the quest to identify a property that may reliably predict the spontaneity of a process, we have identified a very promising candidate: entropy. Processes that involve an increase in entropy *of the system* ($\Delta S > 0$) are very often spontaneous; however, examples to the contrary are plentiful. By expanding consideration of entropy changes to include *the surroundings*, we may reach a significant conclusion regarding the relation between this property and spontaneity. In thermodynamic models, the system and surroundings comprise everything, that is, the universe, and so the following is true:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \tag{8.3.1}$$

To illustrate this relation, consider again the process of heat flow between two objects, one identified as the system and the other as the surroundings. There are three possibilities for such a process:

1. The objects are at different temperatures, and heat flows from the hotter to the cooler object. *This is always observed to occur spontaneously.* Designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{\text{sys}} = \frac{-q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T_{\text{surr}}} \tag{8.3.2}$$

   The arithmetic signs of q_{rev} denote the loss of heat by the system and the gain of heat by the surroundings. Since $T_{\text{sys}} > T_{\text{surr}}$ in this scenario, the magnitude of the entropy change for the surroundings will be greater than that for the system, and so the sum of ΔS_{sys} and ΔS_{surr} will yield a positive value for ΔS_{univ}. *This process involves an increase in the entropy of the universe.*
2. The objects are at different temperatures, and heat flows from the cooler to the hotter object. *This is never observed to occur spontaneously.* Again designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{-q_{\text{rev}}}{T_{\text{surr}}} \tag{8.3.3}$$

   The arithmetic signs of q_{rev} denote the gain of heat by the system and the loss of heat by the surroundings. The magnitude of the entropy change for the surroundings will again be greater than that for the system, but in this case, the signs of the heat changes will yield a negative value for ΔS_{univ}. *This process involves a decrease in the entropy of the universe.*
3. The temperature difference between the objects is infinitesimally small, $T_{\text{sys}} \approx T_{\text{surr}}$, and so the heat flow is thermodynamically reversible. See the previous section's discussion). In this case, the system and surroundings experience entropy changes that are equal in magnitude and therefore sum to yield a value of zero for ΔS_{univ}. *This process involves no change in the entropy of the universe.*

These results lead to a profound statement regarding the relation between entropy and spontaneity known as the second law of thermodynamics: *all spontaneous changes cause an increase in the entropy of the universe.* A summary of these three relations is provided in Table 8.3.1.

Table 8.3.1: The Second Law of Thermodynamics

$\Delta S_{\text{univ}} > 0$	spontaneous
$\Delta S_{\text{univ}} < 0$	nonspontaneous (spontaneous in opposite direction)
$\Delta S_{\text{univ}} = 0$	reversible (system is at equilibrium)

All spontaneous changes cause an increase in the entropy of the universe.

For many realistic applications, the surroundings are vast in comparison to the system. In such cases, the heat gained or lost by the surroundings as a result of some process represents a very small, nearly infinitesimal, fraction of its total thermal energy. For

example, combustion of a fuel in air involves transfer of heat from a system (the fuel and oxygen molecules undergoing reaction) to surroundings that are infinitely more massive (the earth's atmosphere). As a result, q_{surr} is a good approximation of q_{rev}, and the second law may be stated as the following:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \tag{8.3.4}$$

We may use this equation to predict the spontaneity of a process as illustrated in Example 8.3.1.

Example 8.3.1: Will Ice Spontaneously Melt?

The entropy change for the process

$$\mathrm{H_2O}(s) \longrightarrow \mathrm{H_2O}(l)$$

is 22.1 J/K and requires that the surroundings transfer 6.00 kJ of heat to the system. Is the process spontaneous at −10.00 °C? Is it spontaneous at +10.00 °C?

Solution

We can assess the spontaneity of the process by calculating the entropy change of the universe. If ΔS_{univ} is positive, then the process is spontaneous. At both temperatures, ΔS_{sys} = 22.1 J/K and q_{surr} = −6.00 kJ.

At −10.00 °C (263.15 K), the following is true:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \\ &= 22.1\ \text{J/K} + \frac{-6.00 \times 10^3\ \text{J}}{263.15\ \text{K}} = -0.7\ \text{J/K}\end{aligned}$$

$S_{univ} < 0$, so melting is nonspontaneous (*not* spontaneous) at **−10.0 °C**.

At 10.00 °C (283.15 K), the following is true:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \\ &= 22.1\ J/K + \frac{-6.00 \times 10^3\ J}{283.15\ K} = +0.9\ J/K\end{aligned}$$

$S_{univ} > 0$, so melting *is* spontaneous at **10.00 °C.**

Exercise 8.3.1

Using this information, determine if liquid water will spontaneously freeze at the same temperatures. What can you say about the values of S_{univ}?

Answer

Entropy is a state function, and freezing is the opposite of melting. At −10.00 °C spontaneous, +0.7 J/K; at +10.00 °C nonspontaneous, −0.9 J/K.

8.3.2: The Third Law of Thermodynamics

The previous section described the various contributions of matter and energy dispersal that contribute to the entropy of a system. With these contributions in mind, consider the entropy of a pure, perfectly crystalline solid possessing no kinetic energy (that is, at a temperature of absolute zero, 0 K). This system may be described by a single microstate, as its purity, perfect crystallinity and complete lack of motion means there is but one possible location for each identical atom or molecule comprising the crystal (W = 1). According to the Boltzmann equation, the entropy of this system is zero.

$$S = k \ln W = k \ln(1) = 0 \tag{8.3.5}$$

This limiting condition for a system's entropy represents the third law of thermodynamics: *the entropy of a pure, perfect crystalline substance at 0 K is zero.*

Definition: Third Law of Thermodynamics

The entropy of a pure, perfect crystalline substance at 0 K is zero.

We can make careful calorimetric measurements to determine the temperature dependence of a substance's entropy and to derive absolute entropy values under specific conditions. Standard entropies are given the label S°_{298} for values determined for one mole of substance, isolated in its pure form in its own container, at a pressure of 1 bar and a temperature of 298 K.

Definition: Term

The thermodynamic standard state of a substance refers to an isolated sample of that substance, in its own container, at 1.000 bar (0.9869 atm) pressure. If the substance is a solute, the most common standard state is one in which the concentration of the solute is 1.000 molal (sometimes approximated with 1.000 M). There is no defined temperature for the standard state, but most discussions about standard state assume that the temperature is 298.15 K (25ºC) unless otherwise noted.

This may seem like a strange definition, because it requires that each of the reactants and each of the products of a reaction are kept separate from one another, unmixed. The entropy of mixing must be determined separately.

The standard entropy change (Δ*S*°) for any process may be computed from the standard entropies of its reactant and product species like the following:

$$\Delta S^\circ = \sum \nu S^\circ_{298}(\text{products}) - \sum \nu S^\circ_{298}(\text{reactants}) \tag{8.3.6}$$

Here, ν represents stoichiometric coefficients in the balanced equation representing the process. For example, Δ*S*° for the following reaction at room temperature

$$m\text{A} + n\text{B} \longrightarrow x\text{C} + y\text{D} \tag{8.3.7}$$

is computed as the following:

$$= [xS^\circ_{298}(\text{C}) + yS^\circ_{298}(\text{D})] - [mS^\circ_{298}(\text{A}) + nS^\circ_{298}(\text{B})] \tag{8.3.8}$$

Table 8.3.2 lists some standard entropies at 298.15 K. You can find additional standard entropies in Tables T1 or T2.

Table 8.3.2: Standard Entropies (at 298.15 K, 1 atm)

Substance	S°_{298} $\frac{J}{mol\,K}$
carbon	
C(*s*, graphite)	5.740
C(*s*, diamond)	2.38
CO(*g*)	197.7
CO_2(*g*)	213.8
CH_4(*g*)	186.3
C_2H_4(*g*)	219.5
C_2H_6(*g*)	229.5
CH_3OH(*l*)	126.8
C_2H_5OH(*l*)	160.7
hydrogen	
H_2(*g*)	130.57
H(*g*)	114.6

Substance	$S^\circ_{298}\ \frac{J}{mol\,K}$
$H_2O(g)$	188.71
$H_2O(l)$	69.91
HCI(g)	186.8
$H_2S(g)$	205.7
oxygen	
$O_2(g)$	205.03

Example 8.3.2: Determination of ΔS°

Calculate the standard entropy change for the following process:

$$H_2O(g) \longrightarrow H_2O(l)$$

Solution

The value of the standard entropy change at room temperature, ΔS°_{298}, is the difference between the standard entropy of the product, $H_2O(l)$, and the standard entropy of the reactant, $H_2O(g)$.

$$\begin{aligned}\Delta S^\circ_{298} &= S^\circ_{298}(H_2O(l)) - S^\circ_{298}(H_2O(g)) \\ &= (70.0\ J\,mol^{-1}K^{-1}) - (188.8\ Jmol^{-1}K^{-1}) = -118.8\ J\,mol^{-1}K^{-1}\end{aligned}$$

The value for ΔS^o_{298} is negative, as expected for this phase transition (condensation), which the previous section discussed.

Exercise 8.3.2

Calculate the standard entropy change for the following process:

$$H_2(g) + C_2H_4(g) \longrightarrow C_2H_6(g)$$

Answer

−120.6 J mol^{-1} K^{-1}

Example 8.3.3: Determination of ΔS°

Calculate the standard entropy change for the combustion of methanol, CH_3OH at room temperature:

$$2\,CH_3OH(l) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 4\,H_2O(l)$$

Solution

The value of the standard entropy change is equal to the difference between the standard entropies of the products and the entropies of the reactants scaled by their stoichiometric coefficients.

$$\begin{aligned}\Delta S^\circ &= \Delta S^\circ_{298} = \sum \nu S^\circ_{298}(\text{products}) - \sum \nu S^\circ_{298}(\text{reactants}) \\ &= [2S^\circ_{298}(CO_2(g)) + 4S^\circ_{298}(H_2O(l))] - [2S^\circ_{298}(CH_3OH(l)) + 3S^\circ_{298}(O_2(g))] \\ &= \{[2(213.8) + 4 \times 70.0] - [2(126.8) + 3(205.03)]\} = -161.1\ J/mol \cdot K\end{aligned}$$

Exercise 8.3.3

Calculate the standard entropy change for the following reaction:

$$Ca(OH)_2(s) \longrightarrow CaO(s) + H_2O(l)$$

Answer

24.7 J/mol•K

Summary

The second law of thermodynamics states that a spontaneous process increases the entropy of the universe, $S_{univ} > 0$. If $\Delta S_{univ} < 0$, the process is nonspontaneous, and if $\Delta S_{univ} = 0$, the system is at equilibrium. The third law of thermodynamics establishes the zero for entropy as that of a perfect, pure crystalline solid at 0 K. With only one possible microstate, the entropy is zero. We may compute the standard entropy change for a process by using standard entropy values for the reactants and products involved in the process.

8.3.3: Key Equations

- $\Delta S^\circ = \Delta S^\circ_{298} = \sum \nu S^\circ_{298}(\text{products}) - \sum \nu S^\circ_{298}(\text{reactants})$
- $\Delta S = \frac{q_{rev}}{T}$
- $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$
- $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = \Delta S_{sys} + \frac{q_{surr}}{T}$

Glossary

second law of thermodynamics

entropy of the universe increases for a spontaneous process

standard entropy (*S*°)

entropy for a substance at 1 bar pressure; tabulated values are usually determined at 298.15 K and denoted S°_{298}

standard entropy change (Δ*S*°)

change in entropy for a reaction calculated using the standard entropies, usually at room temperature and denoted ΔS°_{298}

third law of thermodynamics

entropy of a perfect crystal at absolute zero (0 K) is zero

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8.4: Gibbs Free Energy

Learning Objectives

- Define Gibbs free energy, and describe its relation to spontaneity
- Calculate the standard free energy change for a process using standard free energies of formation for its reactants and products
- Calculate standard free energy change for a process using senthalpies of formation and the entropies for its reactants and products
- Explain how temperature affects the spontaneity of some processes
- Relate standard free energy changes to equilibrium constants

One of the challenges of using the second law of thermodynamics to determine if a chemical reaction is spontaneous is that we must determine the entropy change for the system *and* the entropy change for the surroundings. A second challenge when working with a chemical reaction is that we need to take into account the mixing of the substances, an issue that does not occur when observing the phase change if a pure substance. An alternative approach involving a new thermodynamic property defined in terms of system properties only was introduced in the late nineteenth century by American mathematician Josiah Willard Gibbs. This new property is called the Gibbs free energy (G) (or simply the *free energy*), and it is defined in terms of a system's enthalpy and entropy as the following:

$$G = H - TS$$

Free energy is a state function, and at constant temperature and pressure, the standard free energy change (ΔG°) may be expressed as the following:

$$\Delta G^\circ_{\text{sys}} = \Delta H^\circ_{\text{sys}} - T\Delta S^\circ_{\text{sys}}$$

(For simplicity's sake, the subscript "sys" will be omitted henceforth.) We can understand the relationship between this system property and the spontaneity of a process by recalling the previously derived second law expression:

$$\Delta S_{\text{univ}} = \Delta S + \frac{q_{\text{surr}}}{T}$$

The first law requires that $q_{surr} = -q_{sys}$, and at constant pressure $q_{sys} = \Delta H$, and so this expression may be rewritten as the following:

$$\Delta S_{\text{univ}} = \Delta S - \frac{\Delta H}{T}$$

ΔH is the enthalpy change of the system. Multiplying both sides of this equation by −T, and rearranging yields the following:

$$-T\Delta S_{\text{univ}} = \Delta H - T\Delta S$$

Comparing this equation to the previous one for free energy change shows the following relation:

$$\Delta G = -T\Delta S_{\text{univ}} \tag{8.4.1}$$

The free energy change is therefore a reliable indicator of the spontaneity of a process, being directly related to the previously identified spontaneity indicator, ΔS_{univ}. Table 8.4.1 summarizes the relation between the spontaneity of a process and the arithmetic signs of these indicators.

Table 8.4.1: Relation between Process Spontaneity and Signs of Thermodynamic Properties

$\Delta S_{univ} > 0$	$\Delta G < 0$	moves spontaneously in the forward direction, as written, to reach equilibrium
$\Delta S_{univ} < 0$	$\Delta G > 0$	nonspontaneous in the forward direction, as written, but moves spontaneously in the reverse direction, as written, to reach equilibrium

$\Delta S_{univ} = 0$	$\Delta G = 0$	reversible (at equilibrium)

8.4.1: Calculating Free Energy Change

Free energy is a state function, so its value depends only on the conditions of the initial and final states of the system that have undergone some change. A convenient and common approach to the calculation of free energy changes for physical changes and chemical reactions is by use of widely available compilations of standard state thermodynamic data. One method involves the use of standard enthalpies and entropies to compute standard free energy changes according to the following relation as demonstrated in Example 8.4.1.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{8.4.2}$$

It is important to understand that for phase changes, ΔG° tells you if the phase change is spontaneous or not; will it happen, or not happen. For chemical reactions, ΔG° tells you the **extent** of a reaction. In other words, ΔG° for a reaction tells you how much product will be present at equilibrium. A reaction with $\Delta G^\circ < 0$ is considered **product-favored at equilibrium**; there will be more products than reactants when the reaction reaches equilibrium. A reaction with $\Delta G^\circ > 0$ is considered **reactant-favored at equilibrium**; there will be more reactants than products when the reaction reaches equilibrium.

Example 8.4.1: Evaluation of ΔG° for a Phase Change of a Pure Substance

Use standard enthalpy and entropy data from Tables T1 or T2 to calculate the standard free energy change for the vaporization of water at room temperature (298 K). What does the computed value for ΔG° say about the spontaneity of this physical change for a pure substance?

Solution

The process of interest is the following:

$$\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g) \tag{8.4.3}$$

The standard change in free energy may be calculated using the following equation:

$$\Delta G^\circ_{298} = \Delta H^\circ - T\Delta S^\circ \tag{8.4.4}$$

From Tables T1 or T2, here are the data:

Data from Tables T1 or T2

Substance	ΔH_f° (kJ/mol)	S°_{298} (J/K·mol)
$H_2O(l)$	−286.83	70.0
$H_2O(g)$	−241.82	188.8

Combining at 298 K:

$$\begin{aligned}
\Delta H^\circ &= \Delta H^\circ_{298} = \Delta H_f^\circ(\mathrm{H_2O}(g)) - \Delta H_f^\circ(\mathrm{H_2O}(l)) \\
&= [-241.82\ kJ - (-285.83)]\ kJ/mol \\
&= 44.01\ kJ/mol \\
\Delta S^\circ &= \Delta S^\circ_{298} = S^\circ_{298}(\mathrm{H_2O}(g)) - S^\circ_{298}(\mathrm{H_2O}(l)) \\
&= 188.8\ J/mol \cdot K - 70.0\ J/K \\
&= 118.8\ J/mol \cdot K
\end{aligned}$$

then use Equation 8.4.2:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Converting everything into kJ and combining at 298 K:

$$\Delta G^\circ_{298} = \Delta H^\circ - T\Delta S^\circ$$

$$= 44.01\ kJ/mol - (298\ K \times 118.8\ J/mol \cdot K) \times \frac{1\ kJ}{1000\ J}$$

$$44.01\ \text{kJ/mol} - 35.4\ \text{kJ/mol} = 8.6\ \text{kJ/mol}$$

At 298 K (25 °C) $\Delta G^\circ_{298} > 0$, and so boiling is nonspontaneous (not spontaneous) at 298 K.

? Exercise 8.4.1: Evaluation of ΔG° for a Chemical Reaction

Use standard enthalpy and entropy data from Tables T1 or T2 to calculate the standard free energy change for the reaction shown here (298 K). What does the computed value for ΔG° say about the extent of this reaction at 298 K?

$$\text{C}_2\text{H}_6(g) \longrightarrow \text{H}_2(g) + \text{C}_2\text{H}_4(g)$$

Answer

$\Delta G^\circ_{298} = 102.0\ \text{kJ/mol}$; the reaction is reactant-favored at equilibrium at 25 °C. There will be more $\text{C}_2\text{H}_6(g)$ than $\text{H}_2(g)$ and $\text{C}_2\text{H}_4(g)$ at equilibrium

Free energy changes may also use the standard free energy of formation $(\Delta G^\circ_\text{f})$, for each of the reactants and products involved in the reaction. The standard free energy of formation is the free energy change that accompanies the formation of one mole of a substance from its elements in their standard states. Similar to the standard enthalpies of formation, $(\Delta G^\circ_\text{f})$ is by definition zero for elemental substances under standard state conditions. The approach to computing the free energy change for a reaction using this approach is the same as that demonstrated previously for enthalpy and entropy changes. For the reaction

$$m\text{A} + n\text{B} \longrightarrow x\text{C} + y\text{D},$$

the standard free energy change at room temperature may be calculated as

$$\Delta G^\circ_{298} = \Delta G^\circ \tag{8.4.5}$$

$$= \sum \nu \Delta G^\circ_{298}(\text{products}) - \sum \nu \Delta G^\circ_{298}(\text{reactants}) \tag{8.4.6}$$

$$= [x\Delta G^\circ_\text{f}(\text{C}) + y\Delta G^\circ_\text{f}(\text{D})] - [m\Delta G^\circ_\text{f}(\text{A}) + n\Delta G^\circ_\text{f}(\text{B})]. \tag{8.4.7}$$

✓ Example 8.4.2: Calculation of ΔG°_{298}

Consider the decomposition of yellow mercury(II) oxide.

$$\text{HgO}(s,\ \text{yellow}) \longrightarrow \text{Hg}(l) + \tfrac{1}{2}\text{O}_2(\text{g})$$

Calculate the standard free energy change at room temperature, ΔG°_{298}, using:

a. standard free energies of formation and
b. standard enthalpies of formation and standard entropies.

Do the results indicate the reaction to be product-favored or reactant-favored at equilibrium?

Solution

The required data are available in Tables T1 or T2 and are shown here.

Required data for Tables T1 or T2

Compound	ΔG°_f (kJ/mol)	ΔH°_f (kJ/mol)	S°_{298} (J/K·mol)
HgO (*s*, yellow)	−58.43	−90.46	71.13
Hg(*l*)	0	0	75.9
$O_2(g)$	0	0	205.2

(a) Using free energies of formation:

$$\begin{aligned}\Delta G^\circ_{298} &= \sum \nu GS^\circ_{298}(\text{products}) - \sum \nu \Delta G^\circ_{298}(\text{reactants}) \\ &= \left[1\Delta G^\circ_{298}\text{Hg}(l) + \frac{1}{2}\Delta G^\circ_{298}\text{O}_2(g)\right] - 1\Delta G^\circ_{298}\text{HgO}(s,\text{ yellow}) \\ &= \left[1\text{ mol}(0\text{ kJ/mol}) + \frac{1}{2}\text{mol}(0\text{ kJ/mol})\right] - 1\text{ mol}(-58.43\text{ kJ/mol}) = 58.43\text{ kJ/mol}\end{aligned}$$

(b) Using enthalpies and entropies of formation:

$$\begin{aligned}\Delta H^\circ_{298} &= \sum \nu \Delta H^\circ_{298}(\text{products}) - \sum \nu \Delta H^\circ_{298}(\text{reactants}) \\ &= \left[1\Delta H^\circ_{298}\text{Hg}(l) + \frac{1}{2}\Delta H^\circ_{298}\text{O}_2(g)\right] - 1\Delta H^\circ_{298}\text{HgO}(s,\text{ yellow}) \\ &= [1\text{ mol}(0\text{ kJ/mol}) + \frac{1}{2}\text{mol}(0\text{ kJ/mol})] - 1\text{ mol}(-90.46\text{ kJ/mol}) = 90.46\text{ kJ/mol} \\ \Delta S^\circ_{298} &= \sum \nu \Delta S^\circ_{298}(\text{products}) - \sum \nu \Delta S^\circ_{298}(\text{reactants}) \\ &= \left[1\Delta S^\circ_{298}\text{Hg}(l) + \frac{1}{2}\Delta S^\circ_{298}\text{O}_2(g)\right] - 1\Delta S^\circ_{298}\text{HgO}(s,\text{ yellow}) \\ &= \left[1\text{ mol}(75.9\text{ J/mol K}) + \frac{1}{2}\text{mol}(205.2\text{ J/mol K})\right] - 1\text{ mol}(71.13\text{ J/mol K}) = 107.4\text{ J/mol K}\end{aligned}$$

then we can use Equation \ref7} directly:

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= 90.46\text{ kJ} - 298.15\text{ K} \times 107.4\text{ J/K}\cdot\text{mol} \times \frac{1\text{ kJ}}{1000\text{ J}} \\ &= (90.46 - 32.01)\text{ kJ/mol} = 58.45\text{ kJ/mol}\end{aligned}$$

Both ways to calculate the standard free energy change at 25 °C give the same numerical value (to three significant figures), and both predict that the process is reactant-favored at equilibrium at room temperature.

? Exercise 8.4.2

Calculate ΔG° using (a) free energies of formation and (b) enthalpies of formation and entropies (Tables T1 or T2). Do the results indicate the reaction to be product-favored or reactant-favored at equilibrium at 25 °C?

$$\text{C}_2\text{H}_4(g) \longrightarrow \text{H}_2(g) + \text{C}_2\text{H}_2(g)$$

Answer

141.5 kJ/mol, reactant-favored at equilibrium

8.4.2: Temperature Dependence of Spontaneity and Extent of Reaction

As was previously demonstrated in this chapter's section on entropy, the spontaneity of a process may depend upon the temperature of the system. Phase transitions, for example, will proceed spontaneously in one direction or the other depending upon the temperature of the substance in question. In a similar, but not identical fashion, some chemical reactions can switch from being product-favored at equilibrium, to being reactant-favored at equilibrium, depending on the temperature.

Note

The numerical value of ΔG° is always dependent on the temperature. In this section we are determining whether or not the sign of ΔG° is dependent on the temperature.

To illustrate this concept, the equation relating free energy change to the enthalpy and entropy changes for the process is considered:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

The extent of a process, as reflected in the arithmetic sign of its standard free energy change, is then determined by the signs of the enthalpy and entropy changes and, in some cases, the absolute temperature. Since T is the absolute (Kelvin) temperature, it can only have positive values. Four possibilities therefore exist with regard to the signs of the enthalpy and entropy changes:

1. **Both ΔH^o and ΔS^o are positive.** This condition describes an endothermic process that involves an increase in system entropy. In this case, ΔG^o will be negative if the magnitude of the $T\Delta S^o$ term is greater than ΔH^o. If the $T\Delta S^o$ term is less than ΔH^o, the free energy change will be positive. Such a process is spontaneous or *product-favored at high temperatures and reactant-favored at low temperatures.*
2. **Both ΔH^o and ΔS^o are negative.** This condition describes an exothermic process that involves a decrease in system entropy. In this case, ΔG^o will be negative if the magnitude of the $T\Delta S^o$ term is less than ΔH^o. If the $T\Delta S^o$ term's magnitude is greater than ΔH^o, the free energy change will be positive. Such a process is *product-favored at low temperatures* and *reactant-favored at high temperatures.*
3. **ΔH^o is positive and ΔS^o is negative.** This condition describes an endothermic process that involves a decrease in system entropy. In this case, ΔG^o will be positive regardless of the temperature. Such a process is *reactant-favored at all temperatures.*
4. **ΔH^o is negative and ΔS^o is positive.** This condition describes an exothermic process that involves an increase in system entropy. In this case, ΔG^o will be negative regardless of the temperature. Such a process is *product-favored at all temperatures.*

These four scenarios are summarized in Table 8.4.1

Table 8.4.1

Sign of ΔH^o	Sign of ΔS^o	Sign of ΔG^o	Temperature Dependence of ΔG^o
-	+	-	The sign of ΔG^o does not depend on the temperature.The reaction is product-favored at all temperatures.
+	-	+	The sign of ΔG^o does not depend on the temperature.The reaction is reactant-favored at all temperatures.
-	-	- or +	The sign of ΔG^o **does** depend on the temperature. The reaction will be product-favored at lower temperatures.
+	+	- or +	The sign of ΔG^o **does** depend on the temperature. The reaction will be product-favored at high temperatures.

Example 8.4.3: Predicting the Temperature Dependence of Spontaneity

The incomplete combustion of carbon is described by the following equation:

$$2\,\mathrm{C}(s) + \mathrm{O}_2(g) \longrightarrow 2\,\mathrm{CO}(g)$$

Does the sign of ΔG° of this process depend upon temperature?

Solution

Combustion processes are exothermic ($\Delta H^\circ < 0$). This particular reaction involves an increase in entropy due to the accompanying increase in the amount of gaseous species (net gain of one mole of gas, $\Delta S^\circ > 0$). The reaction is therefore product-favored at equilibrium ($\Delta G^\circ < 0$) at all temperatures.

? Exercise 8.4.3

Popular chemical hand warmers generate heat by the air-oxidation of iron:

$$4\,\mathrm{Fe}(s) + 3\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{Fe_2O_3}(s)$$

Does the sign of ΔG^o of this process depend upon temperature?

Answer

ΔH^o and ΔS^o are both negative; the reaction is product-favored at equilibrium at low temperatures.

When considering the conclusions drawn regarding the temperature dependence of the sign of ΔG^o, it is important to keep in mind what the terms "high" and "low" mean. Since these terms are adjectives, the temperatures in question are deemed high or low relative to some reference temperature. A process that is reactant-favored at equilibrium at one temperature but product-favored at equilibrium at another temperature will necessarily undergo a change in "extent" (as reflected by its ΔG^o) as temperature varies. This is clearly illustrated by a graphical presentation of the free energy change equation, in which ΔG^o is plotted on the *y* axis versus *T* on the *x* axis:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$y = b + mx$$

Such a plot is shown in Figure 8.4.2. A process whose enthalpy and entropy changes are of the same arithmetic sign will exhibit a temperature-dependence for the sign of ΔG^o as depicted by the two yellow lines in the plot. Each line crosses from one spontaneity domain (positive or negative ΔG^o) to the other at a temperature that is characteristic of the process in question. This temperature is represented by the *x*-intercept of the line, that is, the value of *T* for which ΔG^o is zero:

$$\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

Thus, saying a process is product-favored at equilibrium at "high" or "low" temperatures means the temperature is above or below, respectively, that temperature at which ΔG^o for the process is zero.

Note

In this discussion, we have used two different descriptions for the meaning of the sign of ΔG^o. You should be aware of the meaning of each description.

a) **Extent of Reaction:** This description is used to predict the ratio of the product and reactant concentrations at equilibrium. In this description, we use the thermodynamic term ΔG^o to tell us the same information as the equilibrium constant, K. When $\Delta G^o < 0$, K > 1, and the reaction will be product-favored at equilibrium. When $\Delta G^o > 0$, K< 1, and the reaction is reactant-favored at equilibrium. When $\Delta G^o = 0$, K =1, and the reaction will have roughly equal amounts of products and reactants at equilibrium. In all cases, the reaction will form a mixture of products and reactants at equilibrium. We use the sign and magnitude of ΔG^o to tell us how much product will be made if the reaction is allowed to reach equilibrium.

b) **Spontaneity:** This description is much more complicated because it involves two different interpretations of how a reaction at standard state occurs. One interpretation involves the hypothetical process in which the reaction proceeds from a starting point of pure reactants to a finishing point of pure products, with all substances isolated in their own containers under standard state conditions. In the second, more realistic interpretation, the reaction starts with all reactants and all products in their standard state in one container. We then allow this specific mixture to react an infinitesimally small amount so that we can obtain a rate of change in free energy with respect to the extent of reaction when all reactants and products are mixed and

(essentially) in their standard states. Although each interpretation describes a different reaction scenario, the value of the difference in free energy and the value of the rate of change in free energy are the same number. If $\Delta G^o < 0$, we say that the reaction is spontaneous, meaning that the reaction would proceed in the forward direction, as written, to form pure products in their standard state. If $\Delta G^o > 0$, we say that the reaction is nonspontaneous, meaning that the reaction would proceed in the reverse direction, as written, to form pure reactants in their standard state. If $\Delta G^o = 0$, we say that the neither the reactants nor the products are favored to be formed.

A detailed treatment of the meaning of ΔGº can be found in the paper, "Free Energy versus Extent of Reaction" by Richard S. Treptow, Journal of Chemical Education, **1996**, Volume 73 (1), 51-54.

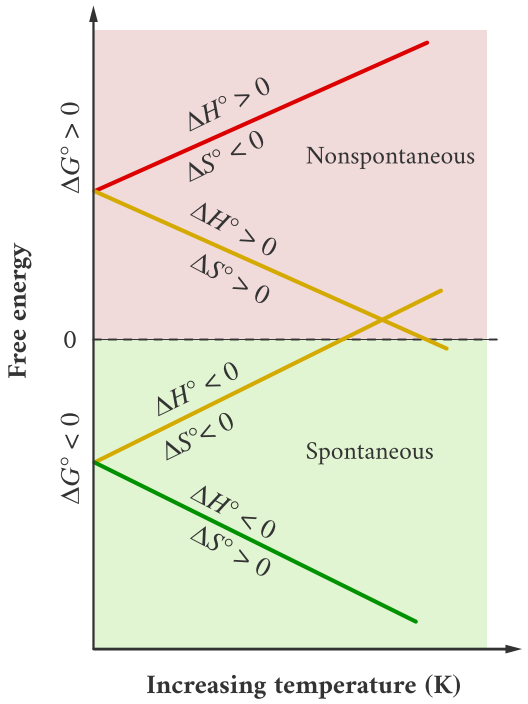


Figure 8.4.2: These plots show the variation in ΔGº with temperature for the four possible combinations of arithmetic sign for ΔHº and ΔSº. Note that in this graph of ΔGº, "spontaneous" is synonymous with "product-favored at equilibrium", and "nonspontaneous" is synonymous with "reactant-favored at equilibrium".

Example 8.4.4: Equilibrium Temperature for a Phase Transition

As defined in the chapter on liquids and solids, the boiling point of a liquid is the temperature at which its solid and liquid phases are in equilibrium (that is, when vaporization and condensation occur at equal rates). Use the information in Tables T1 or T2 to estimate the boiling point of water.

Solution

The process of interest is the following phase change:

$$\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g)$$

When this process is at equilibrium, $\Delta G = 0$, so the following is true:

$$0 = \Delta H^\circ - T\Delta S^\circ \qquad \text{or} \qquad T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

Using the standard thermodynamic data from Tables T1 or T2,

$$\begin{aligned} \Delta H^\circ &= \Delta H_\mathrm{f}^\circ(\mathrm{H_2O}(g)) - \Delta H_\mathrm{f}^\circ(\mathrm{H_2O}(l)) \\ &= -241.82\ \mathrm{kJ/mol} - (-285.83\ \mathrm{kJ/mol}) = 44.01\ \mathrm{kJ/mol} \end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= \Delta S^\circ_{298}(\mathrm{H_2O}(g)) - \Delta S^\circ_{298}(\mathrm{H_2O}(l)) \\ &= 188.8\ \mathrm{J/K \cdot mol} - 70.0\ \mathrm{J/K \cdot mol} = 118.8\ \mathrm{J/K \cdot mol}\end{aligned}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{44.01 \times 10^3\ \mathrm{J/mol}}{118.8\ \mathrm{J/K \cdot mol}} = 370.5\ \mathrm{K} = 97.3\ ^\circ\mathrm{C}$$

The accepted value for water's normal boiling point is 373.2 K (100.0 °C), and so this calculation is in reasonable agreement. Note that the values for enthalpy and entropy changes data used were derived from standard data at 298 K (Tables T1 or T2.). If desired, you could obtain more accurate results by using enthalpy and entropy changes determined at (or at least closer to) the actual boiling point.

? Exercise 8.4.4

Use the information in Tables T1 or T2 to estimate the boiling point of CS_2.

Answer

313 K (accepted value 319 K).

8.4.3: Free Energy and Equilibrium

The free energy change for a process may be viewed as a measure of its driving force. A negative value for ΔG represents a finite driving force for the process in the forward direction, while a positive value represents a driving force for the process in the reverse direction. When ΔG is zero, the forward and reverse driving forces are equal, and so the process occurs in both directions at the same rate (the system is at equilibrium).

In the chapter on equilibrium the *reaction quotient*, *Q*, was introduced as a convenient measure of the status of an equilibrium system. Recall that *Q* is the numerical value of the mass action expression for the system, and that you may use its value to identify the direction in which a reaction will proceed in order to achieve equilibrium. When *Q* is lesser than the equilibrium constant, *K*, the reaction will proceed in the forward direction until equilibrium is reached and *Q* = *K*. Conversely, if *Q* > *K*, the process will proceed in the reverse direction until equilibrium is achieved.

The free energy change for a process taking place with reactants and products present under nonstandard conditions, ΔG, is related to the standard free energy change, $\Delta G°$, according to this equation:

$$\Delta G = \Delta G^\circ + RT \ln Q \tag{8.4.8}$$

R is the gas constant (8.314 J/K mol), *T* is the kelvin or absolute temperature, and *Q* is the reaction quotient. We may use this equation to predict the spontaneity for a process under any given set of conditions as illustrated in Example 8.4.1.

✓ Example 8.4.5: Calculating ΔG under Nonstandard Conditions

What is the free energy change for the process shown here under the specified conditions?

T = 25 °C, $P_{\mathrm{N_2}} = 0.870$ atm, $P_{\mathrm{H_2}} = 0.250$ atm, and $P_{\mathrm{NH_3}} = 12.9$ atm

$$2\,\mathrm{NH_3}(g) \longrightarrow 3\,\mathrm{H_2}(g) + \mathrm{N_2}(g) \quad \Delta G^\circ = 33.0\ \mathrm{kJ/mol}$$

Solution

Equation 8.4.8 relates free energy change to standard free energy change and reaction quotient and may be used directly:

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT \ln Q \\ &= 33.0\ \frac{\mathrm{kJ}}{\mathrm{mol}} + \left(8.314\ \frac{\mathrm{J}}{\mathrm{mol\ K}} \times 298\ \mathrm{K} \times \ln \frac{(0.250^3) \times 0.870}{12.9^2}\right) \\ &= 9680\ \frac{\mathrm{J}}{\mathrm{mol}} \text{ or } 9.68\ \mathrm{kJ/mol}\end{aligned}$$

Since the computed value for ΔG is positive, the reaction is nonspontaneous under these conditions. The reaction will proceed in the reverse direction to reach equilibrium.

Exercise 8.4.5

Calculate the free energy change for this same reaction at 875 °C in a 5.00 L mixture containing 0.100 mol of each gas. Is the reaction spontaneous under these conditions?

Answer

ΔG = −47 kJ; yes, the reaction proceeds in the forward direction, as written, to reach equilibrium.

For a system at equilibrium, $Q = K$ and $\Delta G = 0$, and the Equation 8.4.8 may be written as

$$\underbrace{0 = \Delta G^\circ + RT \ln K}_{\text{at equilibrium}}$$

$$\Delta G^\circ = -RT \ln K \tag{8.4.9}$$

or alternatively

$$K = e^{-\frac{\Delta G^\circ}{RT}} \tag{8.4.10}$$

This form of the equation provides a useful link between these two essential thermodynamic properties, and it can be used to derive equilibrium constants from standard free energy changes and vice versa. The relations between standard free energy changes and equilibrium constants are summarized in Table 8.4.1.

Table 8.4.2: Relations between Standard Free Energy Changes and Equilibrium Constants

K	ΔG°	Comments
< 1	> 0	Reactants are more abundant at equilibrium.
= 1	= 0	Reactants and products are equally abundant at equilibrium.
> 1	< 0	Products are more abundant at equilibrium.

Example 8.4.6: Equilibrium Constant using Standard Free Energy Change

Given that the standard free energies of formation of $Ag^+(aq)$, $Cl^-(aq)$, and $AgCl(s)$ are 77.1 kJ/mol, −131.2 kJ/mol, and −109.8 kJ/mol, respectively, calculate the solubility product, K_{sp}, for AgCl.

Solution

The reaction of interest is the following:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \quad K_{sp} = [Ag^+][Cl^-]$$

The standard free energy change for this reaction is first computed using standard free energies of formation for its reactants and products:

$$\begin{aligned} \Delta G^\circ = \Delta G^\circ_{298} &= [\Delta G^\circ_f(Ag^+(aq)) + \Delta G^\circ_f(Cl^-(aq))] - [\Delta G^\circ_f(AgCl(s))] \\ &= [77.1\ kJ/mol - 131.2\ kJ/mol] - [-109.8\ kJ/mol] \\ &= 55.7\ kJ/mol \end{aligned}$$

The equilibrium constant for the reaction may then be derived from its standard free energy change via Equation 8.4.10:

$$K_{sp} = e^{-\frac{\Delta G^\circ}{RT}} = \exp\left(-\frac{\Delta G^\circ}{RT}\right)$$
$$= \exp\left(-\frac{55.7 \times 10^3\ \text{J/mol}}{8.314\ \text{J/mol}\cdot\text{K} \times 298.15\ \text{K}}\right)$$
$$= \exp(-22.470) = e^{-22.470} = 1.74 \times 10^{-10}$$

? Exercise 8.4.6: dissociation of dinitrogen tetroxide

Use the thermodynamic data provided in Tables T1 or T2 to calculate the equilibrium constant for the dissociation of dinitrogen tetroxide at 25 °C.

$$NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$$

Answer

K = 6.9

To further illustrate the relation between these two essential thermodynamic concepts, consider the observation that reactions spontaneously proceed in a direction that ultimately establishes equilibrium. As may be shown by plotting the free energy change versus the extent of the reaction (for example, as reflected in the value of Q), equilibrium is established when the system's free energy is minimized (Figure 8.4.3). If a system is present with reactants and products present in nonequilibrium amounts ($Q \neq K$), the reaction will proceed spontaneously in the direction necessary to establish equilibrium.

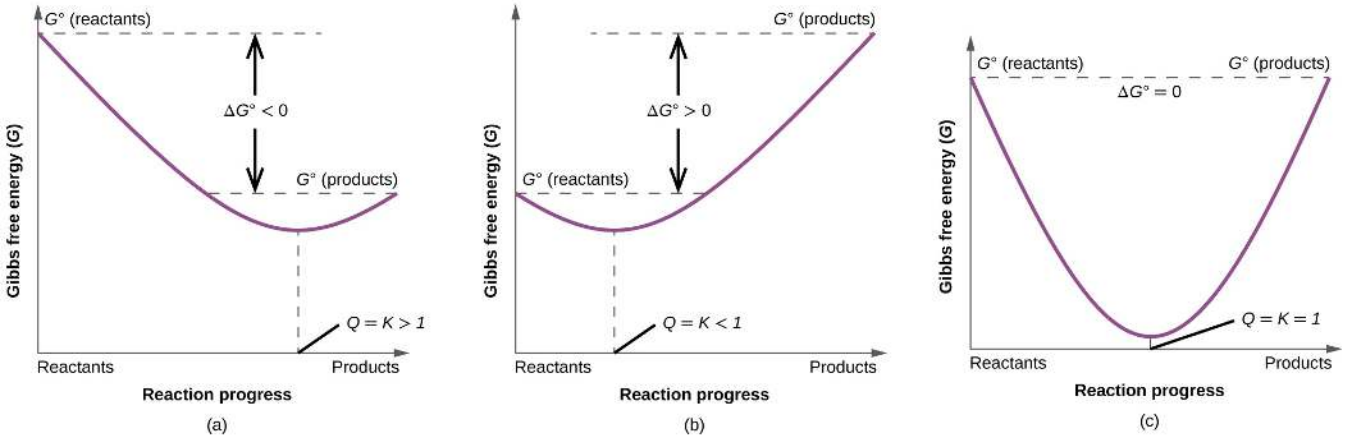


Figure 8.4.3: These plots show the free energy versus reaction progress for systems whose standard free changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium. Note that reactions with K equal to exactly 1.000 are rare.

Summary

Gibbs free energy (G) is a state function defined with regard to system quantities only and may be used to predict the spontaneity of a process. A negative value for ΔG indicates that the process will proceed in the forward direction to reach equilibrium; a positive ΔG indicates that the process will proceed in the reverse direction to reach equilibrium ; and a ΔG of zero indicates that the system is at equilibrium. A negative value for ΔG^o means that the reaction is product-favored at equilibrium. A positive value for ΔG^o means that the reaction is reactant-favored at equilibrium. If ΔG^o equals 0 (a rare occurrence), the reaction has roughly equal amounts of reactants and products at equilibrium.A number of approaches to the computation of free energy changes are possible.

8.4.4: Key Equations

- $\Delta G = \Delta H - T\Delta S$
- $\Delta G = \Delta G° + RT \ln Q$
- $\Delta G° = -RT \ln K$

Glossary

Gibbs free energy change (*G*)

thermodynamic property defined in terms of system enthalpy and entropy; all spontaneous processes involve a decrease in *G*

standard free energy change (Δ*G*°)

change in free energy for a process occurring under standard conditions (1 bar pressure for gases, 1 M concentration for solutions)

standard free energy of formation (ΔG_f°)

change in free energy accompanying the formation of one mole of substance from its elements in their standard states

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8.E: Entropy and Free Energy (Exercises)

8.1: Spontaneity

Exercise 8.E.1

What is a spontaneous reaction?

Answer

A reaction has a natural tendency to occur and takes place without the continual input of energy from an external source.

Exercise 8.E.2

Indicate whether the following processes are spontaneous or nonspontaneous.

a. Liquid water freezing at a temperature below its freezing point
b. Liquid water freezing at a temperature above its freezing point
c. The combustion of gasoline
d. A ball thrown into the air
e. A raindrop falling to the ground
f. Iron rusting in a moist atmosphere

Answer

a. spontaneous

b. nonspontaneous

c. spontaneous

d. nonspontaneous

e. spontaneous

f. spontaneous

Exercise 8.E.3

Many plastic materials are organic polymers that contain carbon and hydrogen. The oxidation of these plastics in air to form carbon dioxide and water is a spontaneous process; however, plastic materials tend to persist in the environment. Explain.

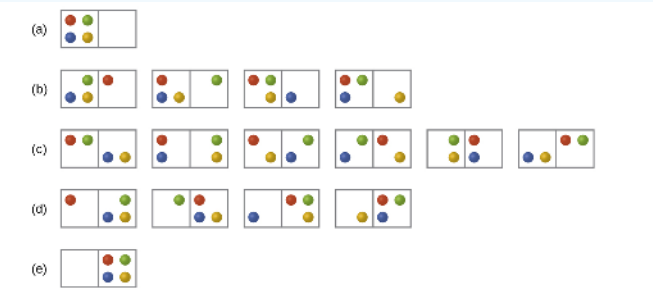
Answer

Although the oxidation of plastics is spontaneous, the rate of oxidation is very slow. Plastics are therefore kinetically stable and do not decompose appreciably even over relatively long periods of time.

8.2: Entropy

Exercise 8.E.4

In the figure below all of the possible distributions and microstates are shown for four different particles shared between two boxes. Determine the entropy change, ΔS, for the system when it is converted from distribution to distribution (d).



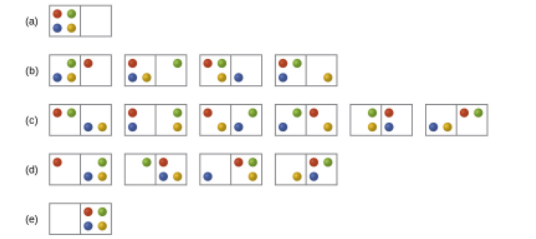
Answer

There are four initial microstates and four final microstates.

$$\Delta S = k \ln \frac{W_f}{W_i} = 1.38 \times 10^{-23}\ \text{J/K} \times \ln \frac{4}{4} = 0 \tag{8.E.1}$$

Exercise 8.E.5

Consider a system similar to the one below, except that it contains six particles instead of four. What is the probability of having all the particles in only one of the two boxes in the case? Compare this with the similar probability for the system of four particles that we have derived to be equal to $\frac{1}{8}$. What does this comparison tell us about even larger systems?



Answer

The probability for all the particles to be on one side is $\frac{1}{32}$. This probability is noticeably lower than the $\frac{1}{8}$ result for the four-particle system. The conclusion we can make is that the probability for all the particles to stay in only one part of the system will decrease rapidly as the number of particles increases, and, for instance, the probability for all molecules of gas to gather in only one side of a room at room temperature and pressure is negligible since the number of gas molecules in the room is very large.

Exercise 8.E.6

At room temperature, the entropy of the halogens increases from I_2 to Br_2 to Cl_2. Explain.

Answer

The masses of these molecules would suggest the opposite trend in their entropies. The observed trend is a result of the more significant variation of entropy with a physical state. At room temperature, I_2 is a solid, Br_2 is a liquid, and Cl_2 is a gas.

Exercise 8.E.7

Indicate which substance in the given pairs has the higher entropy value. Explain your choices.

a. $C_2H_5OH(l)$ or $C_3H_7OH(l)$
b. $C_2H_5OH(l)$ or $C_2H_5OH(g)$
c. 2Hor H(g)

Answer

$C_3H_7OH(l)$ as it is a larger molecule (more complex and more massive), and so more microstates describing its motions are available at any given temperature. $C_2H_5OH(g)$ as it is in the gaseous state. 2H(g), since entropy is an extensive property, and so two H atoms (or two moles of H atoms) possess twice as much entropy as one atom (or one mole of atoms).

Exercise 8.E.8

Predict the sign of the enthalpy change for the following processes. Give a reason for your prediction.

a. $Pb^{2+}(aq) + S^{2-}(aq) \longrightarrow PbS(s)$
b. $2\,Fe(s) + 3\,O_2(g) \longrightarrow Fe_2O_3(s)$
c. $2\,C_6H_{14}(l) + 19\,O_2(g) \longrightarrow 14\,H_2O(g) + 12\,CO_2(g)$

Answer

Negative. The relatively ordered solid precipitating decreases the number of mobile ions in solution. Negative. There is a net loss of three moles of gas from reactants to products. Positive. There is a net increase of seven moles of gas from reactants to products.

Exercise 8.E.9

Write the balanced chemical equation for the combustion of benzene, $C_6H_6(l)$, to give carbon dioxide and water vapor. Would you expect ΔS to be positive or negative in this process?

Answer

$$C_6H_6(l) + 7.5O_2(g) \longrightarrow 3\,H_2O(g) + 6\,CO_2(g) \tag{8.E.2}$$

There are 7.5 moles of gas initially, and 3 + 6 = 9 moles of gas in the end. Therefore, it is likely that the entropy increases as a result of this reaction, and ΔS is positive.

8.3: The Second and Third law

Exercise 8.E.10

Calculate ΔS°_{298} for the following changes.

a. $SnCl_4(l) \longrightarrow SnCl_4(g)$
b. $CS_2(g) \longrightarrow CS_2(l)$
c. $Cu(s) \longrightarrow Cu(g)$
d. $H_2O(l) \longrightarrow H_2O(g)$
e. $2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l)$
f. $2\,HCl(g) + Pb(s) \longrightarrow PbCl_2(s) + H_2(g)$
g. $Zn(s) + CuSO_4(s) \longrightarrow Cu(s) + ZnSO_4(s)$

Answer

107 J/K; −86.4 J/K; 133.2 J/K; 118.8 J/K; −326.6 J/K; −171.9 J/K; (g) −7.2 J/K

Exercise 8.E.11

Determine the entropy change for the combustion of gaseous propane, C_3H_8, under standard state conditions to give gaseous carbon dioxide and water.

Answer

100.6 J/K

Exercise 8.E.12

Using the relevant S°_{298} values listed in Resource Table 2, calculate S°_{298} for the following changes:

a. $\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \longrightarrow 2\,\mathrm{NH_3}(g)$

b. $\mathrm{N_2}(g) + \frac{5}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{N_2O_5}(g)$

Answer

−198.1 J/K; −348.9 J/K

Exercise 8.E.13

By calculating ΔS_{univ} at each temperature, determine if the melting of 1 mole of NaCl(s) is spontaneous at 500 °C and at 700 °C.

S^\circ_{\ce{NaCl}(s)}=\mathrm{72.11\:\dfrac{J}{mol·K}}\hspace{40px} S^\circ_{\ce{NaCl}(l)}=\mathrm{95.06\:\dfrac{J}{mol·K}}\hspace{40px ΔH^\circ_\ce{fusion}=\mathrm{27.95\: kJ/mol}

$$S^\circ_{\mathrm{NaCl}(s)} = 72.11\,\frac{\mathrm{J}}{\mathrm{mol}\cdot\mathrm{K}} \quad S^\circ_{\mathrm{NaCl}(l)} = 95.06\,\frac{\mathrm{J}}{\mathrm{mol}\cdot\mathrm{K}} \quad \Delta H^\circ_{\text{fusion}} = 27.95\ \mathrm{kJ/mol} \tag{8.E.3}$$

What assumptions are made about the thermodynamic information (entropy and enthalpy values) used to solve this problem?

Answer

As $\Delta S_{\text{univ}} < 0$ at each of these temperatures, melting is not spontaneous at either of them. The given values for entropy and enthalpy are for NaCl at 298 K. It is assumed that these do not change significantly at the higher temperatures used in the problem.

Exercise 8.E.14

Use the standard entropy data in Resource Table T1 to determine the change in entropy for each of the reactions listed. All are run under standard state conditions and 25 °C.

a.

$$\mathrm{C}(s,\ \text{graphite}) + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) \tag{8.E.4}$$

b.

$$\mathrm{O_2}(g) + \mathrm{N_2}(g) \longrightarrow 2\mathrm{NO}(g) \tag{8.E.5}$$

c.

$$2\mathrm{Cu}(s) + \mathrm{S}(g) \longrightarrow \mathrm{Cu_2\,S}(s) \tag{8.E.6}$$

d.

$$\mathrm{CaO}(s) + \mathrm{H_2O}(l) \longrightarrow \mathrm{Ca(OH)_2}(s) \tag{8.E.7}$$

e.

$$\mathrm{Fe_2O_3}(s) + 3\mathrm{CO}(g) \longrightarrow 2\mathrm{Fe}(s) + 3\mathrm{CO_2}(g) \tag{8.E.8}$$

f.

$$\mathrm{CaSO_4 \cdot 2H_2O}(s) \longrightarrow \mathrm{CaSO_4}(s) + 2\mathrm{H_2O}(g) \tag{8.E.9}$$

Answer

(a) 2.86 J/K; (b) 24.8 J/K; (c) −113.2 J/K; (d) −24.7 J/K; (e) 15.5 J/K; (f) 290.0 J/K

Q16.3.0

What is the difference between ΔS, $\Delta S°$, and ΔS°_{298} for a chemical change?

Q16.3.1

Calculate ΔS°_{298} for the following changes.

a. $\mathrm{SnCl_4}(l) \longrightarrow \mathrm{SnCl_4}(g)$

b. $\mathrm{CS_2}(g) \longrightarrow \mathrm{CS_2}(l)$

c. $\mathrm{Cu}(s) \longrightarrow \mathrm{Cu}(g)$
d. $\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g)$
e. $2\,\mathrm{H_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{H_2O}(l)$
f. $2\,\mathrm{HCl}(g) + \mathrm{Pb}(s) \longrightarrow \mathrm{PbCl_2}(s) + \mathrm{H_2}(g)$
g. $\mathrm{Zn}(s) + \mathrm{CuSO_4}(s) \longrightarrow \mathrm{Cu}(s) + \mathrm{ZnSO_4}(s)$

S16.3.1

107 J/K; −86.4 J/K; 133.2 J/K; 118.8 J/K; −326.6 J/K; −171.9 J/K; (g) −7.2 J/K

Q16.3.2

Determine the entropy change for the combustion of liquid ethanol, C_2H_5OH, under standard state conditions to give gaseous carbon dioxide and liquid water.

Q16.3.3

Determine the entropy change for the combustion of gaseous propane, C_3H_8, under standard state conditions to give gaseous carbon dioxide and water.

S16.3.3

100.6 J/K

Q16.3.4

“Thermite” reactions have been used for welding metal parts such as railway rails and in metal refining. One such thermite reaction is:

$$\mathrm{Fe_2O_3}(s) + 2\,\mathrm{Al}(s) \longrightarrow \mathrm{Al_2O_3}(s) + 2\,\mathrm{Fe}(s) \tag{8.E.10}$$

Is the reaction spontaneous at room temperature under standard conditions? During the reaction, the surroundings absorb 851.8 kJ/mol of heat.

Q16.3.5

Using the relevant S°_{298} values listed in Appendix G, calculate S°_{298} for the following changes:

a. $\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \longrightarrow 2\,\mathrm{NH_3}(g)$
b. $\mathrm{N_2}(g) + \frac{5}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{N_2O_5}(g)$

S16.3.5

−198.1 J/K; −348.9 J/K

Q16.3.6

From the following information, determine ΔS°_{298} for the following:

a. $\mathrm{N}(g) + \mathrm{O}(g) \longrightarrow \mathrm{NO}(g) \quad \Delta S^\circ_{298} = ?$
b. $\mathrm{N_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{NO}(g) \quad \Delta S^\circ_{298} = 24.8\ \mathrm{J/K}$
c. $\mathrm{N_2}(g) \longrightarrow 2\,\mathrm{N}(g) \quad \Delta S^\circ_{298} = 115.0\ \mathrm{J/K}$
d. $\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{O}(g) \quad \Delta S^\circ_{298} = 117.0\ \mathrm{J/K}$

Q16.3.7

By calculating ΔS_{univ} at each temperature, determine if the melting of 1 mole of NaCl(s) is spontaneous at 500 °C and at 700 °C.

S^\circ_{\ce{NaCl}(s)}=\mathrm{72.11\:\dfrac{J}{mol·K}}\hspace{40px} S^\circ_{\ce{NaCl}(l)}=\mathrm{95.06\:\dfrac{J}{mol·K}}\hspace{40px} ΔH^\circ_\ce{fusion}=\mathrm{27.95\: kJ/mol}

What assumptions are made about the thermodynamic information (entropy and enthalpy values) used to solve this problem?

S16.3.7

As $\Delta S_{univ} < 0$ at each of these temperatures, melting is not spontaneous at either of them. The given values for entropy and enthalpy are for NaCl at 298 K. It is assumed that these do not change significantly at the higher temperatures used in the problem.

Q16.3.8

Use the standard entropy data in Appendix G to determine the change in entropy for each of the reactions listed in [link]. All are run under standard state conditions and 25 °C.

Q16.3.8

2.86 J/K; 24.8 J/K; −113.2 J/K; −24.7 J/K; 15.5 J/K; 290.0 J/K

16.4: Free Energy

Q16.4.1

What is the difference between ΔG, $\Delta G°$, and ΔG°_{298} for a chemical change?

Q16.4.2

A reactions has ΔH°_{298} = 100 kJ/mol and $\Delta S^\circ_{298} = 250\ \mathrm{J/mol{\cdot}K}$. Is the reaction spontaneous at room temperature? If not, under what temperature conditions will it become spontaneous?

S16.4.2

The reaction is nonspontaneous at room temperature. Above 400 K, ΔG will become negative, and the reaction will become spontaneous.

Q16.4.3

Explain what happens as a reaction starts with $\Delta G < 0$ (negative) and reaches the point where $\Delta G = 0$.

Use the standard free energy of formation data in Appendix G to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these conditions.

a. $\mathrm{MnO_2}(s) \longrightarrow \mathrm{Mn}(s) + \mathrm{O_2}(g)$

b. $H_2(g) + Br_2(l) \longrightarrow 2\,HBr(g)$
c. $Cu(s) + S(g) \longrightarrow CuS(s)$
d. $2\,LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(g)$
e. $CH_4(g) + O_2(g) \longrightarrow C(s,\text{ graphite}) + 2\,H_2O(g)$
f. $CS_2(g) + 3\,Cl_2(g) \longrightarrow CCl_4(g) + S_2Cl_2(g)$

S16.4.3

465.1 kJ nonspontaneous; −106.86 kJ spontaneous; −53.6 kJ spontaneous; −83.4 kJ spontaneous; −406.7 kJ spontaneous; −30.0 kJ spontaneous

Q16.4.4

Use the standard free energy data in Appendix G to determine the free energy change for each of the following reactions, which are run under standard state conditions and 25 °C. Identify each as either spontaneous or nonspontaneous at these conditions.

a. $C(s,\text{ graphite}) + O_2(g) \longrightarrow CO_2(g)$
b. $O_2(g) + N_2(g) \longrightarrow 2\,NO(g)$
c. $2\,Cu(s) + S(g) \longrightarrow Cu_2S(s)$
d. $CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s)$
e. $Fe_2O_3(s) + 3\,CO(g) \longrightarrow 2\,Fe(s) + 3\,CO_2(g)$
f. $CaSO_4 \cdot 2\,H_2O(s) \longrightarrow CaSO_4(s) + 2\,H_2O(g)$

Given:

$$P_4(s) + 5\,O_2(g) \longrightarrow P_4O_{10}(s) \quad \Delta G^\circ_{298} = -2697.0\text{ kJ/mol} \tag{8.E.11}$$

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g) \quad \Delta G^\circ_{298} = -457.18\text{ kJ/mol} \tag{8.E.12}$$

$$6\,H_2O(g) + P_4O_{10}(g) \longrightarrow 4\,H_3PO_4(l) \quad \Delta G^\circ_{298} = -428.66\text{ kJ/mol} \tag{8.E.13}$$

Q16.4.5

a. Determine the standard free energy of formation, ΔG°_f, for phosphoric acid.
b. How does your calculated result compare to the value in Appendix G? Explain.

S16.4.5

−1124.3 kJ/mol for the standard free energy change. The calculation agrees with the value in Appendix G because free energy is a state function (just like the enthalpy and entropy), so its change depends only on the initial and final states, not the path between them.

Q16.4.6

Is the formation of ozone ($O_3(g)$) from oxygen ($O_2(g)$) spontaneous at room temperature under standard state conditions?

Q16.4.7

Consider the decomposition of red mercury(II) oxide under standard state conditions.

$$2\,HgO(s,\text{ red}) \longrightarrow 2\,Hg(l) + O_2(g) \tag{8.E.14}$$

a. Is the decomposition spontaneous under standard state conditions?
b. Above what temperature does the reaction become spontaneous?

S16.4.7

The reaction is nonspontaneous; Above 566 °C the process is spontaneous.

Q16.4.8

Among other things, an ideal fuel for the control thrusters of a space vehicle should decompose in a spontaneous exothermic reaction when exposed to the appropriate catalyst. Evaluate the following substances under standard state conditions as suitable candidates for fuels.

a. Ammonia: $2\,NH_3(g) \longrightarrow N_2(g) + 3\,H_2(g)$
b. Diborane: $B_2H_6(g) \longrightarrow 2\,B(g) + 3\,H_2(g)$
c. Hydrazine: $N_2H_4(g) \longrightarrow N_2(g) + 2\,H_2(g)$
d. Hydrogen peroxide: $H_2O_2(l) \longrightarrow H_2O(g) + \frac{1}{2}O_2(g)$

Q16.4.9

Calculate $\Delta G°$ for each of the following reactions from the equilibrium constant at the temperature given.

a. $N_2(g) + O_2(g) \longrightarrow 2\,NO(g) \quad T = 2000\ ^\circ C \quad K_p = 4.1 \times 10^{-4}$
b. $H_2(g) + I_2(g) \longrightarrow 2\,HI(g) \quad T = 400\ ^\circ C \quad K_p = 50.0$
c. $CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g) \quad T = 980\ ^\circ C \quad K_p = 1.67$
d. $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g) \quad T = 900\ ^\circ C \quad K_p = 1.04$
e. $HF(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + F^-(aq) \quad T = 25\ ^\circ C \quad K_p = 7.2 \times 10^{-4}$
f. $AgBr(s) \longrightarrow Ag^+(aq) + Br^-(aq) \quad T = 25\ ^\circ C \quad K_p = 3.3 \times 10^{-13}$

S16.4.9

1.5×10^2 kJ; −21.9 kJ; −5.34 kJ; −0.383 kJ; 18 kJ; 71 kJ

Q16.4.10

Calculate $\Delta G°$ for each of the following reactions from the equilibrium constant at the temperature given.

a. $Cl_2(g) + Br_2(g) \longrightarrow 2\,BrCl(g) \quad T = 25\ ^\circ C \quad K_p = 4.7 \times 10^{-2}$
b. $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g) \quad T = 500\ ^\circ C \quad K_p = 48.2$
c. $H_2O(l) \rightleftharpoons H_2O(g) \quad T = 60\ ^\circ C \quad K_p = 0.196\text{ atm}$
d. $CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g) \quad T = 550\ ^\circ C \quad K_p = 4.90 \times 10^2$

e. $CH_3NH_2(aq) + H_2O(l) \longrightarrow CH_3NH_3^+(aq) + OH^-(aq) \quad T = 25\ ^\circ C \quad K_p = 4.4 \times 10^{-4}$
f. $PbI_2(s) \longrightarrow Pb^{2+}(aq) + 2\,I^-(aq) \quad T = 25\ ^\circ C \quad K_p = 8.7 \times 10^{-9}$

Q16.4.11

Calculate the equilibrium constant at 25 °C for each of the following reactions from the value of Δ*G*° given.

a. $O_2(g) + 2\,F_2(g) \longrightarrow 2\,OF_2(g) \quad \Delta G^\circ = -9.2\ kJ$
b. $I_2(s) + Br_2(l) \longrightarrow 2\,IBr(g) \quad \Delta G^\circ = 7.3\ kJ$
c. $2\,LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(g) \quad \Delta G^\circ = -79\ kJ$
d. $N_2O_3(g) \longrightarrow NO(g) + NO_2(g) \quad \Delta G^\circ = -1.6\ kJ$
e. $SnCl_4(l) \longrightarrow SnCl_4(l) \quad \Delta G^\circ = 8.0\ kJ$

S16.4.11

K = 41; *K* = 0.053; *K* = 6.9 × 10^{13}; *K* = 1.9; *K* = 0.04

Q16.4.2

Calculate the equilibrium constant at 25 °C for each of the following reactions from the value of Δ*G*° given.

a. $I_2(s) + Cl_2(g) \longrightarrow 2\,ICl(g) \quad \Delta G^\circ = -10.88\ kJ$
b. $H_2(g) + I_2(s) \longrightarrow 2\,HI(g) \quad \Delta G^\circ = 3.4\ kJ$
c. $CS_2(g) + 3\,Cl_2(g) \longrightarrow CCl_4(g) + S_2Cl_2(g) \quad \Delta G^\circ = -39\ kJ$
d. $2\,SO_2(g) + O_2(g) \longrightarrow 2\,SO_3(g) \quad \Delta G^\circ = -141.82\ kJ$
e. $CS_2(g) \longrightarrow CS_2(l) \quad \Delta G^\circ = -1.88\ kJ$

Q16.4.13

Calculate the equilibrium constant at the temperature given.

a. (a) $O_2(g) + 2\,F_2(g) \longrightarrow 2\,F_2O(g) \quad (T = 100\ ^\circ C)$
b. $I_2(s) + Br_2(l) \longrightarrow 2\,IBr(g) \quad (T = 0.0\ ^\circ C)$
c. $2\,LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(g) \quad (T = 575\ ^\circ C)$
d. $N_2O_3(g) \longrightarrow NO(g) + NO_2(g) \quad (T = -10.0\ ^\circ C)$
e. $SnCl_4(l) \longrightarrow SnCl_4(g) \quad (T = 200\ ^\circ C)$

S16.4.13

In each of the following, the value of Δ*G* is not given at the temperature of the reaction. Therefore, we must calculate Δ*G*° from the values Δ*H*° and Δ*S*° and then calculate Δ*G* from the relation ΔG° = ΔH° − TΔS°.

a. *K* = 1.29
b. *K* = 2.51 × 10^{-3}
c. *K* = 4.83 × 10^{3}
d. *K* = 0.219
e. *K* = 16.1

Q16.4.14

Calculate the equilibrium constant at the temperature given.

a. (a) $I_2(s) + Cl_2(g) \longrightarrow 2\,ICl(g) \quad (T = 100\ ^\circ C)$
b. $H_2(g) + I_2(s) \longrightarrow 2\,HI(g) \quad (T = 0.0\ ^\circ C)$
c. $CS_2(g) + 3\,Cl_2(g) \longrightarrow CCl_4(g) + S_2Cl_2(g) \quad (T = 125\ ^\circ C)$
d. $2\,SO_2(g) + O_2(g) \longrightarrow 2\,SO_3(g) \quad (T = 675\ ^\circ C)$
e. $CS_2(g) \longrightarrow CS_2(l) \quad (T = 90\ ^\circ C)$

Q16.4.15

Consider the following reaction at 298 K:

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \quad K_P = 0.142 \tag{8.E.15}$$

What is the standard free energy change at this temperature? Describe what happens to the initial system, where the reactants and products are in standard states, as it approaches equilibrium.

S16.4.16

The standard free energy change is $\Delta G^\circ_{298} = -RT \ln K = 4.84\ kJ/mol$. When reactants and products are in their standard states (1 bar or 1 atm), *Q* = 1. As the reaction proceeds toward equilibrium, the reaction shifts left (the amount of products drops while the amount of reactants increases): *Q* < 1, and ΔG_{298} becomes less positive as it approaches zero. At equilibrium, *Q* = *K*, and Δ*G* = 0.

Q16.4.17

Determine the normal boiling point (in kelvin) of dichloroethane, CH_2Cl_2. Find the actual boiling point using the Internet or some other source, and calculate the percent error in the temperature. Explain the differences, if any, between the two values.

Q16.4.18

Under what conditions is $N_2O_3(g) \longrightarrow NO(g) + NO_2(g)$ spontaneous?

S16.4.18

The reaction will be spontaneous at temperatures greater than 287 K.

Q16.4.19

At room temperature, the equilibrium constant (K_w) for the self-ionization of water is 1.00 × 10^{-14}. Using this information, calculate the standard free energy change for the aqueous reaction of hydrogen ion with hydroxide ion to produce water. (Hint: The reaction is the reverse of the self-ionization reaction.)

Q16.4.20

Hydrogen sulfide is a pollutant found in natural gas. Following its removal, it is converted to sulfur by the reaction $2\,H_2S(g) + SO_2(g) \rightleftharpoons \frac{3}{8}S_8(s,\text{ rhombic}) + 2\,H_2O(l)$. What is the equilibrium constant for this reaction? Is the reaction endothermic or exothermic?

S16.4.20

$K = 5.35 \times 10^{15}$

The process is exothermic.

Q16.4.21

Consider the decomposition of $CaCO_3$(s) into CaO(s) and CO_2(g). What is the equilibrium partial pressure of CO_2 at room temperature?

Q16.4.22

In the laboratory, hydrogen chloride (HCl(g)) and ammonia (NH_3(g)) often escape from bottles of their solutions and react to form the ammonium chloride (NH_4Cl(s)), the white glaze often seen on glassware. Assuming that the number of moles of each gas that escapes into the room is the same, what is the maximum partial pressure of HCl and NH_3 in the laboratory at room temperature? (Hint: The partial pressures will be equal and are at their maximum value when at equilibrium.)

S16.4.22

1.0×10^{-8} atm. This is the maximum pressure of the gases under the stated conditions.

Q16.4.23

Benzene can be prepared from acetylene. $3\,C_2H_2(g) \rightleftharpoons C_6H_6(g)$. Determine the equilibrium constant at 25 °C and at 850 °C. Is the reaction spontaneous at either of these temperatures? Why is all acetylene not found as benzene?

Q16.4.24

Carbon dioxide decomposes into CO and O_2 at elevated temperatures. What is the equilibrium partial pressure of oxygen in a sample at 1000 °C for which the initial pressure of CO_2 was 1.15 atm?

$$x = 1.29 \times 10^{-5}\text{ atm} = P_{O_2} \tag{8.E.16}$$

Q16.4.25

Carbon tetrachloride, an important industrial solvent, is prepared by the chlorination of methane at 850 K.

$$CH_4(g) + 4\,Cl_2(g) \longrightarrow CCl_4(g) + 4\,HCl(g) \tag{8.E.17}$$

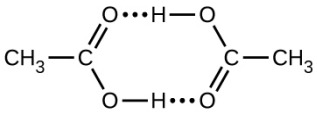
What is the equilibrium constant for the reaction at 850 K? Would the reaction vessel need to be heated or cooled to keep the temperature of the reaction constant?

Q16.4.25B

Acetic acid, CH_3CO_2H, can form a dimer, $(CH_3CO_2H)_2$, in the gas phase.

$$2\,CH_3CO_2H(g) \longrightarrow (CH_3CO_2H)_2(g) \tag{8.E.18}$$

The dimer is held together by two hydrogen bonds with a total strength of 66.5 kJ per mole of dimer.



At 25 °C, the equilibrium constant for the dimerization is 1.3×10^3 (pressure in atm). What is $\Delta S°$ for the reaction?

S16.4.25B

−0.16 kJ

Q16.4.26

Nitric acid, HNO_3, can be prepared by the following sequence of reactions:

$$4\,NH_3(g) + 5\,O_2(g) \longrightarrow 4\,NO(g) + 6\,H_2O(g) \tag{8.E.19}$$

$$2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g) \tag{8.E.20}$$

$$3\,NO_2(g) + H_2O(l) \longrightarrow 2\,HNO_3(l) + NO(g) \tag{8.E.21}$$

How much heat is evolved when 1 mol of NH_3(g) is converted to HNO_3(l)? Assume standard states at 25 °C.

Q16.4.27A

Determine ΔG for the following reactions.

(a) Antimony pentachloride decomposes at 448 °C. The reaction is:

$$SbCl_5(g) \longrightarrow SbCl_3(g) + Cl_2(g) \tag{8.E.22}$$

An equilibrium mixture in a 5.00 L flask at 448 °C contains 3.85 g of $SbCl_5$, 9.14 g of $SbCl_3$, and 2.84 g of Cl_2.

Chlorine molecules dissociate according to this reaction:

$$Cl_2(g) \longrightarrow 2\,Cl(g) \tag{8.E.23}$$

1.00% of Cl_2 molecules dissociate at 975 K and a pressure of 1.00 atm.

S16.4.27A

a. (a) −22.1 kJ;
b. 61.6 kJ/mol

Q16.4.27

Given that the ΔG_f° for $Pb^{2+}(aq)$ and $Cl^-(aq)$ is −24.3 kJ/mole and −131.2 kJ/mole respectively, determine the solubility product, K_{sp}, for $PbCl_2(s)$.

Q16.4.28

Determine the standard free energy change, ΔG_f°, for the formation of $S^{2-}(aq)$ given that the ΔG_f° for $Ag^+(aq)$ and $Ag_2S(s)$ are 77.1 k/mole and −39.5 kJ/mole respectively, and the solubility product for $Ag_2S(s)$ is 8×10^{-51}.

S16.4.28

90 kJ/mol

Q16.4.29

Determine the standard enthalpy change, entropy change, and free energy change for the conversion of diamond to graphite. Discuss the spontaneity of the conversion with respect to the enthalpy and entropy changes. Explain why diamond spontaneously changing into graphite is not observed.

Q16.4.30

The evaporation of one mole of water at 298 K has a standard free energy change of 8.58 kJ.

$$\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2O}(g) \quad \Delta G^\circ_{298} = 8.58\ \mathrm{kJ} \tag{8.E.24}$$

a. (a) Is the evaporation of water under standard thermodynamic conditions spontaneous?
b. Determine the equilibrium constant, K_P, for this physical process.
c. By calculating ΔG, determine if the evaporation of water at 298 K is spontaneous when the partial pressure of water, $P_{\mathrm{H_2O}}$, is 0.011 atm.
d. If the evaporation of water were always nonspontaneous at room temperature, wet laundry would never dry when placed outside. In order for laundry to dry, what must be the value of $P_{\mathrm{H_2O}}$ in the air?

S16.4.30

(a) Under standard thermodynamic conditions, the evaporation is nonspontaneous; K_p = 0.031; The evaporation of water is spontaneous; $P_{\mathrm{H_2O}}$ must always be less than K_p or less than 0.031 atm. 0.031 atm represents air saturated with water vapor at 25 °C, or 100% humidity.

Q16.4.31

In glycolysis, the reaction of glucose (Glu) to form glucose-6-phosphate (G6P) requires ATP to be present as described by the following equation:

$$\mathrm{Glu} + \mathrm{ATP} \longrightarrow \mathrm{G6P} + \mathrm{ADP} \quad \Delta G^\circ_{298} = -17\ \mathrm{kJ} \tag{8.E.25}$$

In this process, ATP becomes ADP summarized by the following equation:

$$\mathrm{ATP} \longrightarrow \mathrm{ADP} \quad \Delta G^\circ_{298} = -30\ \mathrm{kJ} \tag{8.E.26}$$

Determine the standard free energy change for the following reaction, and explain why ATP is necessary to drive this process:

$$\mathrm{Glu} \longrightarrow \mathrm{G6P} \quad \Delta G^\circ_{298} = ? \tag{8.E.27}$$

Q16.4.32

One of the important reactions in the biochemical pathway glycolysis is the reaction of glucose-6-phosphate (G6P) to form fructose-6-phosphate (F6P):

$$\mathrm{G6P} \rightleftharpoons \mathrm{F6P} \quad \Delta G^\circ_{298} = 1.7\ \mathrm{kJ} \tag{8.E.28}$$

a. (a) Is the reaction spontaneous or nonspontaneous under standard thermodynamic conditions?
b. Standard thermodynamic conditions imply the concentrations of G6P and F6P to be 1 *M*, however, in a typical cell, they are not even close to these values. Calculate ΔG when the concentrations of G6P and F6P are 120 μ*M* and 28 μ*M* respectively, and discuss the spontaneity of the forward reaction under these conditions. Assume the temperature is 37 °C.

S16.4.32

(a) Nonspontaneous as $\Delta G^\circ_{298} > 0$; $\Delta G^\circ_{298} = -RT\ln K$, $\Delta G = 1.7 \times 10^3 + \left(8.314 \times 335 \times \ln\frac{28}{128}\right) = -2.5$ kJ . The forward reaction to produce F6P is spontaneous under these conditions.

Q16.4.33

Without doing a numerical calculation, determine which of the following will reduce the free energy change for the reaction, that is, make it less positive or more negative, when the temperature is increased. Explain.

a. (a) $\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \longrightarrow 2\,\mathrm{NH_3}(g)$
b. $\mathrm{HCl}(g) + \mathrm{NH_3}(g) \longrightarrow \mathrm{NH_4Cl}(s)$
c. $\mathrm{(NH_4)_2Cr_2O_7}(s) \longrightarrow \mathrm{Cr_2O_3}(s) + 4\,\mathrm{H_2O}(g) + \mathrm{N_2}(g)$
d. $2\,\mathrm{Fe}(s) + 3\,\mathrm{O_2}(g) \longrightarrow \mathrm{Fe_2O_3}(s)$

When ammonium chloride is added to water and stirred, it dissolves spontaneously and the resulting solution feels cold. Without doing any calculations, deduce the signs of ΔG, ΔH, and ΔS for this process, and justify your choices.

S16.4.33

ΔG is negative as the process is spontaneous. ΔH is positive as with the solution becoming cold, the dissolving must be endothermic. ΔS must be positive as this drives the process, and it is expected for the dissolution of any soluble ionic compound.

Q16.4.34

An important source of copper is from the copper ore, chalcocite, a form of copper(I) sulfide. When heated, the Cu_2S decomposes to form copper and sulfur described by the following equation:

$$\mathrm{Cu_2S}(s) \longrightarrow \mathrm{Cu}(s) + \mathrm{S}(s) \tag{8.E.29}$$

a. (a) Determine ΔG°_{298} for the decomposition of $\mathrm{Cu_2S}(s)$.
b. The reaction of sulfur with oxygen yields sulfur dioxide as the only product. Write an equation that describes this reaction, and determine ΔG°_{298} for the process.
c. The production of copper from chalcocite is performed by roasting the $\mathrm{Cu_2S}$ in air to produce the Cu. By combining the equations from Parts (a) and (b), write the equation that describes the roasting of the chalcocite, and explain why coupling these reactions together makes for a more efficient process for the production of the copper.

Q16.4.35

What happens to ΔG°_{298} (becomes more negative or more positive) for the following chemical reactions when the partial pressure of oxygen is increased?

a. (a) $\mathrm{S}(s) + \mathrm{O_2}(g) \longrightarrow \mathrm{SO_2}(g)$
b. $2\,\mathrm{SO_2}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{SO_3}(g)$
c. $\mathrm{HgO}(s) \longrightarrow \mathrm{Hg}(l) + \mathrm{O_2}(g)$

S16.4.35

a. (a) Increasing $P_{\mathrm{O_2}}$ will shift the equilibrium toward the products, which increases the value of *K*. ΔG°_{298} therefore becomes more negative.
b. Increasing $P_{\mathrm{O_2}}$ will shift the equilibrium toward the products, which increases the value of *K*. ΔG°_{298} therefore becomes more negative.
c. Increasing $P_{\mathrm{O_2}}$ will shift the equilibrium the reactants, which decreases the value of *K*. ΔG°_{298} therefore becomes more positive.

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8.S: Entropy and Free Energy (Study Guide)

8.1 Spontaneity

Chemical and physical processes have a natural tendency to occur in one direction under certain conditions. A spontaneous process occurs without the need for a continual input of energy from some external source, while a nonspontaneous process requires such. Systems undergoing a spontaneous process may or may not experience a gain or loss of energy, but they will experience a change in the way matter and/or energy is distributed within the system.

8.2 Entropy

Entropy (S) is a state function that can be related to the number of microstates for a system (the number of ways the system can be arranged) and to the ratio of reversible heat to kelvin temperature. It may be interpreted as a measure of the dispersal or distribution of matter and/or energy in a system, and it is often described as representing the “disorder” of the system.

For a given substance, entropy depends on phase with $S_{solid} < S_{liquid} < S_{gas}$. For different substances in the same physical state at a given temperature, entropy is typically greater for heavier atoms or more complex molecules. Entropy increases when a system is heated and when solutions form. Using these guidelines, the sign of entropy changes for some chemical reactions and physical changes may be reliably predicted.

8.3 The Second and Third Laws of Thermodynamics

The second law of thermodynamics states that a spontaneous process increases the entropy of the universe, $S_{univ} > 0$. If $\Delta S_{univ} < 0$, the process is nonspontaneous, and if $\Delta S_{univ} = 0$, the system is at equilibrium. The third law of thermodynamics establishes the zero for entropy as that of a perfect, pure crystalline solid at 0 K. With only one possible microstate, the entropy is zero. We may compute the standard entropy change for a process by using standard entropy values for the reactants and products involved in the process.

8.4 Gibbs Free Energy

Gibbs free energy (G) is a state function defined with regard to system quantities only and may be used to predict the spontaneity of a process. A negative value for ΔG indicates a spontaneous process; a positive ΔG indicates a nonspontaneous process; and a ΔG of zero indicates that the system is at equilibrium. A number of approaches to the computation of free energy changes are possible.

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CHAPTER OVERVIEW

9: Electrochemistry

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General Chemistry

Electrochemistry deals with chemical reactions that produce electricity and the changes associated with the passage of electrical current through matter. The reactions involve electron transfer, and so they are oxidation-reduction (or redox) reactions. Many metals may be purified or electroplated using electrochemical methods. Devices such as automobiles, smartphones, electronic tablets, watches, pacemakers, and many others use batteries for power. Batteries use chemical reactions that produce electricity spontaneously and that can be converted into useful work. All electrochemical systems involve the transfer of electrons in a reacting system. In many systems, the reactions occur in a region known as the cell, where the transfer of electrons occurs at electrodes.

9.1: Balancing Oxidation-Reduction Reactions
9.2: Galvanic Cells
9.3: Standard Reduction Potentials
9.4: The Nernst Equation
9.5: Batteries and Fuel Cells
9.6: Electrolysis
9.E: Exercises on Electrochemistry
9.S: Electrochemistry (Study Guide)

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9.1: Balancing Oxidation-Reduction Reactions

Learning Objectives

- Define electrochemistry and a number of important associated terms
- Split oxidation-reduction reactions into their oxidation half-reactions and reduction half-reactions
- Produce balanced oxidation-reduction equations for reactions in acidic or basic solution
- Identify oxidizing agents and reducing agents

Electricity refers to a number of phenomena associated with the presence and flow of electric charge. Electricity includes such diverse things as lightning, static electricity, the current generated by a battery as it discharges, and many other influences on our daily lives. The flow or movement of charge is an electric current (Figure 9.1.1). Electrons or ions may carry the charge. The elementary unit of charge is the charge of a proton, which is equal in magnitude to the charge of an electron. The SI unit of charge is the coulomb (C) and the charge of a proton is 1.602×10^{-19} C. The presence of an electric charge generates an electric field. Electric current is the rate of flow of charge.



Figure 9.1.1: Electricity-related phenomena include lightning, accumulation of static electricity, and current produced by a battery. (credit left: modification of work by Thomas Bresson; credit middle: modification of work by Chris Darling; credit right: modification of work by Windell Oskay).

The SI unit for electrical current is the SI base unit called the ampere (A), which is a flow rate of 1 coulomb of charge per second (1 A = 1 C/s). An electric current flows in a path, called an electric circuit. In most chemical systems, it is necessary to maintain a closed path for current to flow. The flow of charge is generated by an electrical potential difference, or potential, between two points in the circuit. Electrical potential is the ability of the electric field to do work on the charge. The SI unit of electrical potential is the volt (V). When 1 coulomb of charge moves through a potential difference of 1 volt, it gains or loses 1 joule (J) of energy. Table 9.1.1 summarizes some of this information about electricity.

Table 9.1.1: Common Electrical Terms

Quantity	Definition	Measure or Unit
Electric charge	Charge on a proton	1.602×10^{-19} C
Electric current	The movement of charge	ampere = A = 1 C/s
Electric potential	The force trying to move the charge	volt = V = J/C
Electric field	The force acting upon other charges in the vicinity	

Electrochemistry studies oxidation-reduction reactions, which were first discussed in an earlier chapter, where we learned that oxidation was the loss of electrons and reduction was the gain of electrons. The reactions discussed tended to be rather simple, and conservation of mass (atom counting by type) and deriving a correctly balanced chemical equation were relatively simple. In this section, we will concentrate on the half-reaction method for balancing oxidation-reduction reactions. The use of half-reactions is important partly for balancing more complicated reactions and partly because many aspects of electrochemistry are easier to discuss in terms of half-reactions. There are alternate methods of balancing these reactions; however, there are no good alternatives to half-reactions for discussing what is occurring in many systems. The half-reaction method splits oxidation-reduction reactions into their oxidation “half” and reduction “half” to make finding the overall equation easier.

Electrochemical reactions frequently occur in solutions, which could be acidic, basic, or neutral. When balancing oxidation-reduction reactions, the nature of the solution may be important. It helps to see this in an actual problem. Consider the following unbalanced oxidation-reduction reaction in acidic solution:

$$\mathrm{MnO_4^-}(aq) + \mathrm{Fe^{2+}}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq) + \mathrm{Fe^{3+}}(aq)$$

We can start by collecting the species we have so far into an unbalanced oxidation half-reaction and an unbalanced reduction half-reaction. Each of these half-reactions contain the same element in two different oxidation states. The Fe^{2+} has lost an electron to become Fe^{3+}; therefore, the iron underwent oxidation. The reduction is not as obvious; however, the manganese gained five electrons to change from Mn^{7+} to Mn^{2+}.

$$\text{oxidation (unbalanced): } \mathrm{Fe^{2+}}(aq) \longrightarrow \mathrm{Fe^{3+}}(aq)$$
$$\text{reduction (unbalanced): } \mathrm{MnO_4^-}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq)$$

In acidic solution, there are hydrogen ions present, which are often useful in balancing half-reactions. It may be necessary to use the hydrogen ions directly or as a reactant that may react with oxygen to generate water. Hydrogen ions are very important in acidic solutions where the reactants or products contain hydrogen and/or oxygen. In this example, the oxidation half-reaction involves neither hydrogen nor oxygen, so hydrogen ions are not necessary to the balancing. However, the reduction half-reaction does involve oxygen. It is necessary to use hydrogen ions to convert this oxygen to water.

$$\text{charge not balanced: } \mathrm{MnO_4^-}(aq) + 8\,\mathrm{H^+}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\,\mathrm{H_2O}(l)$$

The situation is different in basic solution because the hydrogen ion concentration is lower and the hydroxide ion concentration is higher. After finishing this example, we will examine how basic solutions differ from acidic solutions. A neutral solution may be treated as acidic or basic, though treating it as acidic is usually easier.

The iron atoms in the oxidation half-reaction are balanced (mass balance); however, the charge is unbalanced, since the charges on the ions are not equal. It is necessary to use electrons to balance the charge. The way to balance the charge is by *adding* electrons to one side of the equation. Adding a single electron on the right side gives a balanced oxidation half-reaction:

$$\text{oxidation (balanced): } \mathrm{Fe^{2+}}(aq) \longrightarrow \mathrm{Fe^{3+}}(aq) + \mathrm{e^-}$$

You should check the half-reaction for the number of each atom type and the total charge on each side of the equation. The charges include the actual charges of the ions times the number of ions and the charge on an electron times the number of electrons.

$$\text{Fe: Does } (1 \times 1) = (1 \times 1)\text{? Yes.}$$
$$\text{Charge: Does } [1 \times (+2)] = [1 \times (+3) + 1 \times (-1)]\text{? Yes.}$$

If the atoms and charges balance, the half-reaction is balanced. In oxidation half-reactions, electrons appear as products (on the right). As discussed in the earlier chapter, since iron underwent oxidation, iron is the reducing agent.

Now return to the reduction half-reaction equation:

$$\text{reduction (unbalanced): } \mathrm{MnO_4^-}(aq) + 8\,\mathrm{H^+}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\,\mathrm{H_2O}(l)$$

The atoms are balanced (mass balance), so it is now necessary to check for charge balance. The total charge on the left of the reaction arrow is [(−1) × (1) + (8) × (+1)], or +7, while the total charge on the right side is [(1) × (+2) + (4) × (0)], or +2. The difference between +7 and +2 is five; therefore, it is necessary to add five electrons to the left side to achieve charge balance.

$$\text{Reduction (balanced): } \mathrm{MnO_4^-}(aq) + 8\,\mathrm{H^+}(aq) + 5\,\mathrm{e^-} \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\,\mathrm{H_2O}(l)$$

You should check this half-reaction for each atom type and for the charge, as well:

$$\text{Mn: Does } (1 \times 1) = (1 \times 1)\text{? Yes.}$$
$$\text{H: Does } (8 \times 1) = (4 \times 2)\text{? Yes.}$$
$$\text{O: Does } (1 \times 4) = (4 \times 1)\text{? Yes.}$$
$$\text{Charge: Does } [1 \times (-1) + 8 \times (+1) + 5 \times (-1)] = [1 \times (+2)]\text{? Yes.}$$

Now that this half-reaction is balanced, it is easy to see it involves reduction because electrons were gained when MnO_4^- was reduced to Mn^{2+}. In all reduction half-reactions, electrons appear as reactants (on the left side). As discussed in the earlier chapter, the species that was reduced, MnO_4^- in this case, is also called the oxidizing agent. We now have two balanced half-reactions.

$$\text{oxidation: } \mathrm{Fe^{2+}}(aq) \longrightarrow \mathrm{Fe^{3+}}(aq) + \mathrm{e^-}$$
$$\text{reduction: } \mathrm{MnO_4^-}(aq) + 8\,\mathrm{H^+}(aq) + 5\,\mathrm{e^-} \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\,\mathrm{H_2O}(l)$$

It is now necessary to combine the two halves to produce a whole reaction. The key to combining the half-reactions is the electrons. The electrons lost during oxidation must go somewhere. These electrons go to cause reduction. The number of electrons transferred from the oxidation half-reaction to the reduction half-reaction must be equal. There can be no missing or excess electrons. In this example, the oxidation half-reaction generates one electron, while the reduction half-reaction requires five. The lowest common multiple of one and five is five; therefore, it is necessary to multiply every term in the oxidation half-reaction by five and every term in the reduction half-reaction by one. (In this case, the multiplication of the reduction half-reaction generates no change; however, this will not always be the case.) The multiplication of the two half-reactions by the appropriate factor followed by addition of the two halves gives

$$\begin{aligned}&\text{oxidation: } 5 \times (\mathrm{Fe^{2+}}(aq) \longrightarrow \mathrm{Fe^{3+}}(aq) + \mathrm{e^-})\\ &\text{reduction: } \mathrm{MnO_4^-}(aq) + 8\,\mathrm{H^+}(aq) + 5\,\mathrm{e^-} \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\,\mathrm{H_2O}(l)\\ \hline &\text{overall: } 5\,\mathrm{Fe^{2+}}(aq) + \mathrm{MnO_4^-}(aq) + 8\,\mathrm{H^+}(aq) \longrightarrow 5\,\mathrm{Fe^{3+}}(aq) + \mathrm{Mn^{2+}}(aq) + 4\,\mathrm{H_2O}(l)\end{aligned}$$

The electrons do not appear in the final answer because the oxidation electrons are the same electrons as the reduction electrons and they “cancel.” Carefully check each side of the overall equation to verify everything was combined correctly:

$$\begin{aligned}&\text{Fe: Does } (5 \times 1) = (5 \times 1)\text{? Yes.}\\ &\text{Mn: Does } (1 \times 1) = (1 \times 1)\text{? Yes.}\\ &\text{H: Does } (8 \times 1) = (4 \times 2)\text{? Yes.}\\ &\text{O: Does } (1 \times 4) = (4 \times 1)\text{? Yes.}\\ &\text{Charge: Does } [5 \times (+2) + 1 \times (-1) + 8 \times (+1)] = [5 \times (+3) + 1 \times (+2)]\text{? Yes.}\end{aligned}$$

Everything checks, so this is the overall equation in acidic solution. If something does not check, the most common error occurs during the multiplication of the individual half-reactions.

Now suppose we wanted the solution to be basic. Recall that basic solutions have excess hydroxide ions. Some of these hydroxide ions will react with hydrogen ions to produce water. The simplest way to generate the balanced overall equation in basic solution is to start with the balanced equation in acidic solution, then “convert” it to the equation for basic solution. However, it is necessary to exercise caution when doing this, as many reactants behave differently under basic conditions and many metal ions will precipitate as the metal hydroxide. We just produced the following reaction, which we want to change to a basic reaction:

$$5\,\mathrm{Fe^{2+}}(aq) + \mathrm{MnO_4^-}(aq) + 8\,\mathrm{H^+}(aq) \longrightarrow 5\,\mathrm{Fe^{3+}}(aq) + \mathrm{Mn^{2+}}(aq) + 4\,\mathrm{H_2O}(l)$$

However, under basic conditions, $\mathrm{MnO_4^-}$ normally reduces to $\mathrm{MnO_2}$ and iron will be present as either $\mathrm{Fe(OH)_2}$ or $\mathrm{Fe(OH)_3}$. For these reasons, under basic conditions, this reaction will be

$$3\,\mathrm{Fe(OH)_2}(s) + \mathrm{MnO_4^-}(aq) + 2\,\mathrm{H_2O}(l) \longrightarrow 3\,\mathrm{Fe(OH)_3}(s) + \mathrm{MnO_2}(s) + \mathrm{OH^-}(aq)$$

(Under very basic conditions $\mathrm{MnO_4^-}$ will reduce to $\mathrm{MnO_4^{2-}}$, instead of $\mathrm{MnO_2}$.)

It is still possible to balance any oxidation-reduction reaction as an acidic reaction and then, when necessary, convert the equation to a basic reaction. This will work if the acidic and basic reactants and products are the same or if the basic reactants and products are used before the conversion from acidic or basic. There are very few examples in which the acidic and basic reactions will involve the same reactants and products. However, balancing a basic reaction as acidic and then converting to basic will work. To convert to a basic reaction, it is necessary to add the same number of hydroxide ions to each side of the equation so that all the hydrogen ions ($\mathrm{H^+}$) are removed and mass balance is maintained. Hydrogen ion combines with hydroxide ion ($\mathrm{OH^-}$) to produce water.

Let us now try a basic equation. We will start with the following basic reaction:

$$\mathrm{Cl^-}(aq) + \mathrm{MnO_4^-}(aq) \longrightarrow \mathrm{ClO_3^-}(aq) + \mathrm{MnO_2}(s)$$

Balancing this as acid gives

$$\mathrm{Cl^-}(aq) + 2\,\mathrm{MnO_4^-}(aq) + 2\,\mathrm{H^+}(aq) \longrightarrow \mathrm{ClO_3^-}(aq) + 2\,\mathrm{MnO_2}(s) + \mathrm{H_2O}(l)$$

In this case, it is necessary to add two hydroxide ions to each side of the equation to convert the two hydrogen ions on the left into water:

$$\mathrm{Cl^-}(aq) + 2\,\mathrm{MnO_4^-}(aq) + (2\,\mathrm{H^+} + 2\,\mathrm{OH^-})(aq) \longrightarrow \mathrm{ClO_3^-}(aq) + 2\,\mathrm{MnO_2}(s) + \mathrm{H_2O}(l) + 2\,\mathrm{OH^-}(aq)$$

$$\mathrm{Cl^-}(aq) + 2\,\mathrm{MnO_4^-}(aq) + (2\,\mathrm{H_2O})(l) \longrightarrow \mathrm{ClO_3^-}(aq) + 2\,\mathrm{MnO_2}(s) + \mathrm{H_2O}(l) + 2\,\mathrm{OH^-}(aq)$$

Note that both sides of the equation show water. Simplifying should be done when necessary, and gives the desired equation. In this case, it is necessary to remove one H_2O from each side of the reaction arrows.

$$\mathrm{Cl^-}(aq) + 2\,\mathrm{MnO_4^-}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{ClO_3^-}(aq) + 2\,\mathrm{MnO_2}(s) + 2\,\mathrm{OH^-}(aq)$$

Again, check each side of the overall equation to make sure there are no errors:

Cl: Does $(1 \times 1) = (1 \times 1)$? Yes.
Mn: Does $(2 \times 1) = (2 \times 1)$? Yes.
H: Does $(1 \times 2) = (2 \times 1)$? Yes.
O: Does $(2 \times 4 + 1 \times 1) = (3 \times 1 + 2 \times 2 + 2 \times 1)$? Yes.
Charge: Does $[1 \times (-1) + 2 \times (-1)] = [1 \times (-1) + 2 \times (-1)]$? Yes.

Everything checks, so this is the overall equation in basic solution.

Example 9.1.1: Balancing Acidic Oxidation-Reduction Reactions

Balance the following reaction equation in acidic solution:

$$\mathrm{MnO_4^-}(aq) + \mathrm{Cr^{3+}}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq) + \mathrm{Cr_2O_7^{2-}}(aq)$$

Solution

This is an oxidation-reduction reaction, so start by collecting the species given into an unbalanced oxidation half-reaction and an unbalanced reduction half-reaction.

$$\text{oxidation (unbalanced): } \mathrm{Cr^{3+}}(aq) \longrightarrow \mathrm{Cr_2O_7^{2-}}(aq)$$
$$\text{reduction (unbalanced): } \mathrm{MnO_4^-}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq)$$

Starting with the oxidation half-reaction, we can balance the chromium

$$\text{oxidation (unbalanced): } 2\,\mathrm{Cr^{3+}}(aq) \longrightarrow \mathrm{Cr_2O_7^{2-}}(aq)$$

In acidic solution, we can use or generate hydrogen ions (H^+). Adding seven water molecules to the left side provides the necessary oxygen; the “left over” hydrogen appears as 14 H^+ on the right:

$$\text{oxidation (unbalanced): } 2\,\mathrm{Cr^{3+}}(aq) + 7\,\mathrm{H_2O}(l) \longrightarrow \mathrm{Cr_2O_7^{2-}}(aq) + 14\,\mathrm{H^+}(aq)$$

The left side of the equation has a total charge of [2 × (+3) = +6], and the right side a total charge of [−2 + 14 × (+1) = +12]. The difference is six; adding six electrons to the right side produces a mass- and charge-balanced oxidation half-reaction (in acidic solution):

$$\text{oxidation (balanced): } 2\,\mathrm{Cr^{3+}}(aq) + 7\,\mathrm{H_2O}(l) \longrightarrow \mathrm{Cr_2O_7^{2-}}(aq) + 14\,\mathrm{H^+}(aq) + 6\,\mathrm{e^-}$$

Checking the half-reaction:

Cr: Does $(2 \times 1) = (1 \times 2)$? Yes.
H: Does $(7 \times 2) = (14 \times 1)$? Yes.
O: Does $(7 \times 1) = (1 \times 7)$? Yes.
Charge: Does $[2 \times (+3)] = [1 \times (-2) + 14 \times (+1) + 6 \times (-1)]$? Yes.

Now work on the reduction. It is necessary to convert the four oxygen atoms in the permanganate into four water molecules. To do this, add eight H^+ to convert the oxygen into four water molecules:

$$\text{reduction (unbalanced): } \mathrm{MnO_4^-}(aq) + 8\,\mathrm{H^+}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\,\mathrm{H_2O}(l)$$

Then add five electrons to the left side to balance the charge:

$$\text{reduction (balanced): } \mathrm{MnO_4^-}(aq) + 8\,\mathrm{H^+}(aq) + 5\,\mathrm{e^-} \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\,\mathrm{H_2O}(l)$$

Make sure to check the half-reaction:

$$\begin{aligned}&\text{Mn: Does } (1\times1)=(1\times1)\text{? Yes.}\\&\text{H: Does } (8\times1)=(4\times2)\text{? Yes.}\\&\text{O: Does } (1\times4)=(4\times1)\text{? Yes.}\\&\text{Charge: Does } [1\times(-1)+8\times(+1)+5\times(-1)]=[1\times(+2)]\text{? Yes.}\end{aligned}$$

Collecting what we have so far:

$$\begin{aligned}&\text{oxidation: } 2\,Cr^{3+}(aq)+7\,H_2O(l)\longrightarrow Cr_2O_7^{2-}(aq)+14\,H^+(aq)+6\,e^-\\&\text{reduction: } MnO_4^-(aq)+8\,H^+(aq)+5\,e^-\longrightarrow Mn^{2+}(aq)+4\,H_2O(l)\end{aligned}$$

The least common multiple for the electrons is 30, so multiply the oxidation half-reaction by five, the reduction half-reaction by six, combine, and simplify:

$$10\,Cr^{3+}(aq)+35\,H_2O(l)+6\,MnO_4^-(aq)+48\,H^+(aq)\longrightarrow 5\,Cr_2O_7^{2-}(aq)+70\,H^+(aq)+6\,Mn^{2+}(aq)+24\,H_2O(l)$$

$$10\,Cr^{3+}(aq)+11\,H_2O(l)+6\,MnO_4^-(aq)\longrightarrow 5\,Cr_2O_7^{2-}(aq)+22\,H^+(aq)+6\,Mn^{2+}(aq)$$

Checking each side of the equation:

$$\begin{aligned}&\text{Mn: Does } (6\times1)=(6\times1)\text{? Yes.}\\&\text{Cr: Does } (10\times1)=(5\times2)\text{? Yes.}\\&\text{H: Does } (11\times2)=(22\times1)\text{? Yes.}\\&\text{O: Does } (11\times1+6\times4)=(5\times7)\text{? Yes.}\\&\text{Charge: Does } [10\times(+3)+6\times(-1)]=[5\times(-2)+22\times(+1)+6\times(+2)]\text{? Yes.}\end{aligned}$$

This is the balanced equation in acidic solution.

? Exercise 9.1.1

Balance the following equation in acidic solution:

$$Hg_2^{2+}+Ag\longrightarrow Hg+Ag^+$$

Answer

$$Hg_2^{2+}(aq)+2\,Ag(s)\longrightarrow 2\,Hg(l)+2\,Ag^+(aq)$$

✓ Example 9.1.2: Balancing Basic Oxidation-Reduction Reactions

Balance the following reaction equation in basic solution:

$$MnO_4^-(aq)+Cr(OH)_3(s)\longrightarrow MnO_2(s)+CrO_4^{2-}(aq)$$

Solution

This is an oxidation-reduction reaction, so start by collecting the species given into an unbalanced oxidation half-reaction and an unbalanced reduction half-reaction

$$\begin{aligned}&\text{oxidation (unbalanced): } Cr(OH)_3(s)\longrightarrow CrO_4^{2-}(aq)\\&\text{reduction (unbalanced): } MnO_4^-(aq)\longrightarrow MnO_2(s)\end{aligned}$$

Starting with the oxidation half-reaction, we can balance the chromium

$$\text{oxidation (unbalanced): } Cr(OH)_3(s)\longrightarrow CrO_4^{2-}(aq)$$

In acidic solution, we can use or generate hydrogen ions (H^+). Adding one water molecule to the left side provides the necessary oxygen; the “left over” hydrogen appears as five H^+ on the right side:

$$\text{oxidation (unbalanced): } Cr(OH)_3(s)+H_2O(l)\longrightarrow CrO_4^{2-}(aq)+5\,H^+(aq)$$

The left side of the equation has a total charge of [0], and the right side a total charge of [−2 + 5 × (+1) = +3]. The difference is three, adding three electrons to the right side produces a mass- and charge-balanced oxidation half-reaction (in acidic solution):

$$\text{oxidation (balanced): } \mathrm{Cr(OH)_3}(s) + \mathrm{H_2O}(l) \longrightarrow \mathrm{CrO_4^{2-}}(aq) + 5\,\mathrm{H^+}(aq) + 3\,\mathrm{e^-}$$

Checking the half-reaction:

$$\begin{aligned}&\text{Cr: Does } (1 \times 1) = (1 \times 1)\text{? Yes.}\\ &\text{H: Does } (1 \times 3 + 1 \times 2) = (5 \times 1)\text{? Yes.}\\ &\text{O: Does } (1 \times 3 + 1 \times 1) = (4 \times 1)\text{? Yes.}\\ &\text{Charge: Does } [0 = [1 \times (-2) + 5 \times (+1) + 3 \times (-1)]\text{? Yes.}\end{aligned}$$

Now work on the reduction. It is necessary to convert the four O atoms in the MnO_4^- minus the two O atoms in MnO_2 into two water molecules. To do this, add four H^+ to convert the oxygen into two water molecules:

$$\text{reduction (unbalanced): } \mathrm{MnO_4^-}(aq) + 4\,\mathrm{H^+}(aq) \longrightarrow \mathrm{MnO_2}(s) + 2\,\mathrm{H_2O}(l)$$

Then add three electrons to the left side to balance the charge:

$$\text{reduction (balanced): } \mathrm{MnO_4^-}(aq) + 4\,\mathrm{H^+}(aq) + 3\,\mathrm{e^-} \longrightarrow \mathrm{MnO_2}(s) + 2\,\mathrm{H_2O}(l)$$

Make sure to check the half-reaction:

$$\begin{aligned}&\text{Mn: Does } (1 \times 1) = (1 \times 1)\text{? Yes.}\\ &\text{H: Does } (4 \times 1) = (2 \times 2)\text{? Yes.}\\ &\text{O: Does } (1 \times 4) = (1 \times 2 + 2 \times 1)\text{? Yes.}\\ &\text{Charge: Does } [1 \times (-1) + 4 \times (+1) + 3 \times (-1)] = [0]\text{? Yes.}\end{aligned}$$

Collecting what we have so far:

$$\begin{aligned}&\text{oxidation: } \mathrm{Cr(OH)_3}(s) + \mathrm{H_2O}(l) \longrightarrow \mathrm{CrO_4^{2-}}(aq) + 5\,\mathrm{H^+}(aq) + 3\,\mathrm{e^-}\\ &\text{reduction: } \mathrm{MnO_4^-}(aq) + 4\,\mathrm{H^+}(aq) + 3\,\mathrm{e^-} \longrightarrow \mathrm{MnO_2}(s) + 2\,\mathrm{H_2O}(l)\end{aligned}$$

In this case, both half reactions involve the same number of electrons; therefore, simply add the two half-reactions together.

$$\mathrm{MnO_4^-}(aq) + 4\,\mathrm{H^+}(aq) + \mathrm{Cr(OH)_3}(s) + \mathrm{H_2O}(l) \longrightarrow \mathrm{CrO_4^{2-}}(aq) + \mathrm{MnO_2}(s) + 2\,\mathrm{H_2O}(l) + 5\,\mathrm{H^+}(aq)$$

$$\mathrm{MnO_4^-}(aq) + \mathrm{Cr(OH)_3}(s) \longrightarrow \mathrm{CrO_4^{2-}}(aq) + \mathrm{MnO_2}(s) + \mathrm{H_2O}(l) + \mathrm{H^+}(aq)$$

Checking each side of the equation:

$$\begin{aligned}&\text{Mn: Does } (1 \times 1) = (1 \times 1)\text{? Yes.}\\ &\text{Cr: Does } (1 \times 1) = (1 \times 1)\text{? Yes.}\\ &\text{H: Does } (1 \times 3) = (2 \times 1 + 1 \times 1)\text{? Yes.}\\ &\text{O: Does } (1 \times 4 + 1 \times 3) = (1 \times 4 + 1 \times 2 + 1 \times 1)\text{? Yes.}\\ &\text{Charge: Does } [1 \times (-1)] = [1 \times (-2) + 1 \times (+1)]\text{? Yes.}\end{aligned}$$

This is the balanced equation in acidic solution. For a basic solution, add one hydroxide ion to each side and simplify:

$$\mathrm{OH^-}(aq) + \mathrm{MnO_4^-}(aq) + \mathrm{Cr(OH)_3}(s) \longrightarrow \mathrm{CrO_4^{2-}}(aq) + \mathrm{MnO_2}(s) + \mathrm{H_2O}(l) + (\mathrm{H^+} + \mathrm{OH^-})(aq)$$

$$\mathrm{OH^-}(aq) + \mathrm{MnO_4^-}(aq) + \mathrm{Cr(OH)_3}(s) \longrightarrow \mathrm{CrO_4^{2-}}(aq) + \mathrm{MnO_2}(s) + 2\,\mathrm{H_2O}(l)$$

Checking each side of the equation:

$$\begin{aligned}&\text{Mn: Does } (1 \times 1) = (1 \times 1)\text{? Yes.}\\ &\text{Cr: Does } (1 \times 1) = (1 \times 1)\text{? Yes.}\\ &\text{H: Does } (1 \times 1 + 1 \times 3) = (2 \times 2)\text{? Yes.}\\ &\text{O: Does } (1 \times 1 + 1 \times 4 + 1 \times 3) = (1 \times 4 + 1 \times 2 + 2 \times 1)\text{? Yes.}\\ &\text{Charge: Does } [1 \times (-1) + 1 \times (-1)] = [1 \times (-2)]\text{? Yes.}\end{aligned}$$

This is the balanced equation in basic solution.

? Exercise 9.1.2

Balance the following in the type of solution indicated.

a. $H_2 + Cu^{2+} \longrightarrow Cu$ (acidic solution)
b. $H_2 + Cu(OH)_2 \longrightarrow Cu$ (basic solution)
c. $Fe + Ag^{+} \longrightarrow Fe^{2+} + Ag$
d. Identify the oxidizing agents in reactions (a), (b), and (c).
e. Identify the reducing agents in reactions (a), (b), and (c).

Answer a

$$H_2(g) + Cu^{2+}(aq) \longrightarrow 2\,H^{+}(aq) + Cu(s)$$

Answer b

$$H_2(g) + Cu(OH)_2(s) \longrightarrow 2\,H_2O(l) + Cu(s)$$

Answer c

$$Fe(s) + 2\,Ag^{+}(aq) \longrightarrow Fe^{2+}(aq) + 2\,Ag(s)$$

Answer d

oxidizing agent = species reduced: Cu^{2+}, $Cu(OH)_2$, Ag^{+}

Answer e

reducing agent = species oxidized: H_2, H_2, Fe.

Summary

An electric current consists of moving charge. The charge may be in the form of electrons or ions. Current flows through an unbroken or closed circular path called a circuit. The current flows through a conducting medium as a result of a difference in electrical potential between two points in a circuit. Electrical potential has the units of energy per charge. In SI units, charge is measured in coulombs (C), current in amperes $\left(\mathrm{A} = \frac{\mathrm{C}}{\mathrm{s}}\right)$, and electrical potential in volts $\left(\mathrm{V} = \frac{\mathrm{J}}{\mathrm{C}}\right)$.

Oxidation is the loss of electrons, and the species that is oxidized is also called the reducing agent. Reduction is the gain of electrons, and the species that is reduced is also called the oxidizing agent. Oxidation-reduction reactions can be balanced using the half-reaction method. In this method, the oxidation-reduction reaction is split into an oxidation half-reaction and a reduction half-reaction. The oxidation half-reaction and reduction half-reaction are then balanced separately. Each of the half-reactions must have the same number of each type of atom on both sides of the equation *and* show the same total charge on each side of the equation. Charge is balanced in oxidation half-reactions by adding electrons as products; in reduction half-reactions, charge is balanced by adding electrons as reactants. The total number of electrons gained by reduction must exactly equal the number of electrons lost by oxidation when combining the two half-reactions to give the overall balanced equation. Balancing oxidation-reduction reaction equations in aqueous solutions frequently requires that oxygen or hydrogen be added or removed from a reactant. In acidic solution, hydrogen is added by adding hydrogen ion (H^{+}) and removed by producing hydrogen ion; oxygen is removed by adding hydrogen ion and producing water, and added by adding water and producing hydrogen ion. A balanced equation in basic solution can be obtained by first balancing the equation in acidic solution, and then adding hydroxide ion to each side of the balanced equation in such numbers that all the hydrogen ions are converted to water.

Glossary

circuit

path taken by a current as it flows because of an electrical potential difference

current

flow of electrical charge; the SI unit of charge is the coulomb (C) and current is measured in amperes $\left(1\ \mathrm{A} = 1\ \frac{\mathrm{C}}{\mathrm{s}}\right)$

electrical potential

energy per charge; in electrochemical systems, it depends on the way the charges are distributed within the system; the SI unit of electrical potential is the volt $\left(1\ \text{V} = 1\ \frac{\text{J}}{\text{C}}\right)$

half-reaction method

method that produces a balanced overall oxidation-reduction reaction by splitting the reaction into an oxidation “half” and reduction “half,” balancing the two half-reactions, and then combining the oxidation half-reaction and reduction half-reaction in such a way that the number of electrons generated by the oxidation is exactly canceled by the number of electrons required by the reduction

oxidation half-reaction

the “half” of an oxidation-reduction reaction involving oxidation; the half-reaction in which electrons appear as products; balanced when each atom type, as well as the charge, is balanced

reduction half-reaction

the “half” of an oxidation-reduction reaction involving reduction; the half-reaction in which electrons appear as reactants; balanced when each atom type, as well as the charge, is balanced

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9.2: Galvanic Cells

Learning Objectives

- Use cell notation to describe galvanic cells
- Describe the basic components of galvanic cells

Galvanic cells, also known as voltaic cells, are electrochemical cells in which spontaneous oxidation-reduction reactions produce electrical energy. In writing the equations, it is often convenient to separate the oxidation-reduction reactions into half-reactions to facilitate balancing the overall equation and to emphasize the actual chemical transformations.

Consider what happens when a clean piece of copper metal is placed in a solution of silver nitrate (Figure 9.2.1). As soon as the copper metal is added, silver metal begins to form and copper ions pass into the solution. The blue color of the solution on the far right indicates the presence of copper ions. The reaction may be split into its two half-reactions. Half-reactions separate the oxidation from the reduction, so each can be considered individually.

$$\text{oxidation: } \mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{2+}(aq) + 2\,\mathrm{e}^- \tag{9.2.1}$$

$$\text{reduction: } 2 \times (\mathrm{Ag}^+(aq) + \mathrm{e}^- \longrightarrow \mathrm{Ag}(s)) \quad \text{or} \quad 2\,\mathrm{Ag}^+(aq) + 2\,\mathrm{e}^- \longrightarrow 2\,\mathrm{Ag}(s) \tag{9.2.2}$$

$$\text{overall: } 2\,\mathrm{Ag}^+(aq) + \mathrm{Cu}(s) \longrightarrow 2\,\mathrm{Ag}(s) + \mathrm{Cu}^{2+}(aq) \tag{9.2.3}$$

The equation for the reduction half-reaction had to be doubled so the number electrons “gained” in the reduction half-reaction equaled the number of electrons “lost” in the oxidation half-reaction.

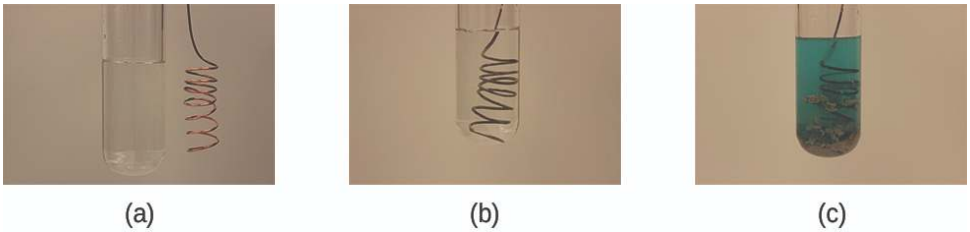


Figure 9.2.1: When a clean piece of copper metal is placed into a clear solution of silver nitrate (a), an oxidation-reduction reaction occurs that results in the exchange of Cu^{2+} for Ag^+ ions in solution. As the reaction proceeds (b), the solution turns blue (c) because of the copper ions present, and silver metal is deposited on the copper strip as the silver ions are removed from solution. (credit: modification of work by Mark Ott)

Galvanic or voltaic cells involve spontaneous electrochemical reactions in which the half-reactions are separated (Figure 9.2.2) so that current can flow through an external wire. The beaker on the left side of the figure is called a half-cell, and contains a 1 *M* solution of copper(II) nitrate [$Cu(NO_3)_2$] with a piece of copper metal partially submerged in the solution. The copper metal is an electrode. The copper is undergoing oxidation; therefore, the copper electrode is the anode. The anode is connected to a voltmeter with a wire and the other terminal of the voltmeter is connected to a silver electrode by a wire. The silver is undergoing reduction; therefore, the silver electrode is the cathode. The half-cell on the right side of the figure consists of the silver electrode in a 1 *M* solution of silver nitrate ($AgNO_3$). At this point, no current flows—that is, no significant movement of electrons through the wire occurs because the circuit is open. The circuit is closed using a salt bridge, which transmits the current with moving ions. The salt bridge consists of a concentrated, nonreactive, electrolyte solution such as the sodium nitrate ($NaNO_3$) solution used in this example. As electrons flow from left to right through the electrode and wire, nitrate ions (anions) pass through the porous plug on the left into the copper(II) nitrate solution. This keeps the beaker on the left electrically neutral by neutralizing the charge on the copper(II) ions that are produced in the solution as the copper metal is oxidized. At the same time, the nitrate ions are moving to the left, sodium ions (cations) move to the right, through the porous plug, and into the silver nitrate solution on the right. These added cations “replace” the silver ions that are removed from the solution as they were reduced to silver metal, keeping the beaker on the right electrically neutral. Without the salt bridge, the compartments would not remain electrically neutral and no significant current would flow. However, if the two compartments are in direct contact, a salt bridge is not necessary. The instant the circuit is completed, the voltmeter reads +0.46 V, this is called the cell potential. The cell potential is created when the two dissimilar metals are connected, and is a measure of the energy per unit charge available from the oxidation-reduction reaction. The volt is the derived SI unit for electrical potential

$$\text{volt} = V = \frac{\text{J}}{\text{C}}$$

In this equation, A is the current in amperes and C the charge in coulombs. Note that volts must be multiplied by the charge in coulombs (C) to obtain the energy in joules (J).

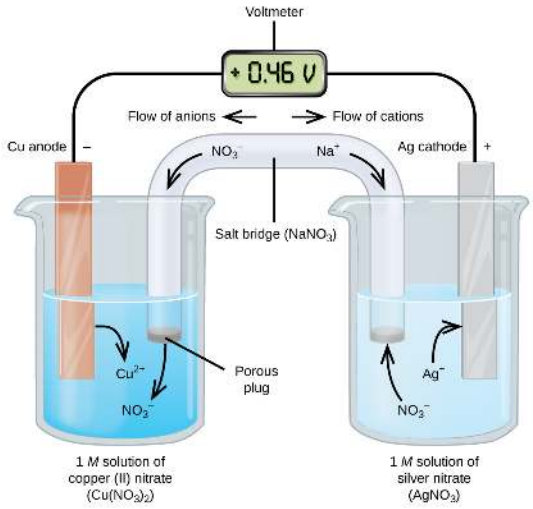


Figure 9.2.2: In this standard galvanic cell, the half-cells are separated; electrons can flow through an external wire and become available to do electrical work.

When the electrochemical cell is constructed in this fashion, a positive cell potential indicates a spontaneous reaction *and* that the electrons are flowing from the left to the right. There is a lot going on in Figure 9.2.2, so it is useful to summarize things for this system:

- Electrons flow from the anode to the cathode: left to right in the standard galvanic cell in the figure.
- The electrode in the left half-cell is the anode because oxidation occurs here. The name refers to the flow of anions in the salt bridge toward it.
- The electrode in the right half-cell is the cathode because reduction occurs here. The name refers to the flow of cations in the salt bridge toward it.
- Oxidation occurs at the anode (the left half-cell in the figure).
- Reduction occurs at the cathode (the right half-cell in the figure).
- The cell potential, +0.46 V, in this case, results from the inherent differences in the nature of the materials used to make the two half-cells.
- The salt bridge must be present to close (complete) the circuit and both an oxidation and reduction must occur for current to flow.

There are many possible galvanic cells, so a shorthand notation is usually used to describe them. The cell notation (sometimes called a cell diagram) provides information about the various species involved in the reaction. This notation also works for other types of cells. A vertical line, $|$, denotes a phase boundary and a double line, $\|$, the salt bridge. Information about the anode is written to the left, followed by the anode solution, then the salt bridge (when present), then the cathode solution, and, finally, information about the cathode to the right. The cell notation for the galvanic cell in Figure 9.2.2 is then

$$\text{Cu}(s)\,|\,\text{Cu}^{2+}(aq,\ 1\ M)\,\|\,\text{Ag}^{+}(aq,\ 1\ M)\,|\,\text{Ag}(s)$$

Note that spectator ions are not included and that the simplest form of each half-reaction was used. When known, the initial concentrations of the various ions are usually included.

One of the simplest cells is the Daniell cell. It is possible to construct this battery by placing a copper electrode at the bottom of a jar and covering the metal with a copper sulfate solution. A zinc sulfate solution is floated on top of the copper sulfate solution; then a zinc electrode is placed in the zinc sulfate solution. Connecting the copper electrode to the zinc electrode allows an electric current to flow. This is an example of a cell without a salt bridge, and ions may flow across the interface between the two solutions.

Some oxidation-reduction reactions involve species that are poor conductors of electricity, and so an electrode is used that does not participate in the reactions. Frequently, the electrode is platinum, gold, or graphite, all of which are inert to many chemical

reactions. One such system is shown in Figure 9.2.3. Magnesium undergoes oxidation at the anode on the left in the figure and hydrogen ions undergo reduction at the cathode on the right. The reaction may be summarized as

$$\text{oxidation: } \mathrm{Mg}(s) \longrightarrow \mathrm{Mg}^{2+}(aq) + 2\,\mathrm{e}^- \tag{9.2.4}$$

$$\text{reduction: } 2\,\mathrm{H}^+(aq) + 2\,\mathrm{e}^- \longrightarrow \mathrm{H}_2(g) \tag{9.2.5}$$

$$\text{overall: } \mathrm{Mg}(s) + 2\,\mathrm{H}^+(aq) \longrightarrow \mathrm{Mg}^{2+}(aq) + \mathrm{H}_2(g) \tag{9.2.6}$$

The cell used an inert platinum wire for the cathode, so the cell notation is

$$\mathrm{Mg}(s)\,|\,\mathrm{Mg}^{2+}(aq)\,\|\,\mathrm{H}^+(aq)\,|\,\mathrm{H}_2(g)\,|\,\mathrm{Pt}(s)$$

The magnesium electrode is an active electrode because it participates in the oxidation-reduction reaction. Inert electrodes, like the platinum electrode in Figure 9.2.3, do not participate in the oxidation-reduction reaction and are present so that current can flow through the cell. Platinum or gold generally make good inert electrodes because they are chemically unreactive.

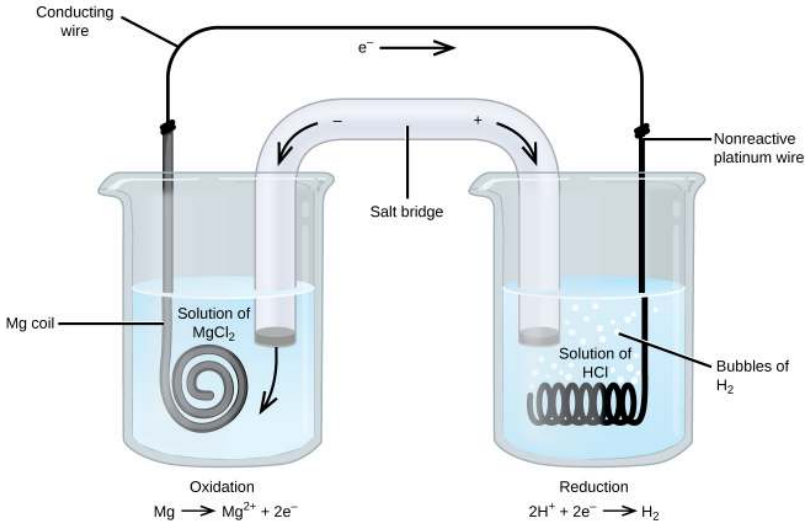


Figure 9.2.2: The oxidation of magnesium to magnesium ion occurs in the beaker on the left side in this apparatus; the reduction of hydrogen ions to hydrogen occurs in the beaker on the right. A nonreactive, or inert, platinum wire allows electrons from the left beaker to move into the right beaker. The overall reaction is: $\mathrm{Mg} + 2\,\mathrm{H}^+ \longrightarrow \mathrm{Mg}^{2+} + \mathrm{H}_2$, *which is represented in cell notation as:* $\mathrm{Mg}(s)\,|\,\mathrm{Mg}^{2+}(aq)\,\|\,\mathrm{H}^+(aq)\,|\,\mathrm{H}_2(g)\,|\,\mathrm{Pt}(s)$

Example 9.2.1: Using Cell Notation

Consider a galvanic cell consisting of

$$2\,\mathrm{Cr}(s) + 3\,\mathrm{Cu}^{2+}(aq) \longrightarrow 2\,\mathrm{Cr}^{3+}(aq) + 3\,\mathrm{Cu}(s)$$

Write the oxidation and reduction half-reactions and write the reaction using cell notation. Which reaction occurs at the anode? The cathode?

Solution

By inspection, Cr is oxidized when three electrons are lost to form Cr^{3+}, and Cu^{2+} is reduced as it gains two electrons to form Cu. Balancing the charge gives

$$\text{oxidation: } 2\,\mathrm{Cr}(s) \longrightarrow 2\,\mathrm{Cr}^{3+}(aq) + 6\,\mathrm{e}^- \tag{9.2.7}$$

$$\text{reduction: } 3\,\mathrm{Cu}^{2+}(aq) + 6\,\mathrm{e}^- \longrightarrow 3\,\mathrm{Cu}(s) \tag{9.2.8}$$

$$\text{overall: } 2\,\mathrm{Cr}(s) + 3\,\mathrm{Cu}^{2+}(aq) \longrightarrow 2\,\mathrm{Cr}^{3+}(aq) + 3\,\mathrm{Cu}(s) \tag{9.2.9}$$

Cell notation uses the simplest form of each of the equations, and starts with the reaction at the anode. No concentrations were specified so:

$$\mathrm{Cr}(s)\,|\,\mathrm{Cr}^{3+}(aq)\,\|\,\mathrm{Cu}^{2+}(aq)\,|\,\mathrm{Cu}(s).$$

Oxidation occurs at the anode and reduction at the cathode.

Example 9.2.2: Using Cell Notation

Consider a galvanic cell consisting of

$$5\,Fe^{2+}(aq) + MnO_4^-(aq) + 8\,H^+(aq) \longrightarrow 5\,Fe^{3+}(aq) + Mn^{2+}(aq) + 4\,H_2O(l)$$

Write the oxidation and reduction half-reactions and write the reaction using cell notation. Which reaction occurs at the anode? The cathode?

Solution

By inspection, Fe^{2+} undergoes oxidation when one electron is lost to form Fe^{3+}, and MnO_4^- is reduced as it gains five electrons to form Mn^{2+}. Balancing the charge gives

$$\text{oxidation: } 5(Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^-) \tag{9.2.10}$$

$$\text{reduction: } MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l) \tag{9.2.11}$$

$$\text{overall: } 5\,Fe^{2+}(aq) + MnO_4^-(aq) + 8\,H^+(aq) \longrightarrow 5\,Fe^{3+}(aq) + Mn^{2+}(aq) + 4\,H_2O(l) \tag{9.2.12}$$

Cell notation uses the simplest form of each of the equations, and starts with the reaction at the anode. It is necessary to use an inert electrode, such as platinum, because there is no metal present to conduct the electrons from the anode to the cathode. No concentrations were specified so:

$$Pt(s)\,|\,Fe^{2+}(aq),\ Fe^{3+}(aq)\,\|\,MnO_4^-(aq),\ H^+(aq),\ Mn^{2+}(aq)\,|\,Pt(s).$$

Oxidation occurs at the anode and reduction at the cathode.

Exercise 9.2.1

Use cell notation to describe the galvanic cell where copper(II) ions are reduced to copper metal and zinc metal is oxidized to zinc ions.

Answer

From the information given in the problem:

$$\text{anode (oxidation): } Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^- \tag{9.2.13}$$

$$\text{cathode (reduction): } Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s) \tag{9.2.14}$$

$$\text{overall: } Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s) \tag{9.2.15}$$

Using cell notation:

$$Zn(s)\,|\,Zn^{2+}(aq)\,\|\,Cu^{2+}(aq)\,|\,Cu(s).$$

Summary

Electrochemical cells typically consist of two half-cells. The half-cells separate the oxidation half-reaction from the reduction half-reaction and make it possible for current to flow through an external wire. One half-cell, normally depicted on the left side in a figure, contains the anode. Oxidation occurs at the anode. The anode is connected to the cathode in the other half-cell, often shown on the right side in a figure. Reduction occurs at the cathode. Adding a salt bridge completes the circuit allowing current to flow. Anions in the salt bridge flow toward the anode and cations in the salt bridge flow toward the cathode. The movement of these ions completes the circuit and keeps each half-cell electrically neutral. Electrochemical cells can be described using cell notation. In this notation, information about the reaction at the anode appears on the left and information about the reaction at the cathode on the right. The salt bridge is represented by a double line, ‖. The solid, liquid, or aqueous phases within a half-cell are separated by a single line, |. The phase and concentration of the various species is included after the species name. Electrodes that participate in the oxidation-reduction reaction are called active electrodes. Electrodes that do not participate in the oxidation-reduction reaction

but are there to allow current to flow are inert electrodes. Inert electrodes are often made from platinum or gold, which are unchanged by many chemical reactions.

Glossary

active electrode
: electrode that participates in the oxidation-reduction reaction of an electrochemical cell; the mass of an active electrode changes during the oxidation-reduction reaction

anode
: electrode in an electrochemical cell at which oxidation occurs; information about the anode is recorded on the left side of the salt bridge in cell notation

cathode
: electrode in an electrochemical cell at which reduction occurs; information about the cathode is recorded on the right side of the salt bridge in cell notation

cell notation
: shorthand way to represent the reactions in an electrochemical cell

cell potential
: difference in electrical potential that arises when dissimilar metals are connected; the driving force for the flow of charge (current) in oxidation-reduction reactions

galvanic cell
: electrochemical cell that involves a spontaneous oxidation-reduction reaction; electrochemical cells with positive cell potentials; also called a voltaic cell

inert electrode
: electrode that allows current to flow, but that does not otherwise participate in the oxidation-reduction reaction in an electrochemical cell; the mass of an inert electrode does not change during the oxidation-reduction reaction; inert electrodes are often made of platinum or gold because these metals are chemically unreactive.

voltaic cell
: another name for a galvanic cell

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9.3: Standard Reduction Potentials

Learning Objectives

- Determine standard cell potentials for oxidation-reduction reactions
- Use standard reduction potentials to determine the better oxidizing or reducing agent from among several possible choices

The cell potential results from the difference in the electrical potentials for each electrode. While it is impossible to determine the electrical potential of a single electrode, we can assign an electrode the value of zero and then use it as a reference. The electrode chosen as the zero is shown in Figure 17.4.1 and is called the standard hydrogen electrode (SHE). The SHE consists of 1 atm of hydrogen gas bubbled through a 1 M HCl solution, usually at room temperature. Platinum, which is chemically inert, is used as the electrode. The reduction half-reaction chosen as the reference is

$$2\,\mathrm{H^+}(aq,\ 1\ M) + 2\,\mathrm{e^-} \rightleftharpoons \mathrm{H_2}(g,\ 1\ \mathrm{atm}) \quad E^\circ = 0\ \mathrm{V}$$

$E°$ is the standard reduction potential. The superscript "°" on the E denotes standard conditions (1 bar or 1 atm for gases, 1 M for solutes). The voltage is defined as zero for all temperatures.

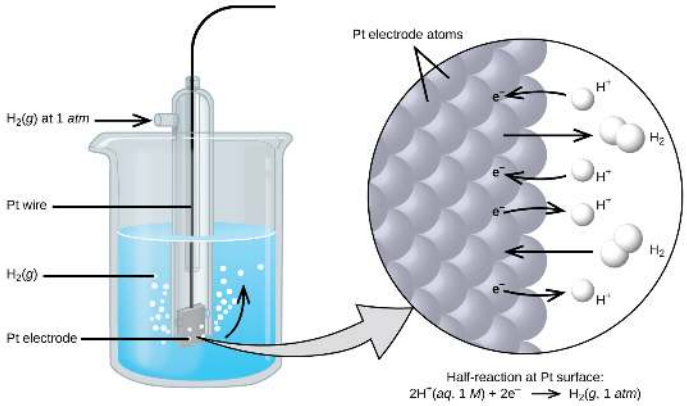


Figure 9.3.1: Hydrogen gas at 1 atm is bubbled through 1 M HCl solution. Platinum, which is inert to the action of the 1 M HCl, is used as the electrode. Electrons on the surface of the electrode combine with H^+ in solution to produce hydrogen gas.

A galvanic cell consisting of a SHE and Cu^{2+}/Cu half-cell can be used to determine the standard reduction potential for Cu^{2+} (Figure 9.3.2). In cell notation, the reaction is

$$\mathrm{Pt}(s)\,|\,\mathrm{H_2}(g,\ 1\ \mathrm{atm})\,|\,\mathrm{H^+}(aq,\ 1\ M)\,\|\,\mathrm{Cu^{2+}}(aq,\ 1\ M)\,|\,\mathrm{Cu}(s)$$

Electrons flow from the anode to the cathode. The reactions, which are reversible, are

$$\begin{aligned}&\text{Anode (oxidation): } \mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-}\\ &\text{Cathode (reduction): } \mathrm{Cu^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Cu}(s)\\ \hline &\text{Overall: } \mathrm{Cu^{2+}}(aq) + \mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H^+}(aq) + \mathrm{Cu}(s)\end{aligned}$$

The standard reduction potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is necessary because oxidation is the reverse of reduction.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$+0.34\ \mathrm{V} = E^\circ_{\mathrm{Cu^{2+}/Cu}} - E^\circ_{\mathrm{H^+/H_2}} = E^\circ_{\mathrm{Cu^{2+}/Cu}} - 0 = E^\circ_{\mathrm{Cu^{2+}/Cu}}$$

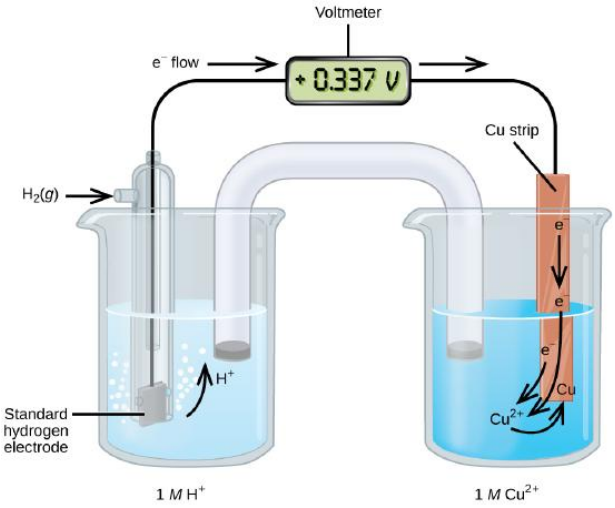


Figure 9.3.2: A galvanic cell can be used to determine the standard reduction potential of Cu^{2+}.

Using the SHE as a reference, other standard reduction potentials can be determined. Consider the cell shown in Figure 9.3.2, where

$$\mathrm{Pt}(s)\,|\,\mathrm{H_2}(g,\ 1\ \mathrm{atm})\,|\,\mathrm{H^+}(aq,\ 1\ M)\,\|\,\mathrm{Ag^+}(aq,\ 1\ M)\,|\,\mathrm{Ag}(s)$$

Electrons flow from left to right, and the reactions are

$$\begin{aligned}&\text{anode (oxidation): } \mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-}\\ &\text{cathode (reduction): } 2\,\mathrm{Ag^+}(aq) + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Ag}(s)\\ \hline &\text{overall: } 2\,\mathrm{Ag^+}(aq) + \mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H^+}(aq) + 2\,\mathrm{Ag}(s)\end{aligned}$$

The standard reduction potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is needed because oxidation is the reverse of reduction.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$+0.80\ \mathrm{V} = E^\circ_{\mathrm{Ag^+/Ag}} - E^\circ_{\mathrm{H^+/H_2}} = E^\circ_{\mathrm{Ag^+/Ag}} - 0 = E^\circ_{\mathrm{Ag^+/Ag}}$$

It is important to note that the potential is *not* doubled for the cathode reaction.

The SHE is rather dangerous and rarely used in the laboratory. Its main significance is that it established the zero for standard reduction potentials. Once determined, standard reduction potentials can be used to determine the standard cell potential, E°_{cell}, for any cell. For example, for the following cell:

$$\mathrm{Cu}(s)\,|\,\mathrm{Cu^{2+}}(aq,\ 1\ M)\,\|\,\mathrm{Ag^+}(aq,\ 1\ M)\,|\,\mathrm{Ag}(s)$$

$$\begin{aligned}&\text{anode (oxidation): } \mathrm{Cu}(s) \longrightarrow \mathrm{Cu^{2+}}(aq) + 2\,\mathrm{e^-}\\ &\text{cathode (reduction): } 2\,\mathrm{Ag^+}(aq) + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Ag}(s)\\ \hline &\text{overall: } \mathrm{Cu}(s) + 2\,\mathrm{Ag^+}(aq) \longrightarrow \mathrm{Cu^{2+}}(aq) + 2\,\mathrm{Ag}(s)\end{aligned}$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{\mathrm{Ag^+/Ag}} - E^\circ_{\mathrm{Cu^{2+}/Cu}} = 0.80\ \mathrm{V} - 0.34\ \mathrm{V} = 0.46\ \mathrm{V}$$

Again, note that when calculating E°_{cell}, standard reduction potentials always remain the same even when a half-reaction is multiplied by a factor. Standard reduction potentials for selected reduction reactions are shown in Table 9.3.1. A more complete list is provided in Tables P1 or P2.

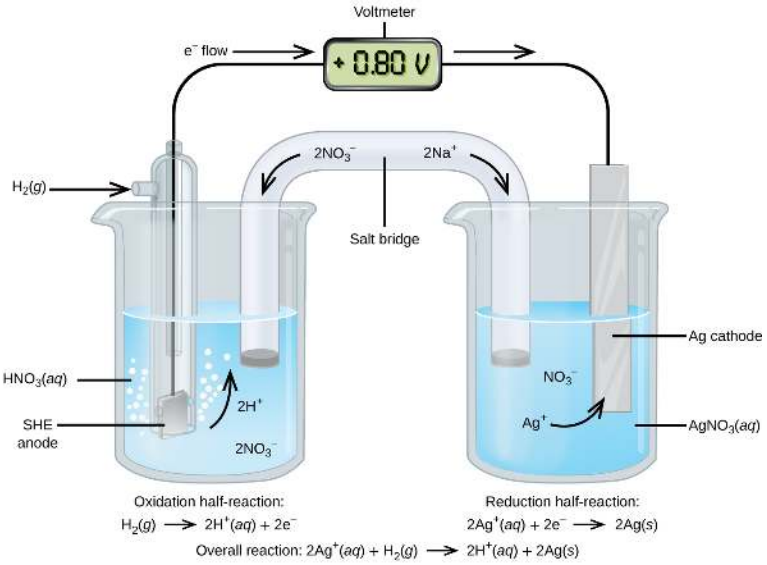


Figure 9.3.3: A galvanic cell can be used to determine the standard reduction potential of Ag^+. The SHE on the left is the anode and assigned a standard reduction potential of zero.

Table 9.3.1: Selected Standard Reduction Potentials at 25 °C

Half-Reaction	E° (V)
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.866
$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$	+1.69
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.507
$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+1.498
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.35827
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$	+1.229
$Pt^{2+}(aq) + 2e^- \longrightarrow Pt(s)$	+1.20
$Br_2(aq) + 2e^- \longrightarrow 2Br^-(aq)$	+1.0873
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.7996
$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+0.7973
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.771
$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$	+0.558
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.5355
$NiO_2(s) + 2H_2O(l) + 2e^- \longrightarrow Ni(OH)_2(s) + 2OH^-(aq)$	+0.49
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.34
$Hg_2Cl_2(s) + 2e^- \longrightarrow 2Hg(l) + 2Cl^-(aq)$	+0.26808
$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)$	+0.22233
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.151
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.1262
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.1375

Half-Reaction	E° (V)
$\mathrm{Ni^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Ni}(s)$	−0.257
$\mathrm{Co^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Co}(s)$	−0.28
$\mathrm{PbSO_4}(s) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Pb}(s) + \mathrm{SO_4^{2-}}(aq)$	−0.3505
$\mathrm{Cd^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Cd}(s)$	−0.4030
$\mathrm{Fe^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Fe}(s)$	−0.447
$\mathrm{Cr^{3+}}(aq) + 3\,\mathrm{e^-} \longrightarrow \mathrm{Cr}(s)$	−0.744
$\mathrm{Mn^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Mn}(s)$	−1.185
$\mathrm{Zn(OH)_2}(s) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Zn}(s) + 2\,\mathrm{OH^-}(aq)$	−1.245
$\mathrm{Zn^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Zn}(s)$	−0.7618
$\mathrm{Al^{3+}}(aq) + 3\,\mathrm{e^-} \longrightarrow \mathrm{Al}(s)$	−1.662
$\mathrm{Mg^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Mg}(s)$	−2.372
$\mathrm{Na^{+}}(aq) + \mathrm{e^-} \longrightarrow \mathrm{Na}(s)$	−2.71
$\mathrm{Ca^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Ca}(s)$	−2.868
$\mathrm{Ba^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Ba}(s)$	−2.912
$\mathrm{K^{+}}(aq) + \mathrm{e^-} \longrightarrow \mathrm{K}(s)$	−2.931
$\mathrm{Li^{+}}(aq) + \mathrm{e^-} \longrightarrow \mathrm{Li}(s)$	−3.04

Tables like this make it possible to determine the standard cell potential for many oxidation-reduction reactions.

Example 9.3.1: Cell Potentials from Standard Reduction Potentials

What is the standard cell potential for a galvanic cell that consists of $\mathrm{Au^{3+}}$/Au and $\mathrm{Ni^{2+}}$/Ni half-cells? Identify the oxidizing and reducing agents.

Solution

Using Table 9.3.1, the reactions involved in the galvanic cell, both written as reductions, are

$$\mathrm{Au^{3+}}(aq) + 3\,\mathrm{e^-} \longrightarrow \mathrm{Au}(s) \quad E^\circ_{\mathrm{Au^{3+}/Au}} = +1.498\ \mathrm{V}$$

$$\mathrm{Ni^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Ni}(s) \quad E^\circ_{\mathrm{Ni^{2+}/Ni}} = -0.257\ \mathrm{V}$$

Galvanic cells have positive cell potentials, and all the reduction reactions are reversible. The reaction at the anode will be the half-reaction with the smaller or more negative standard reduction potential. Reversing the reaction at the anode (to show the oxidation) but *not* its standard reduction potential gives:

$$\text{Anode (oxidation): } \mathrm{Ni}(s) \longrightarrow \mathrm{Ni^{2+}}(aq) + 2\,\mathrm{e^-} \quad E^\circ_{\text{anode}} = E^\circ_{\mathrm{Ni^{2+}/Ni}} = -0.257\ \mathrm{V}$$

$$\text{Cathode (reduction): } \mathrm{Au^{3+}}(aq) + 3\,\mathrm{e^-} \longrightarrow \mathrm{Au}(s) \quad E^\circ_{\text{cathode}} = E^\circ_{\mathrm{Au^{3+}/Au}} = +1.498\ \mathrm{V}$$

The least common factor is six, so the overall reaction is

$$3\,\mathrm{Ni}(s) + 2\,\mathrm{Au^{3+}}(aq) \longrightarrow 3\,\mathrm{Ni^{2+}}(aq) + 2\,\mathrm{Au}(s)$$

The reduction potentials are *not* scaled by the stoichiometric coefficients when calculating the cell potential, and the unmodified standard reduction potentials must be used.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 1.498\ \mathrm{V} - (-0.257\ \mathrm{V}) = 1.755\ \mathrm{V}$$

From the half-reactions, Ni is oxidized, so it is the reducing agent, and Au^{3+} is reduced, so it is the oxidizing agent.

Exercise 9.3.1

A galvanic cell consists of a Mg electrode in 1 *M* $Mg(NO_3)_2$ solution and a Ag electrode in 1 *M* $AgNO_3$ solution. Calculate the standard cell potential at 25 °C.

Answer

$$Mg(s) + 2\,Ag^+(aq) \longrightarrow Mg^{2+}(aq) + 2\,Ag(s) \qquad E^\circ_{cell} = 0.7996\text{ V} - (-2.372\text{ V}) = 3.172\text{ V}$$

Summary

Assigning the potential of the standard hydrogen electrode (SHE) as zero volts allows the determination of standard reduction potentials, *E*°, for half-reactions in electrochemical cells. As the name implies, standard reduction potentials use standard states (1 bar or 1 atm for gases; 1 *M* for solutes, often at 298.15 K) and are written as reductions (where electrons appear on the left side of the equation). The reduction reactions are reversible, so standard cell potentials can be calculated by subtracting the standard reduction potential for the reaction at the anode from the standard reduction for the reaction at the cathode. When calculating the standard cell potential, the standard reduction potentials are *not* scaled by the stoichiometric coefficients in the balanced overall equation.

9.3.1: Key Equations

- $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

Glossary

standard cell potential (E°_{cell})

the cell potential when all reactants and products are in their standard states (1 bar or 1 atm or gases; 1 *M* for solutes), usually at 298.15 K; can be calculated by subtracting the standard reduction potential for the half-reaction at the anode from the standard reduction potential for the half-reaction occurring at the cathode

standard hydrogen electrode (SHE)

the electrode consists of hydrogen gas bubbling through hydrochloric acid over an inert platinum electrode whose reduction at standard conditions is assigned a value of 0 V; the reference point for standard reduction potentials

standard reduction potential (*E*°)

the value of the reduction under standard conditions (1 bar or 1 atm for gases; 1 *M* for solutes) usually at 298.15 K; tabulated values used to calculate standard cell potentials

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9.4: The Nernst Equation

Learning Objectives

- Relate cell potentials to free energy changes
- Use the Nernst equation to determine cell potentials at nonstandard conditions
- Perform calculations that involve converting between cell potentials, free energy changes, and equilibrium constants

We will now extend electrochemistry by determining the relationship between E°_{cell} and the thermodynamics quantities such as $\Delta G°$ (Gibbs free energy) and K (the equilibrium constant). In galvanic cells, chemical energy is converted into electrical energy, which can do work. The electrical work is the product of the charge transferred multiplied by the potential difference (voltage):

$$\text{electrical work} = \text{volts} \times (\text{charge in coulombs}) = \text{J}$$

The charge on 1 mole of electrons is given by Faraday's constant (F)

$$\begin{aligned} F &= \frac{6.022 \times 10^{23}\ e^-}{mol} \times \frac{1.602 \times 10^{-19}\ C}{e^-} \\ &= 9.648 \times 10^4\ \frac{C}{mol} \\ &= 9.648 \times 10^4\ \frac{J}{V \cdot mol} \end{aligned}$$

Therefore

$$\text{total charge} = (\text{number of moles of e}^-) \times F = nF$$

In this equation, n is the number of moles of electrons for the *balanced* oxidation-reduction reaction. The measured cell potential is the maximum potential the cell can produce and is related to the electrical work (w_{ele}) by

$$E_{\text{cell}} = \frac{-w_{\text{ele}}}{nF} \qquad \text{or} \qquad w_{\text{ele}} = -nFE_{\text{cell}}$$

The negative sign for the work indicates that the electrical work is done by the system (the galvanic cell) on the surroundings. In an earlier chapter, the free energy was defined as the energy that was available to do work. In particular, the change in free energy was defined in terms of the maximum work (w_{max}), which, for electrochemical systems, is w_{ele}.

$$\begin{aligned} \Delta G &= w_{\text{max}} = w_{\text{ele}} \\ &= -nFE_{\text{cell}} \end{aligned}$$

We can verify the signs are correct when we realize that n and F are positive constants and that galvanic cells, which have positive cell potentials, involve spontaneous reactions. Thus, spontaneous reactions, which have $\Delta G < 0$, must have $E_{cell} > 0$. If all the reactants and products are in their standard states, this becomes

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

This provides a way to relate standard cell potentials to equilibrium constants, since

$$\Delta G^\circ = -RT \ln K$$

$$-nFE^\circ_{\text{cell}} = -RT \ln K$$

or

$$E^\circ_{\text{cell}} = \frac{RT}{nF} \ln K$$

Most of the time, the electrochemical reactions are run at standard temperature (298.15 K). Collecting terms at this temperature yields

$$
\begin{aligned}
E^\circ_{\text{cell}} &= \frac{RT}{nF}\ln K \\
&= \frac{\left(8.314\ \dfrac{\text{J}}{\text{K·mol}}\right)(298.15\ K)}{n \times 96,485\ \text{C/V·mol}}\ln K \\
&= \frac{0.0257\ \text{V}}{n}\ln K
\end{aligned}
$$

where n is the number of moles of electrons. The logarithm in equations involving cell potentials is often expressed using base 10 logarithms (i.e., $\log_{10}$ or just log), which changes the constant by a factor of 2.303:

$$E^\circ_{\text{cell}} = \frac{0.0592\ \text{V}}{n}\log K$$

Thus, if $\Delta G°$, K, or E°_{cell} is known or can be calculated, the other two quantities can be readily determined. The relationships are shown graphically in Figure 9.4.1.

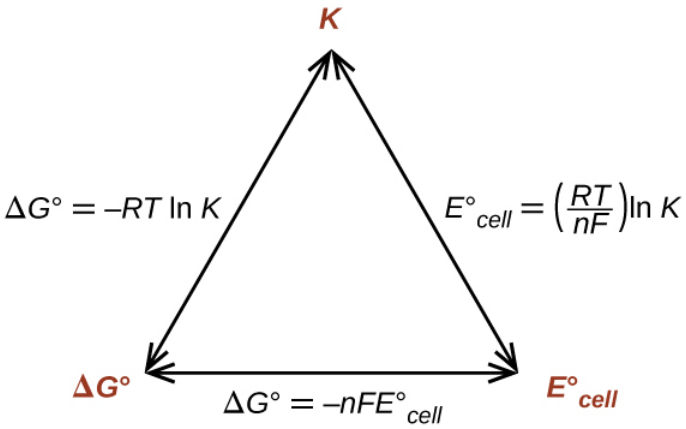


Figure 9.4.1: The relationships between ΔG°, K, and E°_{cell}. *Given any one of the three quantities, the other two can be calculated, so any of the quantities could be used to determine whether a process was spontaneous.*

Given any one of the quantities, the other two can be calculated.

Example 9.4.1: Equilibrium Constants, Potentials, & Free Energy Changes

What is the standard Gibbs free energy change and equilibrium constant for the following reaction at 25 °C?

$$2\,\text{Ag}^+(aq) + \text{Fe}(s) \rightleftharpoons 2\,\text{Ag}(s) + \text{Fe}^{2+}(aq)$$

Solution

The reaction involves an oxidation-reduction reaction, so the standard cell potential can be calculated using the data in Table P1.

$$\text{anode (oxidation): } \text{Fe}(s) \longrightarrow \text{Fe}^{2+}(aq) + 2\,\text{e}^- \qquad E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.447\ \text{V}$$

$$\text{cathode (reduction): } 2 \times (\text{Ag}^+(aq) + \text{e}^- \longrightarrow \text{Ag}(s)) \qquad E^\circ_{\text{Ag}^+/\text{Ag}} = 0.7996\ \text{V}$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Fe}^{2+}/\text{Fe}} = +1.247\ \text{V}$$

Remember that the cell potential for the cathode is not multiplied by two when determining the standard cell potential. With *n* = 2, the equilibrium constant is then

$$E^\circ_{\text{cell}} = \frac{0.0592\ \text{V}}{n}\log K$$

$$K = 10^{n \times E^\circ_{\text{cell}}/0.0592\ \text{V}}$$
$$= 10^{2 \times 1.247\ \text{V}/0.0592\ \text{V}}$$
$$= 10^{42.128}$$
$$= 1.3 \times 10^{42}$$

The standard free energy is then

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$
$$\Delta G^\circ = -2 \times 96,485\ \frac{\text{J}}{\text{V·mol}} \times 1.247\ \text{V} = -240.6\ \frac{\text{kJ}}{\text{mol}}$$

Check your answer: A positive standard cell potential means a spontaneous reaction, so the standard free energy change should be negative, and an equilibrium constant should be >1.

? Exercise 9.4.1

What is the standard Gibbs free energy change and the equilibrium constant for the following reaction at room temperature? Is the reaction spontaneous?

$$\text{Sn}(s) + 2\ \text{Cu}^{2+}(aq) \rightleftharpoons \text{Sn}^{2+}(aq) + 2\ \text{Cu}^{+}(aq)$$

Answer

Spontaneous; $n = 2$; $E^\circ_{\text{cell}} = +0.291\ \text{V}$; $\Delta G^\circ = -56.2\ \frac{\text{kJ}}{\text{mol}}$; $K = 6.8 \times 10^9$.

Now that the connection has been made between the free energy and cell potentials, nonstandard concentrations follow. Recall that

$$\Delta G = \Delta G^\circ + RT \ln Q$$

where Q is the reaction quotient (see the chapter on equilibrium fundamentals). Converting to cell potentials:

$$-nFE_{\text{cell}} = -nFE^\circ_{\text{cell}} + RT \ln Q \tag{9.4.1}$$

or

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q \tag{9.4.2}$$

Equation 9.4.2 is the generalized Nernst equation that is applicable at any temperature. However, is can be simplified for reactions occuring at 25 °C (298.15 K) by rewriting it as

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0257\ \text{V}}{n} \ln Q \tag{9.4.3}$$

or

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592\ \text{V}}{n} \log_{10} Q \tag{9.4.4}$$

If the temperature is not 298.15 K, it is necessary to recalculate the potential with Equation9.4.2. With the Nernst equation, it is possible to calculate the cell potential at nonstandard conditions. This adjustment is necessary because potentials determined under different conditions will have different values.

✓ Example 9.4.2: Cell Potentials at Nonstandard Conditions

Consider the following reaction at room temperature:

$$\text{Co}(s) + \text{Fe}^{2+}(aq,\ 1.94\ M) \longrightarrow \text{Co}^{2+}(aq,\ 0.15\ M) + \text{Fe}(s)$$

Is the process spontaneous?

Solution

There are two ways to solve the problem. If the thermodynamic information in Table T1 were available, you could calculate the free energy change. If the free energy change is negative, the process is spontaneous. The other approach, which we will use, requires information like that given in Table P1. Using those data, the cell potential can be determined. If the cell potential is positive, the process is spontaneous. Collecting information from Table P1 and the problem,

$$\text{Anode (oxidation): } \mathrm{Co}(s) \longrightarrow \mathrm{Co}^{2+}(aq) + 2\,\mathrm{e}^- \qquad E^\circ_{\mathrm{Co}^{2+}/\mathrm{Co}} = -0.28\ \mathrm{V}$$

$$\text{Cathode (reduction): } \mathrm{Fe}^{2+}(aq) + 2\,\mathrm{e}^- \longrightarrow \mathrm{Fe}(s) \qquad E^\circ_{\mathrm{Fe}^{2+}/\mathrm{Fe}} = -0.447\ \mathrm{V}$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = -0.447\ \mathrm{V} - (-0.28\ \mathrm{V}) = -0.17\ \mathrm{V}$$

The process is not spontaneous under standard conditions. Using the Nernst equation and the concentrations stated in the problem and $n = 2$,

$$Q = \frac{[\mathrm{Co}^{2+}]}{[\mathrm{Fe}^{2+}]} = \frac{0.15\ M}{1.94\ M} = 0.077$$

Now we can insert these into the Nernst Equation at room temperature (Equation 9.4.4)

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{0.0592\ \mathrm{V}}{n} \log Q \\ &= -0.17\ \mathrm{V} - \frac{0.0592\ \mathrm{V}}{2} \log 0.077 \\ &= -0.17\ \mathrm{V} + 0.033\ \mathrm{V} = -0.14\ \mathrm{V} \end{aligned}$$

The process is (still) nonspontaneous.

? Exercise 9.4.2

What is the cell potential for the following reaction at room temperature?

$$\mathrm{Al}(s)\,|\,\mathrm{Al}^{3+}(aq,\ 0.15\ M)\,\|\,\mathrm{Cu}^{2+}(aq,\ 0.025\ M)\,|\,\mathrm{Cu}(s)$$

What are the values of *n* and Q for the overall reaction? Is the reaction spontaneous under these conditions?

Answer

n = 6; *Q* = 1440; E_{cell} = +1.97 V, spontaneous.

Finally, we will take a brief look at a special type of cell called a concentration cell. In a concentration cell, the electrodes are the same material and the half-cells differ only in concentration. Since one or both compartments is not standard, the cell potentials will be unequal; therefore, there will be a potential difference, which can be determined with the aid of the Nernst equation.

✓ Example 9.4.3: Concentration Cells

What is the cell potential of the concentration cell described by

$$\mathrm{Zn}(s)\,|\,\mathrm{Zn}^{2+}(aq,\ 0.10\ M)\,\|\,\mathrm{Zn}^{2+}(aq,\ 0.50\ M)\,|\,\mathrm{Zn}(s)$$

Solution

From the information given:

$$\text{Anode: } \mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq,\ 0.10\ M) + 2\,\mathrm{e}^- \qquad E^\circ_{\text{anode}} = -0.7618\ \mathrm{V}$$

$$\text{Cathode: } \mathrm{Zn}^{2+}(aq,\ 0.50\ M) + 2\,\mathrm{e}^- \longrightarrow \mathrm{Zn}(s) \qquad E^\circ_{\text{cathode}} = -0.7618\ \mathrm{V}$$

$$\text{Overall: } \mathrm{Zn}^{2+}(aq,\ 0.50\ M) \longrightarrow \mathrm{Zn}^{2+}(aq,\ 0.10\ M) \qquad E^\circ_{\text{cell}} = 0.000\ \mathrm{V}$$

The standard cell potential is zero because the anode and cathode involve the same reaction; only the concentration of Zn^{2+} changes. Substituting into the Nernst equation,

$$E_{\text{cell}} = 0.000\ \text{V} - \frac{0.0592\ \text{V}}{2} \log \frac{0.10}{0.50} = +0.021\ \text{V}$$

and the process is spontaneous at these conditions.

Check your answer: In a concentration cell, the standard cell potential will always be zero. To get a positive cell potential (spontaneous process) the reaction quotient Q must be <1. $Q < 1$ in this case, so the process is spontaneous.

? Exercise 9.4.3

What value of Q for the previous concentration cell would result in a voltage of 0.10 V? If the concentration of zinc ion at the cathode was 0.50 M, what was the concentration at the anode?

Answer

Q = 0.00042; $[Zn^{2+}]_{cat}$ = 2.1 \times 10^{-4} M.

Summary

Electrical work (w_{ele}) is the negative of the product of the total charge (Q) and the cell potential (E_{cell}). The total charge can be calculated as the number of moles of electrons (n) times the Faraday constant (F = 96,485 C/mol e^-). Electrical work is the maximum work that the system can produce and so is equal to the change in free energy. Thus, anything that can be done with or to a free energy change can also be done to or with a cell potential. The Nernst equation relates the cell potential at nonstandard conditions to the logarithm of the reaction quotient. Concentration cells exploit this relationship and produce a positive cell potential using half-cells that differ only in the concentration of their solutes.

9.4.1: Key Equations

- $E^\circ_{\text{cell}} = \dfrac{RT}{nF} \ln K$
- $E^\circ_{\text{cell}} = \dfrac{0.0257\ \text{V}}{n} \ln K = \dfrac{0.0592\ \text{V}}{n} \log K \qquad (\text{at } 298.15\ K)$
- $E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{RT}{nF} \ln Q \qquad (\text{Nernst equation})$
- $E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{0.0257\ V}{n} \ln Q = E^\circ_{\text{cell}} - \dfrac{0.0592\ \text{V}}{n} \log Q \qquad (\text{at } 298.15\ K)$
- $\Delta G = -nFE_{\text{cell}}$
- $\Delta G^\circ = -nFE^\circ_{\text{cell}}$
- $w_{\text{ele}} = w_{\text{max}} = -nFE_{\text{cell}}$

Glossary

concentration cell

galvanic cell in which the two half-cells are the same except for the concentration of the solutes; spontaneous when the overall reaction is the dilution of the solute

electrical work (w_{ele})

negative of total charge times the cell potential; equal to w_{max} for the system, and so equals the free energy change (ΔG)

Faraday's constant (F)

charge on 1 mol of electrons; F = 96,485 C/mol e^-

Nernst equation

equation that relates the logarithm of the reaction quotient (Q) to nonstandard cell potentials; can be used to relate equilibrium constants to standard cell potentials

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9.5: Batteries and Fuel Cells

Learning Objectives

- Classify batteries as primary or secondary
- List some of the characteristics and limitations of batteries
- Provide a general description of a fuel cell

A battery is an electrochemical cell or series of cells that produces an electric current. In principle, any galvanic cell could be used as a battery. An ideal battery would never run down, produce an unchanging voltage, and be capable of withstanding environmental extremes of heat and humidity. Real batteries strike a balance between ideal characteristics and practical limitations. For example, the mass of a car battery is about 18 kg or about 1% of the mass of an average car or light-duty truck. This type of battery would supply nearly unlimited energy if used in a smartphone, but would be rejected for this application because of its mass. Thus, no single battery is "best" and batteries are selected for a particular application, keeping things like the mass of the battery, its cost, reliability, and current capacity in mind. There are two basic types of batteries: primary and secondary. A few batteries of each type are described next.

Primary Batteries

Primary batteries are single-use batteries because they cannot be recharged. A common primary battery is the dry cell (Figure 9.5.1). The dry cell is a zinc-carbon battery. The zinc can serves as both a container and the negative electrode. The positive electrode is a rod made of carbon that is surrounded by a paste of manganese(IV) oxide, zinc chloride, ammonium chloride, carbon powder, and a small amount of water. The reaction at the anode can be represented as the ordinary oxidation of zinc:

$$\mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq) + 2\,\mathrm{e}^- \qquad E^\circ_{\mathrm{Zn}^{2+}/\mathrm{Zn}} = -0.7618\ \mathrm{V}$$

The reaction at the cathode is more complicated, in part because more than one reaction occurs. The series of reactions that occurs at the cathode is approximately

$$2\,\mathrm{MnO_2}(s) + 2\,\mathrm{NH_4Cl}(aq) + 2\,\mathrm{e}^- \longrightarrow \mathrm{Mn_2O_3}(s) + 2\,\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) + 2\,\mathrm{Cl}^-$$

The overall reaction for the zinc–carbon battery can be represented as

$$2\,\mathrm{MnO_2}(s) + 2\,\mathrm{NH_4Cl}(aq) + \mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq) + \mathrm{Mn_2O_3}(s) + 2\,\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) + 2\,\mathrm{Cl}^-$$

with an overall cell potential which is initially about 1.5 V, but decreases as the battery is used. It is important to remember that the voltage delivered by a battery is the same regardless of the size of a battery. For this reason, D, C, A, AA, and AAA batteries all have the same voltage rating. However, larger batteries can deliver more moles of electrons. As the zinc container oxidizes, its contents eventually leak out, so this type of battery should not be left in any electrical device for extended periods.

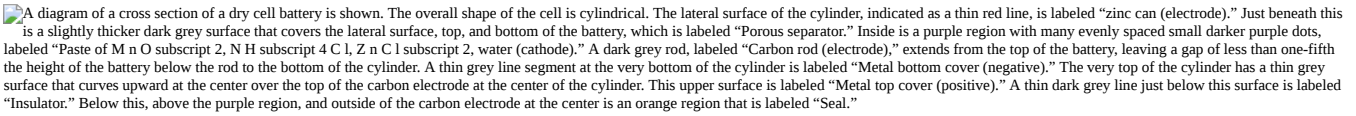

A diagram of a cross section of a dry cell battery is shown. The overall shape of the cell is cylindrical. The lateral surface of the cylinder, indicated as a thin red line, is labeled "zinc can (electrode)." Just beneath this is a slightly thicker dark grey surface that covers the lateral surface, top, and bottom of the battery, which is labeled "Porous separator." Inside is a purple region with many evenly spaced small darker purple dots, labeled "Paste of M n O subscript 2, N H subscript 4 C l, Z n C l subscript 2, water (cathode)." A dark grey rod, labeled "Carbon rod (electrode)," extends from the top of the battery, leaving a gap of less than one-fifth the height of the battery below the rod to the bottom of the cylinder. A thin grey line segment at the very bottom of the cylinder is labeled "Metal bottom cover (negative)." The very top of the cylinder has a thin grey surface that curves upward at the center over the top of the carbon electrode at the center of the cylinder. This upper surface is labeled "Metal top cover (positive)." A thin dark grey line just below this surface is labeled "Insulator." Below this, above the purple region, and outside of the carbon electrode at the center is an orange region that is labeled "Seal."

Figure 9.5.1: The diagram shows a cross section of a flashlight battery, a zinc-carbon dry cell.

Alkaline batteries (Figure 9.5.2) were developed in the 1950s partly to address some of the performance issues with zinc–carbon dry cells. They are manufactured to be exact replacements for zinc-carbon dry cells. As their name suggests, these types of batteries use alkaline electrolytes, often potassium hydroxide. The reactions are

$$\begin{aligned}
&\text{anode: } \mathrm{Zn}(s) + 2\,\mathrm{OH}^-(aq) \longrightarrow \mathrm{ZnO}(s) + \mathrm{H_2O}(l) + 2\,\mathrm{e}^- && E^\circ_{\text{anode}} = -1.28\ \mathrm{V}\\
&\text{cathode: } 2\,\mathrm{MnO_2}(s) + \mathrm{H_2O}(l) + 2\,\mathrm{e}^- \longrightarrow \mathrm{Mn_2O_3}(s) + 2\,\mathrm{OH}^-(aq) && E^\circ_{\text{cathode}} = +0.15\ \mathrm{V}\\
&\text{overall: } \mathrm{Zn}(s) + 2\,\mathrm{MnO_2}(s) \longrightarrow \mathrm{ZnO}(s) + \mathrm{Mn_2O_3}(s) && E^\circ_{\text{cell}} = +1.43\ \mathrm{V}
\end{aligned}$$

An alkaline battery can deliver about three to five times the energy of a zinc-carbon dry cell of similar size. Alkaline batteries are prone to leaking potassium hydroxide, so these should also be removed from devices for long-term storage. While some alkaline

batteries are rechargeable, most are not. Attempts to recharge an alkaline battery that is not rechargeable often leads to rupture of the battery and leakage of the potassium hydroxide electrolyte.

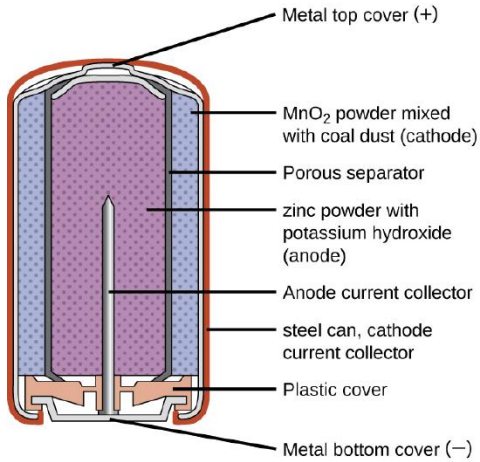


Figure 9.5.2: Alkaline batteries were designed as direct replacements for zinc-carbon (dry cell) batteries.

Secondary Batteries

Secondary batteries are rechargeable. These are the types of batteries found in devices such as smartphones, electronic tablets, and automobiles.

Nickel-cadmium, or NiCd, batteries (Figure 9.5.3) consist of a nickel-plated cathode, cadmium-plated anode, and a potassium hydroxide electrode. The positive and negative plates, which are prevented from shorting by the separator, are rolled together and put into the case. This is a "jelly-roll" design and allows the NiCd cell to deliver much more current than a similar-sized alkaline battery. The reactions are

$$\begin{aligned} &\text{anode: } \mathrm{Cd}(s) + 2\,\mathrm{OH}^-(aq) \longrightarrow \mathrm{Cd(OH)_2}(s) + 2\,\mathrm{e}^- \\ &\text{cathode: } \mathrm{NiO_2}(s) + 2\,\mathrm{H_2O}(l) + 2\,\mathrm{e}^- \longrightarrow \mathrm{Ni(OH)_2}(s) + 2\,\mathrm{OH}^-(aq) \\ &\text{overall: } \mathrm{Cd}(s) + \mathrm{NiO_2}(s) + 2\,\mathrm{H_2O}(l) \longrightarrow \mathrm{Cd(OH)_2}(s) + \mathrm{Ni(OH)_2}(s) \end{aligned}$$

The voltage is about 1.2 V to 1.25 V as the battery discharges. When properly treated, a NiCd battery can be recharged about 1000 times. Cadmium is a toxic heavy metal so NiCd batteries should never be opened or put into the regular trash.

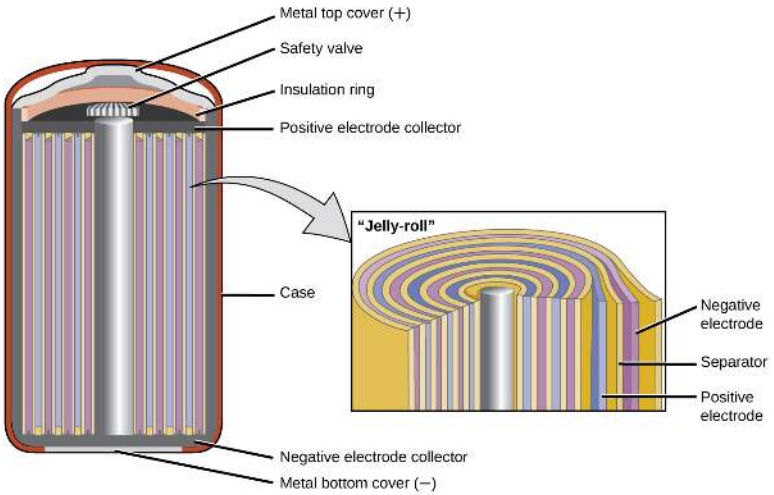


Figure 9.5.3: NiCd batteries use a "jelly-roll" design that significantly increases the amount of current the battery can deliver as compared to a similar-sized alkaline battery.

Lithium ion batteries (Figure 9.5.4) are among the most popular rechargeable batteries and are used in many portable electronic devices. The reactions are

$$\text{anode: } \mathrm{LiCoO_2} \rightleftharpoons \mathrm{Li_{1-x}CoO_2} + x\mathrm{Li^+} + x\mathrm{e^-}$$
$$\text{cathode: } x\mathrm{Li^+} + x\mathrm{e^-} + x\mathrm{C_6} \rightleftharpoons x\mathrm{LiC_6}$$
$$\text{overall: } \mathrm{LiCoO_2} + x\mathrm{C_6} \rightleftharpoons \mathrm{Li_{1-x}CoO_2} + x\mathrm{LiC_6}$$

With the coefficients representing moles, *x* is no more than about 0.5 moles. The battery voltage is about 3.7 V. Lithium batteries are popular because they can provide a large amount current, are lighter than comparable batteries of other types, produce a nearly constant voltage as they discharge, and only slowly lose their charge when stored.

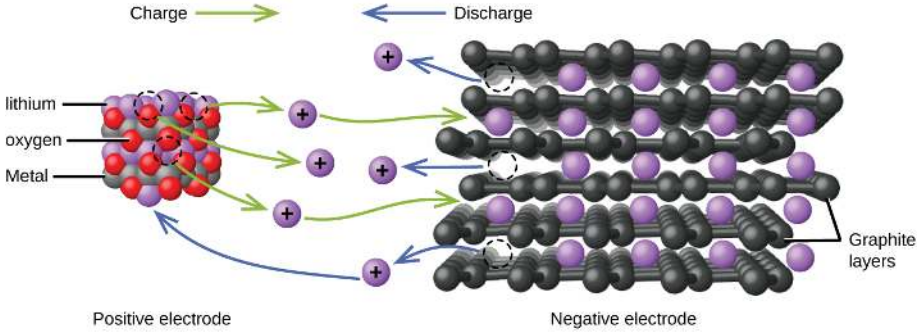


Figure 9.5.4: In a lithium ion battery, charge flows between the electrodes as the lithium ions move between the anode and cathode.

The lead acid battery (Figure 9.5.5) is the type of secondary battery used in your automobile. It is inexpensive and capable of producing the high current required by automobile starter motors. The reactions for a lead acid battery are

$$\text{anode: } \mathrm{Pb}(s) + \mathrm{HSO_4^-}(aq) \longrightarrow \mathrm{PbSO_4}(s) + \mathrm{H^+}(aq) + 2\,\mathrm{e^-}$$
$$\text{cathode: } \mathrm{PbO_2}(s) + \mathrm{HSO_4^-}(aq) + 3\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{PbSO_4}(s) + 2\,\mathrm{H_2O}(l)$$
$$\text{overall: } \mathrm{Pb}(s) + \mathrm{PbO_2}(s) + 2\,\mathrm{H_2SO_4}(aq) \longrightarrow 2\,\mathrm{PbSO_4}(s) + 2\,\mathrm{H_2O}(l)$$

Each cell produces 2 V, so six cells are connected in series to produce a 12-V car battery. Lead acid batteries are heavy and contain a caustic liquid electrolyte, but are often still the battery of choice because of their high current density. Since these batteries contain a significant amount of lead, they must always be disposed of properly.

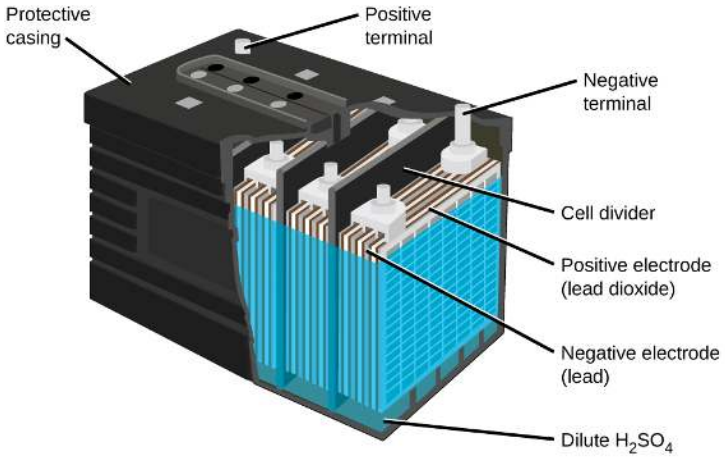


Figure 9.5.5: The lead acid battery in your automobile consists of six cells connected in series to give 12 V. Their low cost and high current output makes these excellent candidates for providing power for automobile starter motors.

Fuel Cells

A fuel cell is a device that converts chemical energy into electrical energy. Fuel cells are similar to batteries but require a continuous source of fuel, often hydrogen. They will continue to produce electricity as long as fuel is available. Hydrogen fuel cells have been used to supply power for satellites, space capsules, automobiles, boats, and submarines (Figure 9.5.6).

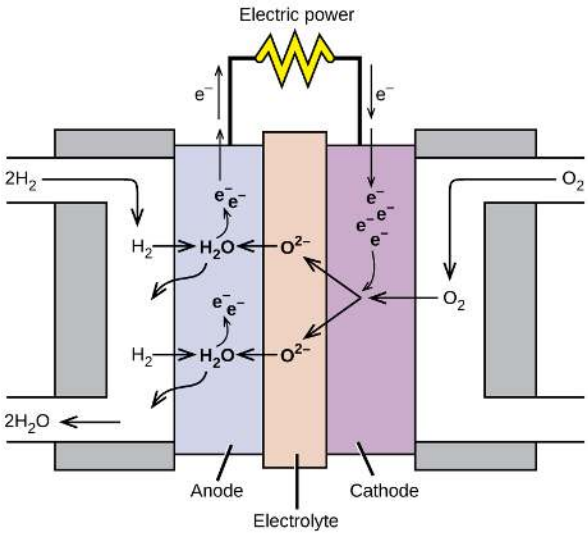


Figure 9.5.6: In this hydrogen fuel-cell schematic, oxygen from the air reacts with hydrogen, producing water and electricity.

In a hydrogen fuel cell, the reactions are

$$\begin{aligned} &\text{anode: } 2\,H_2 + 2\,O^{2-} \longrightarrow 2\,H_2O + 4\,e^- \\ &\text{cathode: } O_2 + 4\,e^- \longrightarrow 2\,O^{2-} \\ &\overline{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad} \\ &\text{overall: } 2\,H_2 + O_2 \longrightarrow 2\,H_2O \end{aligned}$$

The voltage is about 0.9 V. The efficiency of fuel cells is typically about 40% to 60%, which is higher than the typical internal combustion engine (25% to 35%) and, in the case of the hydrogen fuel cell, produces only water as exhaust. Currently, fuel cells are rather expensive and contain features that cause them to fail after a relatively short time.

Summary

Batteries are galvanic cells, or a series of cells, that produce an electric current. When cells are combined into batteries, the potential of the battery is an integer multiple of the potential of a single cell. There are two basic types of batteries: primary and secondary. Primary batteries are “single use” and cannot be recharged. Dry cells and (most) alkaline batteries are examples of primary batteries. The second type is rechargeable and is called a secondary battery. Examples of secondary batteries include nickel-cadmium (NiCd), lead acid, and lithium ion batteries. Fuel cells are similar to batteries in that they generate an electrical current, but require continuous addition of fuel and oxidizer. The hydrogen fuel cell uses hydrogen and oxygen from the air to produce water, and is generally more efficient than internal combustion engines.

alkaline battery

primary battery that uses an alkaline (often potassium hydroxide) electrolyte; designed to be an exact replacement for the dry cell, but with more energy storage and less electrolyte leakage than typical dry cell

battery

galvanic cell or series of cells that produces a current; in theory, any galvanic cell

dry cell

primary battery, also called a zinc-carbon battery; can be used in any orientation because it uses a paste as the electrolyte; tends to leak electrolyte when stored

fuel cell

devices that produce an electrical current as long as fuel and oxidizer are continuously added; more efficient than internal combustion engines

lead acid battery

secondary battery that consists of multiple cells; the lead acid battery found in automobiles has six cells and a voltage of 12 V

lithium ion battery

very popular secondary battery; uses lithium ions to conduct current and is light, rechargeable, and produces a nearly constant potential as it discharges

nickel-cadmium battery

(NiCd battery) secondary battery that uses cadmium, which is a toxic heavy metal; heavier than lithium ion batteries, but with similar performance characteristics

primary battery

single-use nonrechargeable battery

secondary battery

battery that can be recharged

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9.6: Electrolysis

Learning Objectives

- Describe electrolytic cells and their relationship to galvanic cells
- Perform various calculations related to electrolysis

In galvanic cells, chemical energy is converted into electrical energy. The opposite is true for electrolytic cells. In electrolytic cells, electrical energy causes nonspontaneous reactions to occur in a process known as electrolysis. The charging electric barttery shows one such process. Electrical energy is converted into the chemical energy in the battery as it is charged. Once charged, the battery can be used to power the automobile. The same principles are involved in electrolytic cells as in galvanic cells. We will look at three electrolytic cells and the quantitative aspects of electrolysis.

The Electrolysis of Molten Sodium Chloride

In molten sodium chloride, the ions are free to migrate to the electrodes of an electrolytic cell. A simplified diagram of the cell commercially used to produce sodium metal and chlorine gas is shown in Figure 9.6.1. Sodium is a strong reducing agent and chlorine is used to purify water, and is used in antiseptics and in paper production. The reactions are

$$\text{anode: } 2\,\text{Cl}^-(l) \longrightarrow \text{Cl}_2(g) + 2\,\text{e}^- \quad E^\circ_{\text{Cl}_2/\text{Cl}^-} = +1.3\ \text{V} \tag{9.6.1}$$

$$\text{cathode: } \text{Na}^+(l) + \text{e}^- \longrightarrow \text{Na}(l) \quad E^\circ_{\text{Na}^+/\text{Na}} = -2.7\ \text{V} \tag{9.6.2}$$

$$\text{overall: } 2\,\text{Na}^+(l) + 2\,\text{Cl}^-(l) \longrightarrow 2\,\text{Na}(l) + \text{Cl}_2(g) \quad E^\circ_{\text{cell}} = -4.0\ \text{V} \tag{9.6.3}$$

The power supply (battery) must supply a minimum of 4 V, but, in practice, the applied voltages are typically higher because of inefficiencies in the process itself.

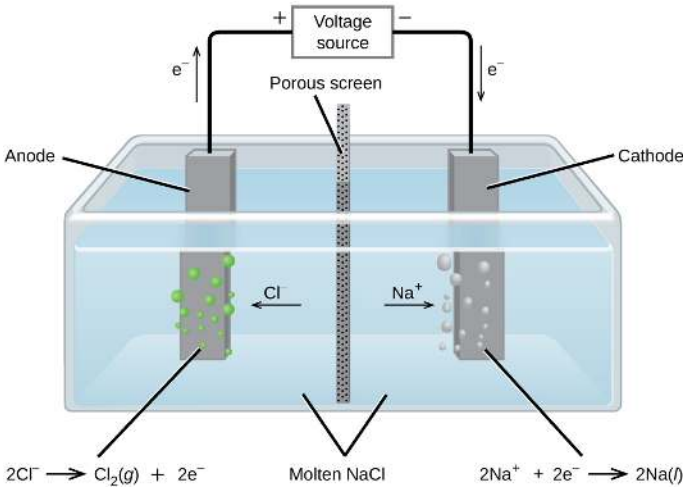


Figure 9.6.1: Passing an electric current through molten sodium chloride decomposes the material into sodium metal and chlorine gas. Care must be taken to keep the products separated to prevent the spontaneous formation of sodium chloride.

The Electrolysis of Water

It is possible to split water into hydrogen and oxygen gas by electrolysis. Acids are typically added to increase the concentration of hydrogen ion in solution (Figure 9.6.2). The reactions are

$$\text{anode: } 2\,\text{H}_2\text{O}(l) \longrightarrow \text{O}_2(g) + 4\,\text{H}^+(aq) + 4\,\text{e}^- \quad E^\circ_{\text{anode}} = +1.229\ \text{V} \tag{9.6.4}$$

$$\text{cathode: } 2\,\text{H}^+(aq) + 2\,\text{e}^- \longrightarrow \text{H}_2(g) \quad E^\circ_{\text{cathode}} = 0\ \text{V} \tag{9.6.5}$$

$$\text{overall: } 2\,\text{H}_2\text{O}(l) \longrightarrow 2\,\text{H}_2(g) + \text{O}_2(g) \quad E^\circ_{\text{cell}} = -1.229\ \text{V} \tag{9.6.6}$$

Note that the sulfuric acid is not consumed and that the volume of hydrogen gas produced is twice the volume of oxygen gas produced. The minimum applied voltage is 1.229 V.

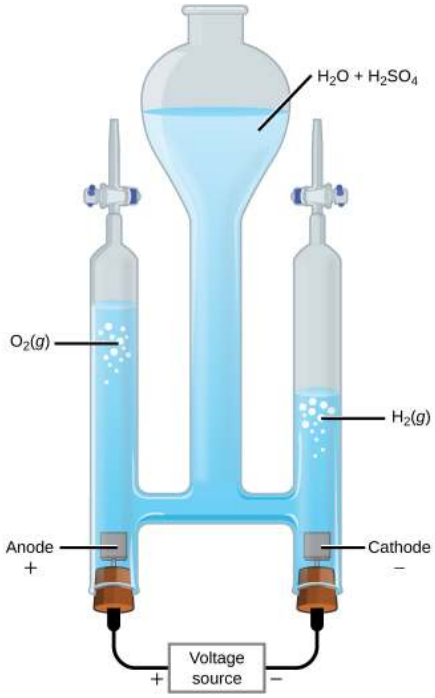


Figure 9.6.2: Water decomposes into oxygen and hydrogen gas during electrolysis. Sulfuric acid was added to increase the concentration of hydrogen ions and the total number of ions in solution, but does not take part in the reaction. The volume of hydrogen gas collected is twice the volume of oxygen gas collected, due to the stoichiometry of the reaction.

The Electrolysis of Aqueous Sodium Chloride

The electrolysis of aqueous sodium chloride is the more common example of electrolysis because more than one species can be oxidized and reduced. Considering the anode first, the possible reactions are

$$\text{(i)}\ 2\,\mathrm{Cl^-}(aq) \longrightarrow \mathrm{Cl_2}(g) + 2\,\mathrm{e^-} \quad E^\circ_{\text{anode}} = +1.35827\ \mathrm{V} \tag{9.6.7}$$

$$\text{(ii)}\ 2\,\mathrm{H_2O}(l) \longrightarrow \mathrm{O_2}(g) + 4\,\mathrm{H^+}(aq) + 4\,\mathrm{e^-} \quad E^\circ_{\text{anode}} = +1.229\ \mathrm{V} \tag{9.6.8}$$

These values suggest that water should be oxidized at the anode because a smaller potential would be needed—using reaction (ii) for the oxidation would give a less-negative cell potential. When the experiment is run, it turns out chlorine, not oxygen, is produced at the anode. The unexpected process is so common in electrochemistry that it has been given the name overpotential. The overpotential is the difference between the theoretical cell voltage and the actual voltage that is necessary to cause electrolysis. It turns out that the overpotential for oxygen is rather high and effectively makes the reduction potential more positive. As a result, under normal conditions, chlorine gas is what actually forms at the anode.

Now consider the cathode. Three reductions could occur:

$$\text{(iii)}\ 2\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2}(g) \quad E^\circ_{\text{cathode}} = 0\ \mathrm{V} \tag{9.6.9}$$

$$\text{(iv)}\ 2\,\mathrm{H_2O}(l) + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2}(g) + 2\,\mathrm{OH^-}(aq) \quad E^\circ_{\text{cathode}} = -0.8277\ \mathrm{V} \tag{9.6.10}$$

$$\text{(v)}\ \mathrm{Na^+}(aq) + \mathrm{e^-} \longrightarrow \mathrm{Na}(s) \quad E^\circ_{\text{cathode}} = -2.71\ \mathrm{V} \tag{9.6.11}$$

Reaction (v) is ruled out because it has such a negative reduction potential. Under standard state conditions, reaction (iii) would be preferred to reaction (iv). However, the pH of a sodium chloride solution is 7, so the concentration of hydrogen ions is only 1×10^{-7} *M*. At such low concentrations, reaction (iii) is unlikely and reaction (iv) occurs. The overall reaction is then

$$\text{overall:}\ 2\,\mathrm{H_2O}(l) + 2\,\mathrm{Cl^-}(aq) \longrightarrow \mathrm{H_2}(g) + \mathrm{Cl_2}(g) + 2\,\mathrm{OH^-}(aq) \quad E^\circ_{\text{cell}} = -2.186\ \mathrm{V}$$

As the reaction proceeds, hydroxide ions replace chloride ions in solution. Thus, sodium hydroxide can be obtained by evaporating the water after the electrolysis is complete. Sodium hydroxide is valuable in its own right and is used for things like oven cleaner, drain opener, and in the production of paper, fabrics, and soap.

Electroplating

An important use for electrolytic cells is in electroplating. Electroplating results in a thin coating of one metal on top of a conducting surface. Reasons for electroplating include making the object more corrosion resistant, strengthening the surface, producing a more attractive finish, or for purifying metal. The metals commonly used in electroplating include cadmium, chromium, copper, gold, nickel, silver, and tin. Common consumer products include silver-plated or gold-plated tableware, chrome-plated automobile parts, and jewelry. We can get an idea of how this works by investigating how silver-plated tableware is produced (Figure 9.6.3).

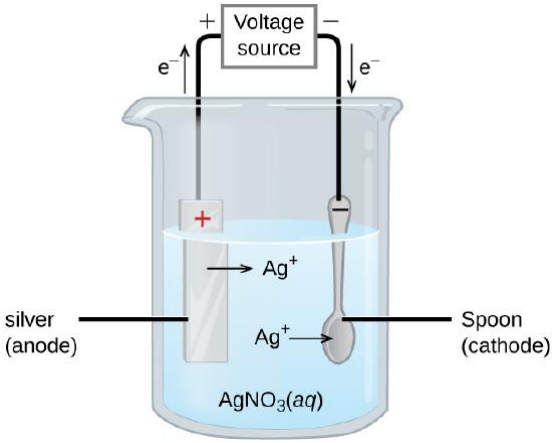


Figure 9.6.3: The spoon, which is made of an inexpensive metal, is connected to the negative terminal of the voltage source and acts as the cathode. The anode is a silver electrode. Both electrodes are immersed in a silver nitrate solution. When a steady current is passed through the solution, the net result is that silver metal is removed from the anode and deposited on the cathode.

In the figure, the anode consists of a silver electrode, shown on the left. The cathode is located on the right and is the spoon, which is made from inexpensive metal. Both electrodes are immersed in a solution of silver nitrate. As the potential is increased, current flows. Silver metal is lost at the anode as it goes into solution.

$$\text{anode: } \mathrm{Ag}(s) \longrightarrow \mathrm{Ag}^{+}(aq) + \mathrm{e}^{-}$$

The mass of the cathode increases as silver ions from the solution are deposited onto the spoon

$$\text{cathode: } \mathrm{Ag}^{+}(aq) + \mathrm{e}^{-} \longrightarrow \mathrm{Ag}(s)$$

The net result is the transfer of silver metal from the anode to the cathode. The quality of the object is usually determined by the thickness of the deposited silver and the rate of deposition.

Quantitative Aspects of Electrolysis

The amount of current that is allowed to flow in an electrolytic cell is related to the number of moles of electrons. The number of moles of electrons can be related to the reactants and products using stoichiometry. Recall that the SI unit for current (I) is the ampere (A), which is the equivalent of 1 coulomb per second (1 A = 1 $\frac{\mathrm{C}}{\mathrm{s}}$). The total charge ($Q$, in coulombs) is given by

$$Q = I \times t = n \times F$$

where

- t is the time in seconds,
- n the number of moles of electrons, and
- F is the Faraday constant.

Moles of electrons can be used in stoichiometry problems. The time required to deposit a specified amount of metal might also be requested, as in the second of the following examples.

Example 9.6.1: Converting Current to Moles of Electrons

In one process used for electroplating silver, a current of 10.23 A was passed through an electrolytic cell for exactly 1 hour. How many moles of electrons passed through the cell? What mass of silver was deposited at the cathode from the silver nitrate solution?

Solution

Faraday's constant can be used to convert the charge (Q) into moles of electrons (n). The charge is the current (I) multiplied by the time

$$n = \frac{Q}{F} = \frac{\frac{10.23\ \text{C}}{\text{s}} \times 1\ \text{hr} \times \frac{60\ \text{min}}{\text{hr}} \times \frac{60\ \text{s}}{\text{min}}}{96,485\ \text{C/mol e}^-} = \frac{36,830\ \text{C}}{96,485\ \text{C/mol e}^-} = 0.3817\ \text{mol e}^-$$

From the problem, the solution contains $AgNO_3$, so the reaction at the cathode involves 1 mole of electrons for each mole of silver

$$\text{cathode: } \text{Ag}^+(aq) + \text{e}^- \longrightarrow \text{Ag}(s)$$

The atomic mass of silver is 107.9 g/mol, so

$$\text{mass Ag} = 0.3817\ \text{mol e}^- \times \frac{1\ \text{mol Ag}}{1\ \text{mol e}^-} \times \frac{107.9\ \text{g Ag}}{1\ \text{mol Ag}} = 41.19\ \text{g Ag}$$

Check your answer: From the stoichiometry, 1 mole of electrons would produce 1 mole of silver. Less than one-half a mole of electrons was involved and less than one-half a mole of silver was produced.

? Exercise 9.6.1

Aluminum metal can be made from aluminum ions by electrolysis. What is the half-reaction at the cathode? What mass of aluminum metal would be recovered if a current of 2.50×10^3 A passed through the solution for 15.0 minutes? Assume the yield is 100%.

Answer

$\text{Al}^{3+}(aq) + 3\,\text{e}^- \longrightarrow \text{Al}(s)$; 7.77 mol Al = 210.0 g Al.

✓ Example 9.6.2: Time Required for Deposition

In one application, a 0.010-mm layer of chromium must be deposited on a part with a total surface area of 3.3 m^2 from a solution of containing chromium(III) ions. How long would it take to deposit the layer of chromium if the current was 33.46 A? The density of chromium (metal) is 7.19 g/cm^3.

Solution This problem brings in a number of topics covered earlier. An outline of what needs to be done is:

- If the total charge can be determined, the time required is just the charge divided by the current
- The total charge can be obtained from the amount of Cr needed and the stoichiometry
- The amount of Cr can be obtained using the density and the volume Cr required
- The volume Cr required is the thickness times the area

Solving in steps, and taking care with the units, the volume of Cr required is

$$\text{volume} = \left(0.010\ \text{mm} \times \frac{1\ \text{cm}}{10\ \text{mm}}\right) \times \left(3.3\ \text{m}^2 \times \left(\frac{10,000\ \text{cm}^2}{1\ \text{m}^2}\right)\right) = 33\ \text{cm}^3$$

Cubic centimeters were used because they match the volume unit used for the density. The amount of Cr is then

$$\text{mass} = \text{volume} \times \text{density} = 33\ \cancel{\text{cm}^3} \times \frac{7.19\ \text{g}}{\cancel{\text{cm}^3}} = 237\ \text{g Cr}$$

$$\text{mol Cr} = 237\ \text{g Cr} \times \frac{1\ \text{mol Cr}}{52.00\ \text{g Cr}} = 4.56\ \text{mol Cr}$$

Since the solution contains chromium(III) ions, 3 moles of electrons are required per mole of Cr. The total charge is then

$$Q = 4.56\ \text{mol Cr} \times \frac{3\ \text{mol e}^-}{1\ \text{mol Cr}} \times \frac{96485\ \text{C}}{\text{mol e}^-} = 1.32 \times 10^6\ \text{C}$$

The time required is then

$$t = \frac{Q}{I} = \frac{1.32 \times 10^6 \text{ C}}{33.46 \text{ C/s}} = 3.95 \times 10^4 \text{ s} = 11.0 \text{ hr}$$

Check your answer: In a long problem like this, a single check is probably not enough. Each of the steps gives a reasonable number, so things are probably correct. Pay careful attention to unit conversions and the stoichiometry.

? Exercise 9.6.2

What mass of zinc is required to galvanize the top of a 3.00 m × 5.50 m sheet of iron to a thickness of 0.100 mm of zinc? If the zinc comes from a solution of $Zn(NO_3)_2$ and the current is 25.5 A, how long will it take to galvanize the top of the iron? The density of zinc is 7.140 g/cm^3.

Answer

231 g Zn required 23,000 minutes.

Summary

Using electricity to force a nonspontaneous process to occur is electrolysis. Electrolytic cells are electrochemical cells with negative cell potentials (meaning a positive Gibbs free energy), and so are nonspontaneous. Electrolysis can occur in electrolytic cells by introducing a power supply, which supplies the energy to force the electrons to flow in the nonspontaneous direction. Electrolysis is done in solutions, which contain enough ions so current can flow. If the solution contains only one material, like the electrolysis of molten sodium chloride, it is a simple matter to determine what is oxidized and what is reduced. In more complicated systems, like the electrolysis of aqueous sodium chloride, more than one species can be oxidized or reduced and the standard reduction potentials are used to determine the most likely oxidation (the half-reaction with the largest [most positive] standard reduction potential) and reduction (the half-reaction with the smallest [least positive] standard reduction potential). Sometimes unexpected half-reactions occur because of overpotential. Overpotential is the difference between the theoretical half-reaction reduction potential and the actual voltage required. When present, the applied potential must be increased, making it possible for a different reaction to occur in the electrolytic cell. The total charge, Q, that passes through an electrolytic cell can be expressed as the current (I) multiplied by time ($Q = It$) or as the moles of electrons (n) multiplied by Faraday's constant ($Q = nF$). These relationships can be used to determine things like the amount of material used or generated during electrolysis, how long the reaction must proceed, or what value of the current is required.

electrolysis

process using electrical energy to cause a nonspontaneous process to occur

electrolytic cell

electrochemical cell in which electrolysis is used; electrochemical cell with negative cell potentials

electroplating

depositing a thin layer of one metal on top of a conducting surface

overpotential

difference between the theoretical potential and actual potential in an electrolytic cell; the "extra" voltage required to make some nonspontaneous electrochemical reaction to occur

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9.E: Exercises on Electrochemistry

9.1 Balancing Oxidation – Reduction reactions

Exercise 9.E.1

Identify each half-reaction below as either oxidation or reduction.

a.

$$\mathrm{Fe^{3+}}(aq) + 3\mathrm{e^-} \longrightarrow \mathrm{Fe}(s) \tag{9.E.1}$$

b.

$$\mathrm{Cr}(s) \longrightarrow \mathrm{Cr^{3+}}(aq) + 3\mathrm{e^-} \tag{9.E.2}$$

c.

$$\mathrm{MnO_4^{2-}}(aq) \longrightarrow \mathrm{MnO_4^-}(aq) + \mathrm{e^-} \tag{9.E.3}$$

d.

$$\mathrm{Li^+}(aq) + \mathrm{e^-} \longrightarrow \mathrm{Li}(s) \tag{9.E.4}$$

Answer

a. reduction; b. oxidation; c. oxidation; d. reduction

Exercise 9.E.2

Assuming each pair of half-reactions below takes place in an acidic solution, write a balanced equation for the overall reaction.

a.

$$\mathrm{Ca} \longrightarrow \mathrm{Ca^{2+}} + 2\mathrm{e^-}, \mathrm{F_2} + 2\mathrm{e^-} \longrightarrow 2\ \mathrm{F^-} \tag{9.E.5}$$

b.

$$\mathrm{Li} \longrightarrow \mathrm{Li^+} + \mathrm{e^-}, \mathrm{Cl_2} + 2\mathrm{e^-} \longrightarrow 2\mathrm{Cl^-} \tag{9.E.6}$$

c.

$$\mathrm{Fe} \longrightarrow \mathrm{Fe^{3+}} + 3\mathrm{e^-}, \mathrm{Br_2} + 2\mathrm{e^-} \longrightarrow 2\mathrm{Br^-} \tag{9.E.7}$$

d.

$$\mathrm{Ag} \longrightarrow \mathrm{Ag^+} + \mathrm{e^-}, \mathrm{MnO_4^-} + 4\mathrm{H^+} + 3\mathrm{e^-} \longrightarrow \mathrm{MnO_2} + 2\mathrm{H_2O} \tag{9.E.8}$$

Answer

$$(a)\mathrm{F_2} + \mathrm{Ca} \longrightarrow 2\ \mathrm{F^-} + \mathrm{Ca^{2+}}; (b)\$\mathrm{Cl_2} + 2\mathrm{Li} \longrightarrow 2\mathrm{Li^+} + 2\mathrm{Cl^-}; (c)3\mathrm{r_2} + 2\mathrm{Fe} \longrightarrow 2\mathrm{Fe^{3+}} + 6\mathrm{Br^-}; (\mathrm{d})\ \mathrm{MnO_4^-} + 4\mathrm{H^+} + 3\mathrm{Ag} \longrightarrow 3\mathrm{Ag^+} + \mathrm{MnO_2} + 2\mathrm{H_2O} \tag{9.E.9}$$

9.2 Galvanic Cells

Exercise 9.E.3

Write cell shorthand notations for the following cell reactions, using platinum as an inert electrode as needed.

a. $\mathrm{Mg(s)+Ni^{2+}(aq) \longrightarrow Mg^{2+}(aq)+Ni(s)}$

b. $\mathrm{2Ag^{+}(aq)+Cu(s) \longrightarrow Cu^{2+}(aq)+2Ag(s)}$

c. $\mathrm{Mn(s)+Sn(NO_3)_2(aq) \longrightarrow Mn(NO_3)_2(aq)+Sn(s)}$

d. $\mathrm{3CuNO_3(aq)+Au(NO_3)_3(aq) \longrightarrow 3Cu(NO_3)_2(aq)+Au(s)}$

Answer

a. $\mathrm{Mg(s) \mid Mg^{2+}(aq) \| Ni^{2+}(aq) \mid Ni(s)}$

b. $\mathrm{Cu(s) \mid Cu^{2+}(aq) \| Ag+(aq) \mid Ag(s)}$

c. $\mathrm{Mn(s) \mid Mn^{2+}(aq) \| Sn^{2+}(aq) \mid Sn(s)}$

d. $\mathrm{Pt(s) \mid Cu^{+}(aq),\ Cu^{2+}(aq) \| Au^{3+}(aq) \mid Au(s)}$

Exercise 9.E.4

Why is a salt bridge necessary in galvanic cells?

Answer

Without the salt bridge, the circuit would be open (or broken) and no current could flow. With a salt bridge, each half-cell remains electrically neutral and current can flow through the circuit.

Exercise 9.E.5

An active (metal) electrode was found to lose mass as the oxidation-reduction reaction was allowed to proceed. Was the electrode an anode or a cathode? Explain.

Answer

Active electrodes participate in the oxidation-reduction reaction. Since metals form cations, the electrode would lose mass if metal atoms in the electrode were to oxidize and go into solution. Oxidation occurs at the anode.

9.3 Standard Reduction Potentials E°cell

Exercise 9.E.6

Identify where each reaction will take place (on the cathode or anode), balance the equation if necessary, and calculate the E°_{cell}.

a. $Fe^{3+}(aq) + Ag(s) \rightarrow Fe^{2+}(aq) + Ag^+(aq)$
b. $Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$
c. $Cd(s) + Cu^{2+}(aq) \rightarrow Cd^{2+} + Cu(s)$
d. $Fe^{2+}(aq) + Cl_2(g) \rightarrow Fe^{3+}(aq) + 2Cl^-(aq)$

Answer

Reduction: $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ at the cathode (reduction occurs at the cathode)

Oxidation: $Ag(s) \rightarrow Ag^+(aq) + e^-$ at the anode

The equation is already balanced.

$E^\circ_{cell} = (0.771 - 0.800) = -0.029\ V$

Reduction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ at the cathode, where reduction occurs

Reduction: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ at the cathode

Oxidation: $2(Fe^{2+}(aq) \rightarrow 2Fe^{3+}(aq) + e^-)$ at the anode

$E^\circ_{cell} = 1.358 - (-0.440) = 1.798\ V$

Oxidation: $Cd(s) \rightarrow Cd^{2+} + 2e^-$ at the anode

Reaction is already balanced

$E^\circ_{cell} = E^\circ_{(right)} - E^\circ_{(left)} = 0.340 - 0.743 = -0.403$

Balance the equation, multiplying the iron half equation by 2 to equal the electrons

Oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ at the anode

Reaction is already balanced

$E^\circ_{cell} = 0.340 - (-0.763) = 1.103\ V$

Reduction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ at the cathode, where reduction occurs

Exercise 9.E.7

Calculate the theoretical cell voltage for the reaction between copper and zinc given that the overall reaction is:
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

Answer

Oxidation: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ $E^\circ = 0.340\ V$
Reduction: $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $E^\circ = -0.763\ V$
$E^\circ_{cell} = -0.763\ V - 0.340\ V = -1.103\ V$

Exercise 9.E.8

Use data from the standard electrode reduction potentials table to predict whether the reactions below are spontaneous in the forward reaction (All reactants and products are in their standard states):

a. $Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$
b. $2Al(s) + 3Zn^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Zn(s)$

c. $Fe^{2+}(aq) + Ag^{+}(aq) \rightarrow Fe^{3+}(aq) + Ag(s)$
d. $2Fe^{2+}(aq) + I_2(s) \rightarrow 2Fe^{3+}(aq) + 2I^{-}(aq)$

Answer

Cell reaction: $Cu(s) + 2Ag^{+}(aq) \rightarrow 2Cu^{2+}(aq) + 2Ag(s)$

Oxidation: $Cu(s) \rightarrow Cu^{2+} + 2e^{-}$
Reduction: $(Ag^{+}(aq) + e^{-} \rightarrow Ag(s) \quad) \times 2$

$$E^{\circ}_{cell} = E^{\circ}_{(reduction)} - E^{\circ}_{(oxidation)} \tag{9.E.10}$$
$$= E^{\circ}_{Ag^{+}/Ag} - E^{\circ}_{Cu/Cu^{2+}} \tag{9.E.11}$$
$$= 0.7991 - 0.3394 = +0.4597\ V \tag{9.E.12}$$

The cell potential is positive, therefore the spontaneous reaction will occur in the forward reaction.

Cell reaction: $2Al(s) + 3Zn^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Zn(s)$

Oxidation: $(Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}(aq)\,) \times 2$
Reduction: $I_2(s) + 2e^{-} \rightarrow 2I^{-}(aq)$

$$E^{\circ}_{cell} = E^{\circ}_{(reduction)} - E^{\circ}_{(oxidation)} \tag{9.E.13}$$
$$= E^{\circ}_{I_2/2I^{-}} - E^{\circ}_{Fe^{2+}/Fe^{3+}} \tag{9.E.14}$$
$$= 0.535 - 0.769 = -0.234\ V \tag{9.E.15}$$

The cell potential is negative, therefore the spontaneous reaction will not occur in the forward reaction.

Oxidation: $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^{-}$
Reduction: $Ag(s) \rightarrow Ag^{+}(aq) + e^{-}$

$$E^{\circ}_{cell} = E^{\circ}_{(reduction)} - E^{\circ}_{(oxidation)} \tag{9.E.16}$$
$$= E^{\circ}_{Ag^{+}/Ag} - E^{\circ}_{Fe^{2+}/Fe^{3+}} \tag{9.E.17}$$
$$= 0.7991 - 0.769 = +0.0301\ V \tag{9.E.18}$$

The cell potential is positive, therefore the spontaneous reaction will occur in the forward reaction.

Cell reaction: $2Fe^{2+}(aq) + I_2(s) \rightarrow 2Fe^{3+}(aq) + 2I^{-}(aq)$

Oxidation: $(Al(s) \rightarrow Al^{3+} + 3e^{-}) \times 2$
Reduction: $(Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)) \times 3$

$$E^{\circ}_{cell} = E^{\circ}_{(reduction)} - E^{\circ}_{(oxidation)} \tag{9.E.19}$$
$$= E^{\circ}_{Zn^{2+}/Zn} - E^{\circ}_{Al/Al^{3+}} \tag{9.E.20}$$
$$= -0.7621 - (-1.676) = +0.9139\ V \tag{9.E.21}$$

The cell potential is positive, therefore the spontaneous reaction will occur in the forward reaction.

Cell reaction: $Fe^{2+}(aq) + Ag^{+}(aq) \rightarrow Fe^{3+}(aq) + Ag(s)$

? Exercise 9.E.9

Write cell reactions for the electrochemical cells diagrammed, and use data from the table of standard electrode potentials to calculate E°_{cell} for each reaction.

a. $Fe(s)|Fe^{2+}(aq)||Zn(s)|Zn^{2+}(aq)$
b. $Na(s)|Na^{+}(aq)||Cl_2(g)|Cl^{-}(aq)$
c. $Co(s)|Co^{2+}(aq)||Mn^{2+}(aq)|Mn(s)$
d. $Pt(s)|Fe^{2+}(aq), Fe^{3+}(aq)||Pb^{2+}(aq)|Pb(s)$

Answer

Oxidation: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-}$ $\quad E^{\circ} = -(-0.440\ V)$

Reduction: $Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$ $\quad E^{\circ} = -0.7621\ V$
Net Reaction: $Fe(s) + Zn^{2+}(aq) \rightarrow Fe^{2+}(aq) + Zn(s)$ $\quad E^{\circ}_{cell} = -0.3321\ V$

Oxidation: $Na(s) \rightarrow Na^{+}(aq) + e^{-}$ $\quad E^{\circ} = -(-2.7144\ V)$

Reduction: $Pb^{2+}(aq) + 2e^{-} \rightarrow Pb(s)$ $\quad E^{\circ} = -0.125\ V$
Net Reaction: $2Fe^{2+} + Pb^{2+}(aq) \rightarrow 2Fe^{3+}(aq) + Pb(s)$ $\quad E^{\circ}_{cell} = -0.896\ V$

Reduction: $Mn^{2+}(aq) + 2e^{-} \rightarrow Mn(s)$ $\quad E^{\circ} = -1.182\ V$
Net Reaction: $Co(s) + Mn^{2+}(aq) \rightarrow Co^{2+}(aq) + Mn(s)$ $\quad E^{\circ}_{cell} = -0.905\ V$

Oxidation: $(Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^{-}) \times 2$ $\quad E^{\circ} = -(-0.771\ V)$

Reduction: $Cl_2(g) + e^{-} \rightarrow 2Cl^{-}(aq)$ $\quad E^{\circ} = 1.3601\ V$
Net Reaction: $Na(s) + Cl_2(g) \rightarrow Na^{+}(aq) + 2Cl^{-}(aq)$ $\quad E^{\circ}_{cell} = -0.905\ V$

Oxidation: $Co(s) \rightarrow Co^{2+}(aq) + 2e^{-}$ $\quad E^{\circ} = -(-0.277\ V)$

Exercise 9.E.10

For each of the following reactions below, draw a voltaic cell. In your drawing include the anode, cathode, and show the flow of electrons. Balance the equation and calculate the E°_{cell}.

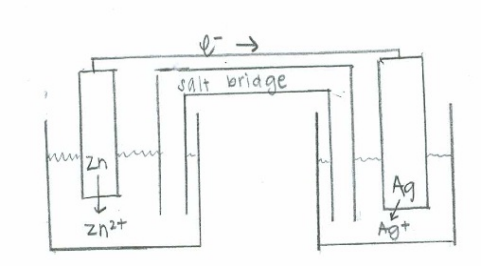
a. $Zn(s) + Ag^+(aq) \rightarrow Ag(s) + Zn^{2+}(aq)$
b. $Rb(s) + Hg^{2+}(aq) \rightarrow Rb^+(aq) + Hg(s)$
c. $F_2(g) + H_2O(l) \rightarrow 4F^-(aq) + O_2(g) + H^+(aq)$
d. $Zn(s) + H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

Answer

Oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $\quad -E^\circ = 0.763\ V$

Reduction: $(e^- + Ag^+(aq) \rightarrow Ag(s)) \times 2$ $\quad E^\circ = 0.337\ V$

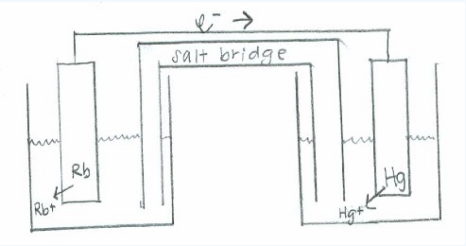
Net: $Zn(s) + 2Ag^+(aq) \rightarrow 2Ag(s) + Zn^{2+}(aq)$ $\quad E^\circ_{cell} = 1.100\ V$



Oxidation: $(Rb(s) \rightarrow Rb^+(aq) + e^-) \times 2$ $\quad -E^\circ = +2.93\ V$

Reduction: $Hg^{2+}(aq) + 2e^- \rightarrow Hg(s)$ $\quad E^\circ = 0.86\ V$

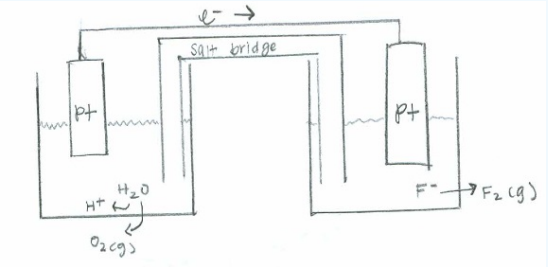
Net: $2Rb(s) + Hg^{2+}(aq) \rightarrow 2Rb^+(aq) + Hg(s)$ $\quad E^\circ_{cell} = 3.79\ V$



Oxidation: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $\quad -E^\circ = -1.229\ V$

Reduction: $(2e^- + F_2(g) \rightarrow 2F^-(aq)) \times 2$ $\quad E^\circ = 2.866\ V$

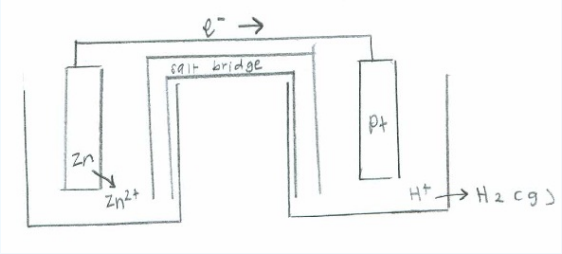
Net: $2F_2(g) + 2H_2O(l) \rightarrow 4F^-(aq) + O_2(g) + 4H^+(aq)$ $\quad E^\circ_{cell} = 1.637\ V$



Oxidation: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $\quad -E^\circ = -1.229\ V$

Reduction: $(2e^- + F_2(g) \rightarrow 2F^-(aq)) \times 2$ $\quad E^\circ = 2.866\ V$

Net: $2F_2(g) + 2H_2O(l) \rightarrow 4F^-(aq) + O_2(g) + 4H^+(aq)$ $\quad E^\circ_{cell} = 1.637\ V$



9.4 The Nernst Equation

? Exercise 9.E.11

What are the ΔG° for the reactions below?

a. $Ti(s) + Cr^{2+}(aq) \rightarrow Ti^{2+}(aq) + Cr(s)$
b. $2Cu^{+}(aq) + Sn^{4+}(aq) \rightarrow 2Cu^{2+}(aq) + Sn^{2+}(aq)$
c. $2Cl_2(g) + 2H_2O(l) \rightarrow O_2(g) + 4H^{+}(aq) + 4Cl^{-}(aq)$

Answer

Oxidation: $Ti(s) \rightarrow Ti^{2+}(aq) + 2e^{-} \qquad -E^\circ = +1.63\ V$

Reduction: $Cr^{2+}(aq) + 2e^{-} \rightarrow Cr(s) \qquad E^\circ = -0.90\ V$

Net: $Ti(s) + Cr^{2+}(aq) \rightarrow Ti^{2+}(aq) + Cr(s) \quad E^\circ_{cell} = 0.73\ V$

$\Delta G^\circ = -nFE^\circ_{cell} = -(2\ mole\ e^{-})(96,485\ C/mol\ e^{-})(0.73\ V) = -140,868.1\ J = -1.41 \times 10^2\ KJ$

Oxidation: $Sn^{2+}(aq) \rightarrow 2e^{-} + Sn^{4+}(aq) \qquad -E^\circ = -0.154\ V$

Reduction: $(Cl_2(g) + 2e^{-} \rightarrow 2Cl^{-}(aq)) \times 2 \qquad E^\circ = 1.358$

Net: $2Cl_2(g) + 2H_2O(l) \rightarrow O_2(g) + 4H^{+}(aq) + 4Cl^{-}(aq) \quad E^\circ_{cell} = 0.129\ V$

$\Delta G^\circ = -nFE^\circ_{cell} = -(4\ mole\ e^{-})(96,485\ C/mol\ e^{-})(0.129\ V) = -49,786.26\ J = -4.98 \times 10^4\ KJ$

Reduction: $(Cu^{2+}(aq) + e^{-} \rightarrow Cu^{+}(aq)) \times 2 \qquad E^\circ = 0.159\ V$

Net: $2Cu^{+}(aq) + Sn^{4+}(aq) \rightarrow 2Cu^{2+}(aq) + Sn^{2+}(aq) \quad E^\circ_{cell} = 0.005\ V$

$\Delta G^\circ = -nFE^\circ_{cell} = -(2\ mole\ e^{-})(96,485\ C/mol\ e^{-})(0.005\ V) = -946.85\ J = -0.965\ KJ$

Oxidation: $2H_2O(l) \rightarrow O_2(g) + 4H^{+}(aq) + 4e^{-} \qquad -E^\circ = -1.229\ V$

? Exercise 9.E.12

Find E°, ΔG°, K, and given that the reactants and products are in their standard state, if they go to completion or not for the following reaction:

$$2BrO_3^{-}(aq) + 12H^{+}(aq) + 10SO_4^{2-}(aq) \rightarrow 5S_2O_8^{2-}(aq) + Br_2(l) + 6H_2O(l)$$

Answer

Oxidation: $(2SO_4^{2-}(aq) \rightarrow S_2O_8^{2-}(aq) + 2e^{-}) \times 5 \qquad -E^\circ = -2.01\ V$

Reduction: $2BrO_3^{-}(aq) + 12H^{+}(aq) + 10e^{-} \rightarrow Br_2(l) + 6H_2O(l) \qquad E^\circ = 1.478\ V$

Net: $2BrO_3^{-}(aq) + 12H^{+}(aq) + 10SO_4^{2-}(aq) \rightarrow 5S_2O_8^{2-}(aq) + Br_2(l) + 6H_2O(l) \quad E^\circ_{cell} = -0.532\ V$

$\Delta G^\circ = -nFE^\circ_{cell} = -(10\ mole\ e^{-})(96,485\ C/mol\ e^{-})(-0.532\ V) = 5.13 \times 10^2\ KJ/mol$

$\Delta G^\circ = -RT \ln K$

$5.13 \times 10^2\ KJ/mol = -(-8.314\ KJ/mol)(298.15\ K) \ln K$

$K = 8.13 \times 10^{-1}$

Since K is small (< 1) the reaction will not go to completion.

? Exercise 9.E.13

A voltaic cell has an E_{cell} value of 1.536 V. What is the concentration of Ag^{+} in the cell?

$$Zn(s)|Zn^{2+}(2.00\ M)||Ag^{+}(x\ M)|Ag(s)$$

Answer

First, determine E°_{cell}:

Oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-} \qquad E^\circ = -0.763\ V$

Reduction: $2Ag^{+}(aq) + 2e^{-} \rightarrow Ag(s) \qquad E^\circ = 0.800\ V$

Net Reaction: $Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + Ag(s) \quad E^\circ_{cell} = 1.563\ V$

Second, use Nernst equation to calculate $[Ag^+]$

$$E = E^\circ_{cell} - \frac{0.0592}{n}\log\frac{[Zn^{2+}]}{[Ag^+]^2}$$
$$1.536 = 1.563 - \frac{0.0592}{2}\log\frac{2}{x^2}$$
$$-0.027\left(\frac{-2}{0.0592}\right) = \log\frac{2}{x^2}$$
$$8.168 = \frac{2}{x^2}$$
$$x^2 = 0.2448$$
$$x = 0.495 = [Ag^+]$$

Exercise 9.E.14

Using the Nernst equation, find E_{cell} for the following cells:

a. $Al(s)|Al^{3+}(0.30\ M)||Fe^{2+}(1.1\ M)|Fe(s)$
b. $Co(s)|Co^{2+}(0.6\ M)||Fe^{3+}(1.0\ M), Fe^{2+}(0.9\ M)|Pt(s)$

Answer

First, determine E°_{cell}

Oxidation: $2Al(s) \rightarrow 2Al^{3+}(aq) + 6e^- \quad E^\circ_{cell} = 1.676\ V$
Reduction: $3Fe^{3+}(aq) + 6e^- \rightarrow 3Fe(s) \quad E^\circ_{cell} = -0.440\ V$
Net Reaction: $2Al(s) + 3Fe^{2+}(1.1\ M) \rightarrow 2Al^{3+}(0.30\ M) + 3Fe(s) \quad E^\circ_{cell} = 1.236\ V$

Second, use Nernst equation to calculate E_{cell}

$$E_{cell} = E^\circ_{cell} - \frac{0.0592}{n}\log\frac{[Al^{3+}]^2}{[Fe^{2+}]^3}$$
$$E_{cell} = 1.236 - \frac{0.0592}{6}\log\frac{(0.3)^2}{(1.1)^3}$$
$$E_{cell} = 1.247$$

First, determine E°_{cell}

Oxidation: $Co(s) \rightarrow Co^{2+}(aq) + 2e^- \quad -E^\circ_{cell} = 0.277\ V$
Reduction: $2Fe^{3+}(aq) + 2e^- \rightarrow 2Fe^{2+}(aq) \quad E^\circ_{cell} = 0.771$
Net Reaction: $Co(s) + 2Fe^{3+}(1.0\ M) \rightarrow Co^{2+}(0.6\ M) + 2Fe^{2+}(0.9\ M) \quad E^\circ_{cell} = 1.048\ V$

Second, use Nernst equation to calculate E_{cell}

$$E_{cell} = E^\circ_{cell} - \frac{0.0592}{n}\log\frac{[Fe^{2+}]^2[Co^{2+}]}{[Fe^{3+}]^2}$$
$$E_{cell} = 1.048 - \frac{0.0592}{2}\log\frac{(0.9)^2(0.6)}{(1.0)^2}$$
$$E_{cell} = 1.057\ V$$

Exercise 9.E.15

If $[Cu^{2+}]$ is maintained at 1.0 M, what is the minimum $[Ag^+]$ for which the reaction given below, is spontaneous in the forward direction?

$$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s) \tag{9.E.22}$$

Answer

Remember - in order for the reaction to be spontaneous, $\Delta G < 0$.

Important equations:

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$
$$0 = E^\circ - \frac{RT}{nF}\ln Q \Rightarrow E^\circ = \frac{RT}{nF}\ln Q$$
$$Q = [Cu^{2+}/Ag^+]$$

Write the equation as a cell diagram:

$Cu(s)|Cu^{2+}(aq)||Ag^+(aq)|Ag(s)$
Oxidation: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^- \quad E^\circ = -0.340$
Reduction: $(Ag^+(aq) + e^- \rightarrow Ag(s)) \times 2 \quad E^\circ = 0.800$
Net reaction: $Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$
$E^\circ_{cell} = 0.800 - 0.340 = 0.46\ V$

$$0.46 = \frac{RT}{2F}\ln\frac{[1]}{[Ag^+]}$$
$$0.46 = \frac{RT}{2F}(\ln 1 - \ln[Ag^+])$$
$$0.46 = -\frac{RT}{2F}\ln[Ag^+]$$
$$0.46 = -\frac{(8.3145)(298)}{2(96485)}\ln[Ag^+]$$
Solve for $[Ag^+]$
$[Ag^+] = 2.76 \times 10^{-16}\ M$

Exercise 9.E.16

Determine the anode and cathode of the following reactions. Then, calculate the reaction's equilibrium constant, K.

a. $Ca^{2+}(aq) + 2\,Li(s) \rightarrow Ca(s) + 2\,Li^+(aq)$
b. $H_2SO_3(aq) + 4\,H^+(aq) + 4\,[Fe(CN)_6]^{4-}(aq) \rightarrow S(s) + 3\,H_2O(l) + 4\,[Fe(CN)_6]^{3-}$

Answer

Cathode: $Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$ $\quad E^\circ = -2.84\ V$
Anode: $2Li(s) \rightarrow 2Li^+(aq) + 2e^-$ $\quad E^\circ = -3.040\ V$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} \tag{9.E.23}$$
$$= -2.84 - (3.040) \tag{9.E.24}$$
$$= 0.2\ V \tag{9.E.25}$$

$$E^\circ_{cell} = \frac{0.026\ V}{n}\ln K$$
$$0.2\ V = \frac{0.026\ V}{2}\ln K$$
$$\ln K = 15.38$$
$$K = 4.8 \times 10^6$$

Cathode: $H_2SO_3(aq) + 4\,H^+(aq) + 4\,e^- \rightarrow S(s) + 3\,H_2O(l)$ $\quad E^\circ = +0.449\ V$
Anode: $4\,[Fe(CN)_6]^{4-}(aq) \rightarrow 4\,[Fe(CN)_6]^{3-}(aq) + 4\,e^-$ $\quad E^\circ = +0.361\ V$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} \tag{9.E.26}$$
$$= 0.449 - 0.361 \tag{9.E.27}$$
$$= 0.088\ V \tag{9.E.28}$$

$$E^\circ_{cell} = \frac{0.026\ V}{n}\ln K$$
$$0.088\ V = \frac{0.026\ V}{4}\ln K$$
$$\ln K = 13.54$$
$$K = 7.6 \times 10^5$$

Exercise 9.E.17

Solve for E_{cell} of the following voltaic cell

$$Cu(s)|Cu^{2+}(0.01\ M)||Cu^{2+}(0.1\ M)|Cu(s)$$

Answer

First solve for E°_{cell}

Oxidation: $Cu(s) \rightarrow Cu^{2+} + 2e^-$ $\quad E^\circ = -0.340$

Reduction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $\quad E^\circ = +0.340$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$
$0.340 - (-0.340) = 0.68$

Then use the Nernst Equation to solve for E_{cell}

$$E_{cell} = E^\circ_{cell} - \frac{0.0257}{2}\ln Q \tag{9.E.29}$$
$$= 0.68 - \frac{0.0257}{2}\ln\frac{0.01\ M}{0.1\ M} \tag{9.E.30}$$
$$E_{cell} = 0.7096\ V \tag{9.E.31}$$

Exercise 9.E.18

a. Determine if the cell reaction for the following cell will proceed spontaneously in the forward direction.

$$\mathrm{Pb(s)|Pb^{2+}(1.00\ M)||Cu^{2+}(1.00\ M)|Cu(s)}$$

b. By using the Nernst equation, $\frac{-0.0592}{2}\log\frac{[\mathrm{Pb^{2+}}]}{[\mathrm{Cu^{2+}}]}$ must be greater than what value in order to make the reaction non-spontaneous?

Answer

Determine $\mathrm{E^\circ_{cell}}$

Oxidation: $\mathrm{Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-}$	$\mathrm{E^\circ_{cell} = -0.125\ V}$
Reduction: $\mathrm{Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)}$	$\mathrm{E^\circ_{cell} = 0.340\ V}$
Net Reaction: $\mathrm{Pb(s) + Cu^{2+}(1.00\ M) \rightarrow Pb^{2+}(1.00\ M) + Cu(s)}$	$\mathrm{E^\circ_{cell} = 0.465\ V}$

$\mathrm{E^\circ_{cell}}$ is positive, therefore the cell reaction for the cell will proceed spontaneously in the forward direction.

$$\frac{-0.0592}{2}\log\frac{[\mathrm{Pb^{2+}}]}{[\mathrm{Cu^{2+}}]} > 0.465$$

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9.S: Electrochemistry (Study Guide)

9.1 Balancing Oxidation – Reduction reactions

Redox reactions are defined by changes in reactant oxidation numbers, and those most relevant to electrochemistry involve actual transfer of electrons. Aqueous phase redox processes often involve water or its characteristic ions, H^+ and OH^-, as reactants in addition to the oxidant and reductant, and equations representing these reactions can be challenging to balance. The half-reaction method is a systematic approach to balancing such equations that involves separate treatment of the oxidation and reduction half-reactions.

- Oxidation-Reduction (redox) processes - net movement of electrons from one reactant to another
- Oxidizing agent – accepts electrons and is reduced
- Reducing agent – loses electrons and is oxidized
- To balance a redox reaction
  - split into **half reactions**
  - balance mass
  - balance electrons

9.2 Galvanic Cells

Galvanic cells are devices in which a spontaneous redox reaction occurs indirectly, with the oxidant and reductant redox couples contained in separate half-cells. Electrons are transferred from the reductant (in the anode half-cell) to the oxidant (in the cathode half-cell) through an external circuit, and inert solution phase ions are transferred between half-cells, through a salt bridge, to maintain charge neutrality. The construction and composition of a galvanic cell may be succinctly represented using chemical formulas and others symbols in the form of a cell schematic (cell notation).

- redox reaction does **electrical work,** pushing electrons through an external circuit connecting the physically **separated** half-cells
- Oxidation at negative anode
- Reduction at positive cathode
- **Conventions:**
  - **oxidation** half-reaction at the **-ve** anode
  - **reduction** half-reaction at the **+ve** cathode
  - electron flow from anode (**-ve**) to cathode (**+ve**)
  - solid electrodes may be **active** (Zn, Cu) or **inactive** (graphite, platinum)
  - porous disc or salt bridge required
- Shorthand notation can be used to describe cells. A vertical line, $|$, denotes a phase boundary and a double line, $\|$, the salt bridge. Information about the anode is written to the left, followed by the anode solution, then the salt bridge (when present), then the cathode solution, and, finally, information about the cathode to the right.

9.3 Standard Reduction Potentials

The property of potential, E, is the energy associated with the separation/transfer of charge. In electrochemistry, the potentials of cells and half-cells are thermodynamic quantities that reflect the driving force or the spontaneity of their redox processes. The cell potential of an electrochemical cell is the difference in between its cathode and anode. To permit easy sharing of half-cell potential data, the standard hydrogen electrode (SHE) is assigned a potential of exactly 0 V and used to define a single electrode potential for any given half-cell. The electrode potential of a half-cell, E_X, is the cell potential of said half-cell acting as a cathode when connected to a SHE acting as an anode. When the half-cell is operating under standard state conditions, its potential is the standard electrode potential, $E°_X$. Standard electrode potentials reflect the relative oxidizing strength of the half-reaction's reactant, with stronger oxidants exhibiting larger (more positive) $E°_X$ values. Tabulations of standard electrode potentials may be used to compute standard cell potentials, $E°_{cell}$, for many redox reactions. The arithmetic sign of a cell potential indicates the spontaneity of the cell reaction, with positive values for spontaneous reactions and negative values for nonspontaneous reactions (spontaneous in the reverse direction).

- The standard hydrogen electrode (SHE) is chosen as the zero and all other half-cells are compared to it

- The standard reduction potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. The minus sign is needed because oxidation is the reverse of reduction.

  $E^o_{cell} = E^o_{cathode} - E^o_{anode}$

- E_{cell} measured in SI unit: **volts (V)**
- for a spontaneous reaction E_{cell} is +ve

9.4 Nernst Equation

Potential is a thermodynamic quantity reflecting the intrinsic driving force of a redox process, and it is directly related to the free energy change and equilibrium constant for the process. For redox processes taking place in electrochemical cells, the maximum (electrical) work done by the system is easily computed from the cell potential and the reaction stoichiometry and is equal to the free energy change for the process. The equilibrium constant for a redox reaction is logarithmically related to the reaction's cell potential, with larger (more positive) potentials indicating reactions with greater driving force that equilibrate when the reaction has proceeded far towards completion (large value of *K*). Finally, the potential of a redox process varies with the composition of the reaction mixture, being related to the reactions standard potential and the value of its reaction quotient, *Q*, as described by the Nernst equation.

- spontaneous reactions, which have ΔG<0, must have Ecell>0

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

$$\Delta G^\circ = -RT\ln K$$

So

$$E^\circ_{\text{cell}} = \frac{RT}{nF}\ln K$$

at standard temperature (298.15 K)

$$\begin{aligned} E^\circ_{\text{cell}} &= \frac{RT}{nF}\ln K \\ &= \frac{0.0257\ \text{V}}{n}\ln K \end{aligned}$$

or

$$E^\circ_{\text{cell}} = \frac{0.0592\ \text{V}}{n}\log K$$

The common form we use is

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF}\ln Q \tag{9.S.1}$$

which for reactions occuring at 25 °C (298.15 K) becomes

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0257\ \text{V}}{n}\ln Q \tag{9.S.2}$$

or

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592\ \text{V}}{n}\log_{10} Q \tag{9.S.3}$$

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Glossary

Sample Word 1 | Sample Definition 1

Accuracy | how closely a measurement aligns with a correct value

Acid anhydride | compound that reacts with water to form an acid or acidic solution

Acid ionization | reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

Acid ionization constant (K_a) | equilibrium constant for the ionization of a weak acid

Acid-base indicator | organic acid or base whose color changes depending on the pH of the solution it is in

Acidic | describes a solution in which [H3O+]>[OH−][H3O+]>[OH−]

Actinide | inner transition metal in the bottom of the bottom two rows of the periodic table

Actinide series | (also, actinoid series) actinium and the elements in the second row or the *f*-block, atomic numbers 89–103

Activated complex | (also, transition state) unstable combination of reactant species representing the highest energy state of a reaction system

Activation energy (E_a) | energy necessary in order for a reaction to take place

Active electrode | electrode that participates in the oxidation-reduction reaction of an electrochemical cell; the mass of an active electrode changes during the oxidation-reduction reaction

Actual yield | amount of product formed in a reaction

Addition reaction | reaction in which a double carbon-carbon bond forms a single carbon-carbon bond by the addition of a reactant. Typical reaction for an alkene.

Adhesive force | force of attraction between molecules of different chemical identities

Alcohol | organic compound with a hydroxyl group (–OH) bonded to a carbon atom

Alkali metal | element in group 1

Alkaline earth metal | element in group 2

Alkaline earth metal | any of the metals (beryllium, magnesium, calcium, strontium, barium, and radium) occupying group 2 of the periodic table; they are reactive, divalent metals that form basic oxides

Alkane | molecule consisting of only carbon and hydrogen atoms connected by single (σ) bonds

Alkene | molecule consisting of carbon and hydrogen containing at least one carbon-carbon double bond

Alkyl group | substituent, consisting of an alkane missing one hydrogen atom, attached to a larger structure

Alkyne | molecule consisting of carbon and hydrogen containing at least one carbon-carbon triple bond

Allotropes | two or more forms of the same element, in the same physical state, with different chemical structures

Alloy | solid mixture of a metallic element and one or more additional elements

Alpha (α) decay | loss of an alpha particle during radioactive decay

Alpha particle | (α or He24He24 or α24α24) high-energy helium nucleus; a helium atom that has lost two electrons and contains two protons and two neutrons

Alpha particle (α particle) | positively charged particle consisting of two protons and two neutrons

Amide | organic molecule that features a nitrogen atom connected to the carbon atom in a carbonyl group

Amine | organic molecule in which a nitrogen atom is bonded to one or more alkyl group

Amorphous | solid material such as a glass that does not have a regular repeating component to its three-dimensional structure; a solid but not a crystal

Amorphous solid | (also, noncrystalline solid) solid in which the particles lack an ordered internal structure

Amphiphilic | molecules possessing both hydrophobic (nonpolar) and a hydrophilic (polar) parts

Amphiprotic | species that may either gain or lose a proton in a reaction

Amphoteric | species that can act as either an acid or a base

Amplitude | extent of the displacement caused by a wave (for sinusoidal waves, it is one-half the difference from the peak height to the trough depth, and the intensity is proportional to the square of the amplitude)

Analyte | chemical species of interest

Angular momentum quantum number (*l*) | quantum number distinguishing the different shapes of orbitals; it is also a measure of the orbital angular momentum

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

Anode | electrode in an electrochemical cell at which oxidation occurs; information about the anode is recorded on the left side of the salt bridge in cell notation

Antimatter | particles with the same mass but opposite properties (such as charge) of ordinary particles

Aqueous solution | solution for which water is the solvent

Aromatic hydrocarbon | cyclic molecule consisting of carbon and hydrogen with delocalized alternating carbon-carbon single and double bonds, resulting in enhanced stability

Arrhenius equation | mathematical relationship between the rate constant and the activation energy of a reaction

Atmosphere (atm) | unit of pressure; 1 atm = 101,325 Pa

Atom | smallest particle of an element that can enter into a chemical combination

Atomic mass | average mass of atoms of an element, expressed in amu

Atomic mass unit (amu) | (also, unified atomic mass unit, u, or Dalton, Da) unit of mass equal to 112112 of the mass of a ^{12}C atom

Atomic number (Z) | number of protons in the nucleus of an atom

Atomic orbital | mathematical function that describes the behavior of an electron in an atom (also called the wavefunction), it can be used to find the probability of locating an electron in a specific region around the nucleus, as well as other dynamical variables

Aufbau principle | procedure in which the electron configuration of the elements is determined by "building" them in order of atomic numbers, adding one proton to the nucleus and one electron to the proper subshell at a time

Autoionization | reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

Average rate | rate of a chemical reaction computed as the ratio of a measured change in amount or concentration of substance to the time interval over which the change occurred

Avogadro's number (N_A) | experimentally determined value of the number of entities comprising 1 mole of substance, equal to $6.022 \times 10^{23}\ mol^{-1}$

Axial position | location in a trigonal bipyramidal geometry in which there is another atom at a 180° angle and the equatorial positions are at a 90° angle

Balanced equation | chemical equation with equal numbers of atoms for each element in the reactant and product

Band of stability | (also, belt of stability, zone of stability, or valley of stability) region of graph of number of protons versus number of neutrons containing stable (nonradioactive) nuclides

Bar | (bar or b) unit of pressure; 1 bar = 100,000 Pa

Barometer | device used to measure atmospheric pressure

Base anhydride | metal oxide that behaves as a base towards acids

Base ionization | reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

Base ionization constant (K_b) | equilibrium constant for the ionization of a weak base

Basic | describes a solution in which $[H_3O^+] < [OH^-]$

Becquerel (Bq) | SI unit for rate of radioactive decay; 1 Bq = 1 disintegration/s

Beta (β) decay | breakdown of a neutron into a proton, which remains in the nucleus, and an electron, which is emitted as a beta particle

Beta particle | (ββ or e−10e−10 or β−10β−10) high-energy electron

Bicarbonate anion | salt of the hydrogen carbonate ion, HCO−3HCO3−

Bidentate ligand | ligand that coordinates to one central metal through coordinate bonds from two different atoms

Binary acid | compound that contains hydrogen and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H^+ ions when dissolved in water)

Binary compound | compound containing two different elements.

Binding energy per nucleon | total binding energy for the nucleus divided by the number of nucleons in the nucleus

Bismuth | heaviest member of group 15; a less reactive metal than other representative metals

Blackbody | idealized perfect absorber of all incident electromagnetic radiation; such bodies emit electromagnetic radiation in characteristic continuous spectra called blackbody radiation

Body-centered cubic (BCC) solid | crystalline structure that has a cubic unit cell with lattice points at the corners and in the center of the cell

Body-centered cubic unit cell | simplest repeating unit of a body-centered cubic crystal; it is a cube containing lattice points at each corner and in the center of the cube

Bohr's model of the hydrogen atom | structural model in which an electron moves around the nucleus only in circular orbits, each with a specific allowed radius; the orbiting electron does not normally emit electromagnetic radiation, but does so when changing from one orbit to another.

Boiling point | temperature at which the vapor pressure of a liquid equals the pressure of the gas above it

Boiling point elevation | elevation of the boiling point of a liquid by addition of a solute

Boiling point elevation constant | the proportionality constant in the equation relating boiling point elevation to solute molality; also known as the ebullioscopic constant

Bomb calorimeter | device designed to measure the energy change for processes occurring under conditions of constant volume; commonly used for reactions involving solid and gaseous reactants or products

Bond angle | angle between any two covalent bonds that share a common atom

Bond dipole moment | separation of charge in a bond that depends on the difference in electronegativity and the bond distance represented by partial charges or a vector

Bond distance | (also, bond length) distance between the nuclei of two bonded atoms

Bond energy | (also, bond dissociation energy) energy required to break a covalent bond in a gaseous substance

Bond length | distance between the nuclei of two bonded atoms at which the lowest potential energy is achieved

Borate | compound containing boron-oxygen bonds, typically with clusters or chains as a part of the chemical structure

Born-Haber cycle | thermochemical cycle relating the various energetic steps involved in the formation of an ionic solid from the relevant elements

Bragg equation | equation that relates the angles at which X-rays are diffracted by the atoms within a crystal

Brønsted-Lowry acid | proton donor

Brønsted-Lowry base | proton acceptor

Buffer | mixture of a weak acid or a weak base and the salt of its conjugate; the pH of a buffer resists change when small amounts of acid or base are added

Buffer capacity | amount of an acid or base that can be added to a volume of a buffer solution before its pH changes significantly (usually by one pH unit)

Buret | device used for the precise delivery of variable liquid volumes, such as in a titration analysis

Calorie (cal) | unit of heat or other energy; the amount of energy required to raise 1 gram of water by 1 degree Celsius; 1 cal is defined as 4.184 J

Calorimeter | device used to measure the amount of heat absorbed or released in a chemical or physical process

Calorimetry | process of measuring the amount of heat involved in a chemical or physical process

Capillary action | flow of liquid within a porous material due to the attraction of the liquid molecules to the surface of the material and to other liquid molecules

Carbonate | salt of the anion $CO2−3CO32−$; often formed by the reaction of carbon dioxide with bases

Catalyst | substance that increases the rate of a reaction without itself being consumed by the reaction

Cathode | electrode in an electrochemical cell at which reduction occurs; information about the cathode is recorded on the right side of the salt bridge in cell notation

Cathodic protection | method of protecting metal by using a sacrificial anode and effectively making the metal that needs protecting the cathode, thus preventing its oxidation

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

Cell notation | shorthand way to represent the reactions in an electrochemical cell

Cell potential | difference in electrical potential that arises when dissimilar metals are connected; the driving force for the flow of charge (current) in oxidation-reduction reactions

Celsius (°C) | unit of temperature; water freezes at 0 °C and boils at 100 °C on this scale

Central metal | ion or atom to which one or more ligands is attached through coordinate covalent bonds

Chain reaction | repeated fission caused when the neutrons released in fission bombard other atoms

Chalcogen | element in group 16

Chelate | complex formed from a polydentate ligand attached to a central metal

Chelating ligand | ligand that attaches to a central metal ion by bonds from two or more donor atoms

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

Chemical equation | symbolic representation of a chemical reaction

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

Chemical reduction | method of preparing a representative metal using a reducing agent

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

Chemical thermodynamics | area of science that deals with the relationships between heat, work, and all forms of energy associated with chemical and physical processes

Chemistry | study of the composition, properties, and interactions of matter

Chemotherapy | similar to internal radiation therapy, but chemical rather than radioactive substances are introduced into the body to kill cancer cells

Chlor-alkali process | electrolysis process for the synthesis of chlorine and sodium hydroxide

Circuit | path taken by a current as it flows because of an electrical potential difference

***cis* configuration** | configuration of a geometrical isomer in which two similar groups are on the same side of an imaginary reference line on the molecule

Clausius-Clapeyron equation | mathematical relationship between the temperature, vapor pressure, and enthalpy of vaporization for a substance

Coefficient | number placed in front of symbols or formulas in a chemical equation to indicate their relative amount

Cohesive force | force of attraction between identical molecules

Colligative property | property of a solution that depends only on the concentration of a solute species

Collision theory | model that emphasizes the energy and orientation of molecular collisions to explain and predict reaction kinetics

Colloid | (also, colloidal dispersion) mixture in which relatively large solid or liquid particles are dispersed uniformly throughout a gas, liquid, or solid

Color-change interval | range in pH over which the color change of an indicator takes place

Combustion analysis | gravimetric technique used to determine the elemental composition of a compound via the collection and weighing of its gaseous combustion products

Common ion effect | effect on equilibrium when a substance with an ion in common with the dissolved species is added to the solution; causes a decrease in the solubility of an ionic species, or a decrease in the ionization of a weak acid or base

Complete ionic equation | chemical equation in which all dissolved ionic reactants and products, including spectator ions, are explicitly represented by formulas for their dissociated ions

Compound | pure substance that can be decomposed into two or more elements

Compressibility factor (Z) | ratio of the experimentally measured molar volume for a gas to its molar volume as computed from the ideal gas equation

Concentrated | qualitative term for a solution containing solute at a relatively high concentration

Concentration | quantitative measure of the relative amounts of solute and solvent present in a solution

Concentration cell | galvanic cell in which the two half-cells are the same except for the concentration of the solutes; spontaneous when the overall reaction is the dilution of the solute

Condensation | change from a gaseous to a liquid state

Conjugate acid | substance formed when a base gains a proton

Conjugate base | substance formed when an acid loses a proton

Containment system | (also, shield) a three-part structure of materials that protects the exterior of a nuclear fission reactor and operating personnel from the high temperatures, pressures, and radiation levels inside the reactor

Continuous spectrum | electromagnetic radiation given off in an unbroken series of wavelengths (e.g., white light from the sun)

Control rod | material inserted into the fuel assembly that absorbs neutrons and can be raised or lowered to adjust the rate of a fission reaction

Coordination compound | stable compound in which the central metal atom or ion acts as a Lewis acid and accepts one or more pairs of electrons

Coordination compound | substance consisting of atoms, molecules, or ions attached to a central atom through Lewis acid-base interactions

Coordination number | number of atoms closest to any given atom in a crystal or to the central metal atom in a complex

Coordination number | number of coordinate covalent bonds to the central metal atom in a complex or the number of closest contacts to an atom in a crystalline form

Coordination sphere | central metal atom or ion plus the attached ligands of a complex

Core electron | electron in an atom that occupies the orbitals of the inner shells

Corrosion | degradation of metal through an electrochemical process

Covalent bond | attractive force between the nuclei of a molecule's atoms and pairs of electrons between the atoms

Covalent bond | bond formed when electrons are shared between atoms

Covalent compound | (also, molecular compound) composed of molecules formed by atoms of two or more different elements

Covalent network solid | solid whose particles are held together by covalent bonds

Covalent radius | one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond

Crenation | process whereby biological cells become shriveled due to loss of water by osmosis

Critical mass | amount of fissionable material that will support a self-sustaining (nuclear fission) chain reaction

Critical point | temperature and pressure above which a gas cannot be condensed into a liquid

Crystal field splitting (Δ_{oct}) | difference in energy between the t_{2g} and e_g sets or t and e sets of orbitals

Crystal field theory | model that explains the energies of the orbitals in transition metals in terms of electrostatic interactions with the ligands but does not include metal ligand bonding

Crystalline solid | solid in which the particles are arranged in a definite repeating pattern

Cubic centimeter (cm^3 or cc) | volume of a cube with an edge length of exactly 1 cm

Cubic closest packing (CCP) | crystalline structure in which planes of closely packed atoms or ions are stacked as a series of three alternating layers of different relative orientations (ABC)

Cubic meter (m^3) | SI unit of volume

Curie (Ci) | larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s

Current | flow of electrical charge; the SI unit of charge is the coulomb (C) and current is measured in amperes (1A=1Cs) (1A=1Cs)

***d* orbital** | region of space with high electron density that is either four lobed or contains a dumbbell and torus shape; describes orbitals with $l = 2$. An electron in this orbital is called a *d* electron

***d*-block element** | one of the elements in groups 3–11 with valence electrons in *d* orbitals

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

Dalton's atomic theory | set of postulates that established the fundamental properties of atoms

Daughter nuclide | nuclide produced by the radioactive decay of another nuclide; may be stable or may decay further

Density | ratio of mass to volume for a substance or object

Deposition | change from a gaseous state directly to a solid state

Diffraction | redirection of electromagnetic radiation that occurs

when it encounters a physical barrier of appropriate dimensions

Dilute | qualitative term for a solution containing solute at a relatively low concentration

Dilution | process of adding solvent to a solution in order to lower the concentration of solutes

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

Dipole moment | property of a molecule that describes the separation of charge determined by the sum of the individual bond moments based on the molecular structure

Dipole-dipole attraction | intermolecular attraction between two permanent dipoles

Diprotic acid | acid containing two ionizable hydrogen atoms per molecule. A diprotic acid ionizes in two steps

Diprotic base | base capable of accepting two protons. The protons are accepted in two steps

Dispersed phase | substance present as relatively large solid or liquid particles in a colloid

Dispersion force | (also, London dispersion force) attraction between two rapidly fluctuating, temporary dipoles; significant only when particles are very close together

Dispersion medium | solid, liquid, or gas in which colloidal particles are dispersed

Disproportionation reaction | chemical reaction where a single reactant is simultaneously reduced and oxidized; it is both the reducing agent and the oxidizing agent

Dissociation | physical process accompanying the dissolution of an ionic compound in which the compound's constituent ions are solvated and dispersed throughout the solution

Dissolved | describes the process by which solute components are dispersed in a solvent

Donor atom | atom in a ligand with a lone pair of electrons that forms a coordinate covalent bond to a central metal

Double bond | covalent bond in which two pairs of electrons are shared between two atoms

Downs cell | electrochemical cell used for the commercial preparation of metallic sodium (and chlorine) from molten sodium chloride

Dynamic equilibrium | state of a system in which reciprocal processes are occurring at equal rates

Effective nuclear charge | charge that leads to the Coulomb force exerted by the nucleus on an electron, calculated as the nuclear charge minus shielding

e_g orbitals | set of two *d* orbitals that are oriented on the Cartesian axes for coordination complexes; in octahedral complexes, they are higher in energy than the t_{2g} orbitals

Electrical potential | energy per charge; in electrochemical systems, it depends on the way the charges are distributed within the system; the SI unit of electrical potential is the volt (1V=1JC)(1V=1JC)

Electrical work (w_{ele}) | negative of total charge times the cell potential; equal to w_{max} for the system, and so equals the free energy change (ΔG)

Electrolyte | substance that produces ions when dissolved in water

Electromagnetic radiation | energy transmitted by waves that have an electric-field component and a magnetic-field component

Electromagnetic spectrum | range of energies that electromagnetic radiation can comprise, including radio, microwaves, infrared, visible, ultraviolet, X-rays, and gamma rays; since electromagnetic radiation energy is proportional to the frequency and inversely proportional to the wavelength, the spectrum can also be specified by ranges of frequencies or wavelengths

Electron | negatively charged, subatomic particle of relatively low mass located outside the nucleus

Electron affinity | energy required to add an electron to a gaseous atom to form an anion

Electron capture | combination of a core electron with a proton to yield a neutron within the nucleus

Electron configuration | electronic structure of an atom in its ground state given as a listing of the orbitals occupied by the electrons

Electron density | a measure of the probability of locating an electron in a particular region of space, it is equal to the squared absolute value of the wave function ψ

Electron volt (eV) | measurement unit of nuclear binding energies, with 1 eV equaling the amount energy due to the moving an electron across an electric potential difference of 1 volt

Electron-pair geometry | arrangement around a central atom of all regions of electron density (bonds, lone pairs, or unpaired electrons)

Electronegativity | tendency of an atom to attract electrons in a bond to itself

Element | substance that is composed of a single type of atom; a substance that cannot be decomposed by a chemical change

Empirical formula | formula showing the composition of a compound given as the simplest whole-number ratio of atoms

Empirical formula mass | sum of average atomic masses for all atoms represented in an empirical formula

Emulsifying agent | amphiphilic substance used to stabilize the particles of some emulsions

Emulsion | colloid formed from immiscible liquids

End point | measured volume of titrant solution that yields the change in sample solution appearance or other property expected for stoichiometric equivalence (see *equivalence point*)

Endothermic process | chemical reaction or physical change that absorbs heat

Energy | capacity to supply heat or do work

Enthalpy (*H*) | sum of a system's internal energy and the mathematical product of its pressure and volume

Enthalpy change (Δ*H*) | heat released or absorbed by a system under constant pressure during a chemical or physical process

Entropy (*S*) | state function that is a measure of the matter and/or energy dispersal within a system, determined by the number of system microstates often described as a measure of the disorder of the system

Equatorial position | one of the three positions in a trigonal bipyramidal geometry with 120° angles between them; the axial positions are located at a 90° angle

Equilibrium | in chemical reactions, the state in which the conversion of reactants into products and the conversion of products back into reactants occur simultaneously at the same rate; state of balance

Equilibrium constant (*K*) | value of the reaction quotient for a system at equilibrium

Equivalence point | volume of titrant solution required to react completely with the analyte in a titration analysis; provides a stoichiometric amount of titrant for the sample's analyte according to the titration reaction

Ether | organic compound with an oxygen atom that is bonded to two carbon atoms

Exact number | number derived by counting or by definition

Excess reactant | reactant present in an amount greater than required by the reaction stoichiometry

Excited state | state having an energy greater than the ground-state energy

Exothermic process | chemical reaction or physical change that releases heat

Expansion work (pressure-volume work) | work done as a system expands or contracts against external pressure

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

External beam radiation therapy | radiation delivered by a machine outside the body

***f* orbital** | multilobed region of space with high electron density, describes orbitals with $l = 3$. An electron in this orbital is called an *f* electron

***f*-block element** | (also, inner transition element) one of the elements with atomic numbers 58–71 or 90–103 that have valence electrons in *f* orbitals; they are frequently shown offset below the periodic table

Face-centered cubic (FCC) solid | crystalline structure consisting of a cubic unit cell with lattice points on the corners and in the center of each face

Face-centered cubic unit cell | simplest repeating unit of a face-centered cubic crystal; it is a cube containing lattice points at each corner and in the center of each face

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

Faraday's constant (F) | charge on 1 mol of electrons; $F = 96{,}485$ C/mol e^-

First law of thermodynamics | internal energy of a system changes due to heat flow in or out of the system or work done on or by the system

First transition series | transition elements in the fourth period of the periodic table (first row of the *d*-block), atomic numbers 21–29

Fissile (or fissionable) | when a material is capable of sustaining a nuclear fission reaction

Fission | splitting of a heavier nucleus into two or more lighter nuclei, usually accompanied by the conversion of mass into large amounts of energy

Formal charge | charge that would result on an atom by taking the number of valence electrons on the neutral atom and subtracting the nonbonding electrons and the number of bonds (one-half of the bonding electrons)

Formula mass | sum of the average masses for all atoms represented in a chemical formula; for covalent compounds, this is also the molecular mass

Fourth transition series | transition elements in the seventh period of the periodic table (fourth row of the *d*-block), atomic numbers 89 and 104–111

Frasch process | important in the mining of free sulfur from enormous underground deposits

Free radical | molecule that contains an odd number of electrons

Freezing | change from a liquid state to a solid state

Freezing point | temperature at which the solid and liquid phases of a substance are in equilibrium; see also *melting point*

Freezing point depression | lowering of the freezing point of a liquid by addition of a solute

Freezing point depression constant | (also, cryoscopic constant) proportionality constant in the equation relating freezing point depression to solute molality

Frequency (νν) | number of wave cycles (peaks or troughs) that pass a specified point in space per unit time

Frequency factor (*A*) | proportionality constant in the Arrhenius equation, related to the relative number of collisions having an orientation capable of leading to product formation

Functional group | part of an organic molecule that imparts a specific chemical reactivity to the molecule

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

Fusion | combination of very light nuclei into heavier nuclei, accompanied by the conversion of mass into large amounts of energy

Fusion reactor | nuclear reactor in which fusion reactions of light nuclei are controlled

Galvanic cell | electrochemical cell that involves a spontaneous oxidation-reduction reaction; electrochemical cells with positive cell potentials; also called a voltaic cell

Galvanized iron | method for protecting iron by covering it with zinc, which will oxidize before the iron; zinc-plated iron

Gamma (γ) emission | decay of an excited-state nuclide accompanied by emission of a gamma ray

Gamma ray | (γ or γ00γ00) short wavelength, high-energy electromagnetic radiation that exhibits wave-particle duality

Gas | state in which matter has neither definite volume nor shape

Geiger counter | instrument that detects and measures radiation via the ionization produced in a Geiger-Müller tube

Gel | colloidal dispersion of a liquid in a solid

Geometric isomers | isomers that differ in the way in which atoms are oriented in space relative to each other, leading to different physical and chemical properties

Gibbs free energy change (*G*) | thermodynamic property defined in terms of system enthalpy and entropy; all spontaneous processes involve a decrease in *G*

Gravimetric analysis | quantitative chemical analysis method involving the separation of an analyte from a sample by a physical or chemical process and subsequent mass measurements of the analyte, reaction product, and/or sample

Gray (Gy) | SI unit for measuring radiation dose; 1 Gy = 1 J absorbed/kg tissue

Ground state | state in which the electrons in an atom, ion, or molecule have the lowest energy possible

Group | vertical column of the periodic table

Haber process | main industrial process used to produce ammonia from nitrogen and hydrogen; involves the use of an iron catalyst and elevated temperatures and pressures

Half-life ($t_{1/2}$) | time required for half of the atoms in a radioactive sample to decay

Half-life of a reaction ($t_{1/2}$) | time required for half of a given amount of reactant to be consumed

Half-reaction method | method that produces a balanced overall oxidation-reduction reaction by splitting the reaction into an oxidation "half" and reduction "half," balancing the two half-reactions, and then combining the oxidation half-reaction and reduction half-reaction in such a way that the number of electrons generated by the oxidation is exactly canceled by the number of electrons required by the reduction

Halide | compound containing an anion of a group 17 element in the 1− oxidation state (fluoride, F^-; chloride, Cl^-; bromide, Br^-; and iodide, I^-)

Hall–Héroult cell | electrolysis apparatus used to isolate pure aluminum metal from a solution of alumina in molten cryolite

Halogen | element in group 17

Heat (*q*) | transfer of thermal energy between two bodies

Heat capacity (*C*) | extensive property of a body of matter that represents the quantity of heat required to increase its temperature by 1 degree Celsius (or 1 kelvin)

Heisenberg uncertainty principle | rule stating that it is impossible to exactly determine both certain conjugate dynamical properties such as the momentum and the position of a particle at the same time. The uncertainty principle is a consequence of quantum particles exhibiting wave–particle duality

Hemolysis | rupture of red blood cells due to the accumulation of excess water by osmosis

Henderson-Hasselbalch equation | equation used to calculate the pH of buffer solutions

Henry's law | law stating the proportional relationship between the concentration of dissolved gas in a solution and the partial pressure of the gas in contact with the solution

Hertz (Hz) | the unit of frequency, which is the number of cycles per second, s^{-1}

Hess's law | if a process can be represented as the sum of several steps, the enthalpy change of the process equals the sum of the enthalpy changes of the steps

Heterogeneous catalyst | catalyst present in a different phase from the reactants, furnishing a surface at which a reaction can occur

Heterogeneous equilibria | equilibria between reactants and products in different phases

Heterogeneous mixture | combination of substances with a composition that varies from point to point

Hexagonal closest packing (HCP) | crystalline structure in which close packed layers of atoms or ions are stacked as a series of two alternating layers of different relative orientations (AB)

High-spin complex | complex in which the electrons maximize the total electron spin by singly populating all of the orbitals before pairing two electrons into the lower-energy orbitals

Hole | (also, interstice) space between atoms within a crystal

Homogeneous catalyst | catalyst present in the same phase as the reactants

Homogeneous equilibria | equilibria within a single phase

Homogeneous mixture | (also, solution) combination of substances with a composition that is uniform throughout

Hund's rule | every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin

Hydrocarbon | compound composed only of hydrogen and carbon; the major component of fossil fuels

Hydrogen bonding | occurs when exceptionally strong dipoles attract; bonding that exists when hydrogen is bonded to one of the three most electronegative elements: F, O, or N

Hydrogen carbonate | salt of carbonic acid, H_2CO_3 (containing the anion HCO−3HCO3−) in which one hydrogen atom has been replaced; an acid carbonate; also known as *bicarbonate ion*

Hydrogen halide | binary compound formed between hydrogen and the halogens: HF, HCl, HBr, and HI

Hydrogen sulfate | HSO−4HSO4− ion

Hydrogen sulfite | HSO−3HSO3− ion

Hydrogenation | addition of hydrogen (H_2) to reduce a compound

Hydrometallurgy | process in which a metal is separated from a mixture by first converting it into soluble ions, extracting the ions, and then reducing the ions to precipitate the pure metal

Hydrostatic pressure | pressure exerted by a fluid due to gravity

Hydroxide | compound of a metal with the hydroxide ion OH^- or the group −OH

Hypertonic | of greater osmotic pressure

Hypervalent molecule | molecule containing at least one main group element that has more than eight electrons in its valence shell

Hypothesis | tentative explanation of observations that acts as a guide for gathering and checking information

Hypotonic | of less osmotic pressure

Ideal solution | solution that forms with no accompanying energy change

Immiscible | of negligible mutual solubility; typically refers to liquid substances

Indicator | substance added to the sample in a titration analysis to permit visual detection of the end point

Induced dipole | temporary dipole formed when the electrons of an atom or molecule are distorted by the instantaneous dipole of a neighboring atom or molecule

Inert electrode | electrode that allows current to flow, but that does not otherwise participate in the oxidation-reduction reaction in an electrochemical cell; the mass of an inert electrode does not change during the oxidation-reduction reaction; inert electrodes are often made of platinum or gold because these metals are chemically unreactive.

Inert gas | (also, noble gas) element in group 18

Inert pair effect | tendency of heavy atoms to form ions in which their valence *s* electrons are not lost

Initial rate | instantaneous rate of a chemical reaction at $t = 0$ s (immediately after the reaction has begun)

Inner transition metal | (also, lanthanide or actinide) element in the bottom two rows; if in the first row, also called lanthanide, or if in the second row, also called actinide

Instantaneous dipole | temporary dipole that occurs for a brief moment in time when the electrons of an atom or molecule are distributed asymmetrically

Instantaneous rate | rate of a chemical reaction at any instant in time, determined by the slope of the line tangential to a graph of concentration as a function of time

Integrated rate law | equation that relates the concentration of a reactant to elapsed time of reaction

Intensity | property of wave-propagated energy related to the amplitude of the wave, such as brightness of light or loudness of sound

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

Interference pattern | pattern typically consisting of alternating bright and dark fringes; it results from constructive and destructive interference of waves

Interhalogen | compound formed from two or more different halogens

Intermolecular force | noncovalent attractive force between atoms, molecules, and/or ions

Internal energy (U) | total of all possible kinds of energy present in a substance or substances

Internal radiation therapy | (also, brachytherapy) radiation from a radioactive substance introduced into the body to kill cancer cells

Interstitial sites | spaces between the regular particle positions in any array of atoms or ions

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

Ion pair | solvated anion/cation pair held together by moderate electrostatic attraction

Ion-dipole attraction | electrostatic attraction between an ion and a polar molecule

Ion-product constant for water (K_w) | equilibrium constant for the autoionization of water

Ionic bond | electrostatic forces of attraction between the oppositely charged ions of an ionic compound

Ionic bond | strong electrostatic force of attraction between cations and anions in an ionic compound

Ionic compound | compound composed of cations and anions combined in ratios, yielding an electrically neutral substance

Ionic solid | solid composed of positive and negative ions held together by strong electrostatic attractions

Ionization energy | energy required to remove an electron from a gaseous atom or ion. The associated number (e.g., second ionization energy) corresponds to the charge of the ion produced (X^{2+})

Ionization isomer | (or coordination isomer) isomer in which an anionic ligand is replaced by the counter ion in the inner coordination sphere

Ionizing radiation | radiation that can cause a molecule to lose an electron and form an ion

Isoelectronic | group of ions or atoms that have identical electron configurations

Isomers | compounds with the same chemical formula but different structures

Isomorphous | possessing the same crystalline structure

Isotonic | of equal osmotic pressure

Isotopes | atoms that contain the same number of protons but different numbers of neutrons

Joule (J) | SI unit of energy; 1 joule is the kinetic energy of an object with a mass of 2 kilograms moving with a velocity of 1 meter per second, 1 J = 1 kg m^2/s and 4.184 J = 1 cal

K_c | equilibrium constant for reactions based on concentrations of reactants and products

Kelvin (K) | SI unit of temperature; 273.15 K = 0 ºC

Kilogram (kg) | standard SI unit of mass; 1 kg = approximately 2.2 pounds

Kinetic energy | energy of a moving body, in joules, equal to 12mv212mv2 (where m = mass and v = velocity)

K_P | equilibrium constant for gas-phase reactions based on partial pressures of reactants and products

Lanthanide | inner transition metal in the top of the bottom two rows of the periodic table

Lanthanide series | (also, lanthanoid series) lanthanum and the elements in the first row or the *f*-block, atomic numbers 57–71

Lattice energy ($\Delta H_{lattice}$) | energy required to separate one mole of an ionic solid into its component gaseous ions

Law | statement that summarizes a vast number of experimental observations, and describes or predicts some aspect of the natural world

Law of conservation of matter | when matter converts from one type to another or changes form, there is no detectable change in the total amount of matter present

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

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

Law of mass action | when a reversible reaction has attained equilibrium at a given temperature, the reaction quotient remains constant

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

Le Chatelier's principle | when a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

Length | measure of one dimension of an object

Leveling effect of water | any acid stronger than H3O+H3O+, or any base stronger than OH^- will react with water to form H3O+H3O+, or OH^-, respectively; water acts as a base to make all strong acids appear equally strong, and it acts as an acid to make all strong bases appear equally strong

Lewis structure | diagram showing lone pairs and bonding pairs of electrons in a molecule or an ion

Lewis symbol | symbol for an element or monatomic ion that uses a dot to represent each valence electron in the element or ion

Ligand | ion or neutral molecule attached to the central metal ion in a coordination compound

Limiting reactant | reactant present in an amount lower than required by the reaction stoichiometry, thus limiting the amount of product generated

Line spectrum | electromagnetic radiation emitted at discrete wavelengths by a specific atom (or atoms) in an excited state

Linear | shape in which two outside groups are placed on opposite sides of a central atom

Linkage isomer | coordination compound that possesses a ligand that can bind to the transition metal in two different ways (CN^- vs. NC^-)

Liquid | state of matter that has a definite volume but indefinite shape

Liter (L) | (also, cubic decimeter) unit of volume; 1 L = 1,000 cm^3

Lone pair | two (a pair of) valence electrons that are not used to form a covalent bond

Low-spin complex | complex in which the electrons minimize the total electron spin by pairing in the lower-energy orbitals before populating the higher-energy orbitals

Macroscopic domain | realm of everyday things that are large enough to sense directly by human sight and touch

Magic number | nuclei with specific numbers of nucleons that are within the band of stability

Magnetic quantum number (m_l) | quantum number signifying the orientation of an atomic orbital around the nucleus; orbitals having different values of m_l but the same subshell value of l have the same energy (are degenerate), but this degeneracy can be removed by application of an external magnetic field

Main-group element | (also, representative element) element in columns 1, 2, and 12–18

Manometer | device used to measure the pressure of a gas trapped in a container

Mass | fundamental property indicating amount of matter

Mass defect | difference between the mass of an atom and the summed mass of its constituent subatomic particles (or the mass “lost” when nucleons are brought together to form a nucleus)

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

Mass percentage | ratio of solute-to-solution mass expressed as a percentage

Mass-energy equivalence equation | Albert Einstein's relationship showing that mass and energy are equivalent

Mass-volume percent | ratio of solute mass to solution volume, expressed as a percentage

Matter | anything that occupies space and has mass

Melting | change from a solid state to a liquid state

Melting point | temperature at which the solid and liquid phases of a substance are in equilibrium; see also *freezing point*

Metal | element that is shiny, malleable, good conductor of heat and electricity

Metal (representative) | atoms of the metallic elements of groups 1, 2, 12, 13, 14, 15, and 16, which form ionic compounds by losing electrons from their outer *s* or *p* orbitals

Metallic solid | solid composed of metal atoms

Metalloid | element that conducts heat and electricity moderately well, and possesses some properties of metals and some properties of nonmetals

Metalloid | element that has properties that are between those of metals and nonmetals; these elements are typically semiconductors

Meter (m) | standard metric and SI unit of length; 1 m = approximately 1.094 yards

Method of initial rates | use of a more explicit algebraic method to determine the orders in a rate law

Microscopic domain | realm of things that are much too small to be sensed directly

Microstate (*W*) | possible configuration or arrangement of matter and energy within a system

Millicurie (mCi) | larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s

Milliliter (mL) | 1/1,000 of a liter; equal to 1 cm^3

Miscible | mutually soluble in all proportions; typically refers to liquid substances

Mixture | matter that can be separated into its components by physical means

Molality (*m*) | a concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms

Molar mass | mass in grams of 1 mole of a substance

Molar solubility | solubility of a compound expressed in units of moles per liter (mol/L)

Molarity (*M*) | unit of concentration, defined as the number of moles of solute dissolved in 1 liter of solution

Mole | amount of substance containing the same number of atoms, molecules, ions, or other entities as the number of atoms in exactly 12 grams of ^{12}C

Molecular compound | (also, covalent compound) composed of molecules formed by atoms of two or more different elements

Molecular equation | chemical equation in which all reactants and products are represented as neutral substances

Molecular formula | formula indicating the composition of a molecule of a compound and giving the actual number of atoms of each element in a molecule of the compound.

Molecular solid | solid composed of neutral molecules held together by intermolecular forces of attraction

Molecular structure | arrangement of atoms in a molecule or ion

Molecular structure | structure that includes only the placement of the atoms in the molecule

Molecule | bonded collection of two or more atoms of the same or different elements

Monatomic ion | ion composed of a single atom

Monodentate | ligand that attaches to a central metal through just one coordinate covalent bond

Monoprotic acid | acid containing one ionizable hydrogen atom per molecule

Multiple equilibrium | system characterized by more than one state of balance between a slightly soluble ionic solid and an aqueous solution of ions working simultaneously

Nernst equation | equation that relates the logarithm of the reaction quotient (Q) to nonstandard cell potentials; can be used to relate equilibrium constants to standard cell potentials

Net ionic equation | chemical equation in which only those dissolved ionic reactants and products that undergo a chemical or physical change are represented (excludes spectator ions)

Neutral | describes a solution in which $[H_3O^+] = [OH^-]$

Neutron | uncharged, subatomic particle located in the nucleus

Nitrate | NO−3NO3− ion; salt of nitric acid

Nitrogen fixation | formation of nitrogen compounds from molecular nitrogen

Noble gas | (also, inert gas) element in group 18

Node | any point of a standing wave with zero amplitude

Node | plane separating different lobes of orbitals, where the probability of finding an electron is zero

Nomenclature | system of rules for naming objects of interest

Nonelectrolyte | substance that does not produce ions when dissolved in water

Nonionizing radiation | radiation that speeds up the movement of atoms and molecules; it is equivalent to heating a sample, but is not energetic enough to cause the ionization of molecules

Nonmetal | element that appears dull, poor conductor of heat and electricity

Nonspontaneous process | process that requires continual input of energy from an

external source

Normal boiling point | temperature at which a liquid's vapor pressure equals 1 atm (760 torr)

Nuclear binding energy | energy lost when an atom's nucleons are bound together (or the energy needed to break a nucleus into its constituent protons and neutrons)

Nuclear chemistry | study of the structure of atomic nuclei and processes that change nuclear structure

Nuclear fuel | fissionable isotope present in sufficient quantities to provide a self-sustaining chain reaction in a nuclear reactor

Nuclear moderator | substance that slows neutrons to a speed low enough to cause fission

Nuclear reaction | change to a nucleus resulting in changes in the atomic number, mass number, or energy state

Nuclear reactor | environment that produces energy via nuclear fission in which the chain reaction is controlled and sustained without explosion

Nuclear transmutation | conversion of one nuclide into another nuclide

Nucleon | collective term for protons and neutrons in a nucleus

Nucleus | massive, positively charged center of an atom made up of protons and neutrons

Nuclide | nucleus of a particular isotope

Nutritional calorie (Calorie) | unit used for quantifying energy provided by digestion of foods, defined as 1000 cal or 1 kcal

Octahedral | shape in which six outside groups are placed around a central atom such that a three-dimensional shape is generated with four groups forming a square and the other two forming the apex of two pyramids, one above and one below the square plane

Octahedral hole | open space in a crystal at the center of six particles located at the corners of an octahedron

Octet rule | guideline that states main group atoms will form structures in which eight valence electrons interact with each nucleus, counting bonding electrons as interacting with both atoms connected by the bond

Optical isomer | (also, enantiomer) molecule that is a nonsuperimposable mirror image with identical chemical and physical properties, except when it reacts with other optical isomers

Orbital diagram | pictorial representation of the electron configuration showing each orbital as a box and each electron as an arrow

Organic compound | natural or synthetic compound that contains carbon

Osmosis | diffusion of solvent molecules through a semipermeable membrane

Osmotic pressure (Π) | opposing pressure required to prevent bulk transfer of solvent molecules through a semipermeable membrane

Ostwald process | industrial process used to convert ammonia into nitric acid

Overall reaction order | sum of the reaction orders for each substance represented in the rate law

Overlap | coexistence of orbitals from two different atoms sharing the same region of space, leading to the formation of a covalent bond

Oxidation half-reaction | the "half" of an oxidation-reduction reaction involving oxidation; the half-reaction in which electrons appear as products; balanced when each atom type, as well as the charge, is balanced

Oxide | binary compound of oxygen with another element or group, typically containing O^{2-} ions or the group –O– or =O

Oxyacid | compound that contains hydrogen, oxygen, and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H^+ ions when dissolved in water)

Oxyacid | compound containing a nonmetal and one or more hydroxyl groups

Oxyanion | polyatomic anion composed of a central atom bonded to oxygen atoms

Ozone | allotrope of oxygen; O_3

***p* orbital** | dumbbell-shaped region of space with high electron density, describes orbitals with $l = 1$. An electron in this orbital is called a *p* electron

Pairing energy (P) | energy required to place two electrons with opposite spins into a single orbital

Parent nuclide | unstable nuclide that changes spontaneously into another (daughter) nuclide

Partially miscible | of moderate mutual solubility; typically refers to liquid substances

Particle accelerator | device that uses electric and magnetic fields to increase the kinetic energy of nuclei used in transmutation reactions

Parts per billion (ppb) | ratio of solute-to-solution mass multiplied by 10^9

Parts per million (ppm) | ratio of solute-to-solution mass multiplied by 10^6

Pascal (Pa) | SI unit of pressure; 1 Pa = 1 N/m^2

Passivation | metals with a protective nonreactive film of oxide or other compound that creates a barrier for chemical reactions; physical or chemical removal of the passivating film allows the metals to demonstrate their expected chemical reactivity

Pauli exclusion principle | specifies that no two electrons in an atom can have the same value for all four quantum numbers

Percent composition | percentage by mass of the various elements in a compound

Percent ionization | ratio of the concentration of the ionized acid to the initial acid concentration, times 100

Percent yield | measure of the efficiency of a reaction, expressed as a percentage of the theoretical yield

Period | (also, series) horizontal row of the periodic table

Periodic law | properties of the elements are periodic function of their atomic numbers.

Periodic table | table of the elements that places elements with similar chemical properties close together

Peroxide | molecule containing two oxygen atoms bonded together or as the anion, $O2−2O22−$

PH | logarithmic measure of the concentration of hydronium ions in a solution

Phase diagram | pressure-temperature graph summarizing conditions under which the phases of a substance can exist

Photon | smallest possible packet of electromagnetic radiation, a particle of light

Photosynthesis | process whereby light energy promotes the reaction of water and carbon dioxide to form carbohydrates and oxygen; this allows photosynthetic organisms to store energy

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

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

Pi bond (π bond) | covalent bond formed by side-by-side overlap of atomic orbitals; the electron density is found on opposite sides of the internuclear axis

Pidgeon process | chemical reduction process used to produce magnesium through the thermal reaction of magnesium oxide with silicon

Plasma | gaseous state of matter containing a large number of electrically charged atoms and/or molecules

Platinum metals | group of six transition metals consisting of ruthenium, osmium, rhodium, iridium, palladium, and platinum that tend to occur in the same minerals and demonstrate similar chemical properties

Pnictogen | element in group 15

POH | logarithmic measure of the concentration of hydroxide ions in a solution

Polar covalent bond | covalent bond between atoms of different electronegativities; a covalent bond with a positive end and a negative end

Polar molecule | (also, dipole) molecule with an overall dipole moment

Polarizability | measure of the ability of a charge to distort a molecule's charge distribution (electron cloud)

Polyatomic ion | ion composed of more than one atom

Polydentate ligand | ligand that is attached to a central metal ion by bonds from two or more donor atoms, named with prefixes specifying how many donors are present (e.g., hexadentate = six coordinate bonds formed)

Polymorph | variation in crystalline structure that results in different physical properties for the resulting compound

Position of equilibrium | concentrations or partial pressures of components of a reaction at equilibrium (commonly used to describe conditions before a disturbance)

Positron (β+10β+10 or e+10e+10) | antiparticle to the electron; it has identical properties to an electron, except for having the opposite (positive) charge

Positron emission | (also, β^+ decay) conversion of a proton into a neutron, which remains in the nucleus, and a positron, which is emitted

Potential energy | energy of a particle or system of particles derived from relative position, composition, or condition

Pounds per square inch (psi) | unit of pressure common in the US

Precision | how closely a measurement matches the same measurement when repeated

Pressure | force exerted per unit area

Principal quantum number (*n*) | quantum number specifying the shell an electron occupies in an atom

Product | substance formed by a chemical or physical change; shown on the right side of the arrow in a chemical equation

Proton | positively charged, subatomic particle located in the nucleus

Pure covalent bond | (also, nonpolar covalent bond) covalent bond between atoms of identical electronegativities

Pure substance | homogeneous substance that has a constant composition

Quantitative analysis | the determination of the amount or concentration of a substance in a sample

Quantization | occurring only in specific discrete values, not continuous

Quantum mechanics | field of study that includes quantization of energy, wave-particle duality, and the Heisenberg uncertainty principle to describe matter

Quantum number | integer number having only specific allowed values and used to characterize the arrangement of electrons in an atom

Radiation absorbed dose (rad) | SI unit for measuring radiation dose, frequently used in medical applications; 1 rad = 0.01 Gy

Radiation dosimeter | device that measures ionizing radiation and is used to determine personal radiation exposure

Radiation therapy | use of high-energy radiation to damage the DNA of cancer cells, which kills them or keeps them from dividing

Radioactive decay | spontaneous decay of an unstable nuclide into another nuclide

Radioactive decay series | chains of successive disintegrations (radioactive decays) that ultimately lead to a stable end-product

Radioactive tracer | (also, radioactive label) radioisotope used to track or follow a substance by monitoring its radioactive emissions

Radioactivity | phenomenon exhibited by an unstable nucleon that spontaneously undergoes change into a nucleon that is more stable; an unstable nucleon is said to be radioactive

Radiocarbon dating | highly accurate means of dating objects 30,000–50,000 years old that were derived from once-living matter; achieved by calculating the ratio of C614:C612C614:C612 in the object vs. the ratio of C614:C612C614:C612 in the present-day atmosphere

Radioisotope | isotope that is unstable and undergoes conversion into a different, more stable isotope

Radiometric dating | use of radioisotopes and their properties to date the formation of objects such as archeological artifacts, formerly living organisms, or geological formations

Raoult's law | the partial pressure exerted by a solution component is equal to the product of the component's mole fraction in the solution and its equilibrium vapor pressure in the pure state

Rare earth element | collection of 17 elements including the lanthanides, scandium, and yttrium that often occur together and have similar chemical properties, making separation difficult

Rate constant (*k*) | proportionality constant in the relationship between reaction rate and concentrations of reactants

Rate expression | mathematical representation relating reaction rate to changes in amount, concentration, or pressure of reactant or product species per unit time

Rate law | (also, rate equation) mathematical equation showing the dependence of reaction rate on the rate constant and the concentration of one or more reactants

Rate of reaction | measure of the speed at which a chemical reaction takes place

Reactant | substance undergoing a chemical or physical change; shown on the left side of the arrow in a chemical equation

Reaction order | value of an exponent in a rate law, expressed as an ordinal number (for example, zero order for 0, first order for 1, second order for 2, and so on)

Reaction quotient (*Q*) | ratio of the product of molar concentrations (or pressures) of the products to that of the reactants, each concentration (or pressure) being raised to the power equal to the coefficient in the equation

Reactor coolant | assembly used to carry the heat produced by fission in a reactor to an external boiler and turbine where it is transformed into electricity

Reduction half-reaction | the "half" of an oxidation-reduction reaction involving reduction; the half-reaction in which electrons appear as reactants; balanced when each atom type, as well as the charge, is balanced

Relative biological effectiveness (RBE) | measure of the relative damage done by radiation

Representative element | (also, main-group element) element in columns 1, 2, and 12–18

Representative element | element where the *s* and *p* orbitals are filling

Representative metal | metal among the representative elements

Resonance | situation in which one Lewis structure is insufficient to describe the bonding in a molecule and the average of multiple structures is observed

Resonance forms | two or more Lewis structures that have the same arrangement of atoms but different arrangements of electrons

Resonance hybrid | average of the resonance forms shown by the individual Lewis structures

Reversible process | process that takes place so slowly as to be capable of reversing direction in response to an infinitesimally small change in conditions; hypothetical construct that can only be approximated by real processes removed

Reversible reaction | chemical reaction that can proceed in both the forward and reverse directions under given conditions

Roentgen equivalent man (rem) | unit for radiation damage, frequently used in medicine; 1 rem = 1 Sv

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

***s* orbital** | spherical region of space with high electron density, describes orbitals with $l = 0$. An electron in this orbital is called an *s* electron

Sacrificial anode | more active, inexpensive metal used as the anode in cathodic protection; frequently made from magnesium or zinc

Saturated | of concentration equal to solubility; containing the maximum concentration of solute possible for a given temperature and pressure

Saturated hydrocarbon | molecule containing carbon and hydrogen that has only single bonds between carbon atoms

Scientific method | 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

Scintillation counter | instrument that uses a scintillator—a material that emits light when excited by ionizing radiation—to detect and measure radiation

Second (s) | SI unit of time

Second law of thermodynamics | entropy of the universe increases for a spontaneous process

Second transition series | transition elements in the fifth period of the periodic table (second row of the *d*-block), atomic numbers 39–47

Selective precipitation | process in which ions are separated using differences in their solubility with a given precipitating reagent

Semipermeable membrane | a membrane that selectively permits passage of certain ions or molecules

Series | (also, period) horizontal row of the period table

Shell | set of orbitals with the same principal quantum number, *n*

SI units (International System of Units) | standards fixed by international agreement in the International System of Units (*Le Système International d'Unités*)

Sievert (Sv) | SI unit measuring tissue damage caused by radiation; takes into account energy and biological effects of radiation

Sigma bond (σ bond) | covalent bond formed by overlap of atomic orbitals along the internuclear axis

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

Silicate | compound containing silicon-oxygen bonds, with silicate tetrahedra connected in rings, sheets, or three-dimensional networks, depending on the other elements involved in the formation of the compounds

Simple cubic structure | crystalline structure with a cubic unit cell with lattice points only at the corners

Simple cubic unit cell | (also, primitive cubic unit cell) unit cell in the simple cubic structure

Single bond | bond in which a single pair of electrons is shared between two atoms

Skeletal structure | shorthand method of drawing organic molecules in which carbon atoms are represented by the ends of lines and bends in between lines, and hydrogen atoms attached to the carbon atoms are not shown (but are understood to be present by the context of the structure)

Smelting | process of extracting a pure metal from a molten ore

Solid | state of matter that is rigid, has a definite shape, and has a fairly constant volume

Solubility | extent to which a solute may be dissolved in water, or any solvent

Solubility product (K_{sp}) | equilibrium constant for the dissolution of a slightly soluble electrolyte

Solute | solution component present in a concentration less than that of the solvent

Solvation | exothermic process in which intermolecular attractive forces between the solute and solvent in a solution are established

Solvent | solution component present in a concentration that is higher relative to other components

Space lattice | all points within a crystal that have identical environments

Spatial isomers | compounds in which the relative orientations of the atoms in space differ

Specific heat capacity (c) | intensive property of a substance that represents the quantity of heat required to raise the temperature of 1 gram of the substance by 1 degree Celsius (or 1 kelvin)

Spectator ion | ion that does not undergo a chemical or physical change during a reaction, but its presence is required to maintain charge neutrality

Spectrochemical series | ranking of ligands according to the magnitude of the crystal field splitting they induce

Spin quantum number (m_s) | number specifying the electron spin direction, either +12+12 or −12−12

Spontaneous change | process that takes place without a continuous input of energy from an external source

Spontaneous process | physical or chemical change that occurs without the addition of energy from an external source

Standard cell potential (E∘cell)(Ecell∘) | the cell potential when all reactants and products are in their standard states (1 bar or 1 atm or gases; 1 M for solutes), usually at 298.15 K; can be calculated by subtracting the standard reduction potential for the half-reaction at the anode from the standard reduction potential for the half-reaction occurring at the cathode

Standard enthalpy of combustion (ΔH∘cΔHc∘) | heat released when one mole of a compound undergoes complete combustion under standard conditions

Standard enthalpy of formation (ΔH∘fΔHf∘) | enthalpy change of a chemical reaction in which 1 mole of a pure substance is formed from its elements in their most stable states under standard state conditions

Standard entropy ($S°$) | entropy for a substance at 1 bar pressure; tabulated values are usually determined at 298.15 K and denoted S∘298S298∘

Standard entropy change ($\Delta S°$) | change in entropy for a reaction calculated using the standard entropies, usually at room temperature and denoted ΔS∘298ΔS298∘

Standard free energy change ($\Delta G°$) | change in free energy for a process occurring under standard conditions (1 bar pressure for gases, 1 M concentration for solutions)

Standard free energy of formation (ΔG∘f)(ΔGf∘) | change in free energy accompanying the formation of one mole of substance from its elements in their standard states

Standard hydrogen electrode (SHE) | the electrode consists of hydrogen gas bubbling through hydrochloric acid over an inert platinum electrode whose reduction at standard conditions is assigned a value of 0 V; the reference point for standard reduction potentials

Standard reduction potential ($E°$) | the value of the reduction under standard conditions (1 bar or 1 atm for gases; 1 M for solutes) usually at 298.15 K; tabulated values used to calculate standard cell potentials

Standard state | set of physical conditions as accepted as common reference conditions for reporting thermodynamic properties; 1 bar of pressure, and solutions at 1 molar concentrations, usually at a temperature of 298.15 K

Standing wave | (also, stationary wave) localized wave phenomenon characterized by discrete wavelengths determined by the boundary conditions used to generate the waves; standing waves are inherently quantized

State function | property depending only on the state of a system, and not the path taken to reach that state

Steel | material made from iron by removing impurities in the iron and adding substances that produce alloys with properties suitable for specific uses

Stepwise ionization | process in which an acid is ionized by losing protons sequentially

Stress | change to a reaction's conditions that may cause a shift in the equilibrium

Strong electrolyte | substance that dissociates or ionizes completely when dissolved in water

Strong nuclear force | force of attraction between nucleons that holds a nucleus together

Strong-field ligand | ligand that causes larger crystal field splittings

Structural formula | shows the atoms in a molecule and how they are connected

Structural isomer | one of two substances that have the same molecular formula but different physical and chemical properties because their atoms are bonded differently

Subcritical mass | amount of fissionable material that cannot sustain a chain reaction; less than a critical mass

Sublimation | change from solid state directly to gaseous state

Subshell | set of orbitals in an atom with the same values of n and l

Substituent | branch or functional group that replaces hydrogen atoms in a larger hydrocarbon chain

Substitution reaction | reaction in which one atom replaces another in a molecule

Sulfate | $SO2−4SO42−$ ion

Sulfite | $SO2−3SO32−$ ion

Superconductor | material that conducts electricity with no resistance

Supercritical fluid | substance at a temperature and pressure higher than its critical point; exhibits properties intermediate between those of gaseous and liquid states

Supercritical mass | amount of material in which there is an increasing rate of fission

Superoxide | oxide containing the anion $O−2O2−$

Supersaturated | of concentration that exceeds solubility; a nonequilibrium state

Surface tension | energy required to increase the area, or length, of a liquid surface by a given amount

Surroundings | all matter other than the system being studied

Symbolic domain | specialized language used to represent components of the macroscopic and microscopic domains, such as chemical symbols, chemical formulas, chemical equations, graphs, drawings, and calculations

System | portion of matter undergoing a chemical or physical change being studied

t_{2g} **orbitals** | set of three d orbitals aligned between the Cartesian axes for coordination complexes; in octahedral complexes, they are lowered in energy compared to the e_g orbitals according to CFT

Temperature | intensive property of matter that is a quantitative measure of “hotness” and “coldness”

Tetrahedral | shape in which four outside groups are placed around a central atom such that a three-dimensional shape is generated with four corners and 109.5° angles between each pair and the central atom

Tetrahedral hole | tetrahedral space formed by four atoms or ions in a crystal

Theoretical yield | amount of product that may be produced from a given amount of reactant(s) according to the reaction stoichiometry

Theory | well-substantiated, comprehensive, testable explanation of a particular aspect of nature

Thermal energy | kinetic energy associated with the random motion of atoms and molecules

Thermochemistry | study of measuring the amount of heat absorbed or released during a chemical reaction or a physical change

Third law of thermodynamics | entropy of a perfect crystal at absolute zero (0 K) is zero

Third transition series | transition elements in the sixth period of the periodic table (third row of the d-block), atomic numbers 57 and 72–79

Titrant | solution containing a known concentration of substance that will react with the analyte in a titration analysis

Titration analysis | quantitative chemical analysis method that involves measuring the volume of a reactant solution required to completely react with the analyte in a sample

Titration curve | plot of the pH of a solution of acid or base versus the volume of base or acid added during a titration

Torr | unit of pressure; $1torr=1760atm1torr=1760atm$

***trans* configuration** | configuration of a geometrical isomer in which two similar groups are on opposite sides of an imaginary reference line on the molecule

Transition metal | element in columns 3–11

Transmutation reaction | bombardment of one type of nuclei with other nuclei or neutrons

Transuranium element | element with an atomic number greater than 92; these elements do not occur in nature

Trigonal bipyramidal | shape in which five outside groups are placed around a central atom such that three form a flat triangle with 120° angles between each pair and the central atom, and the other two form the apex of two pyramids, one above and one below the triangular plane

Trigonal planar | shape in which three outside groups are placed in a flat triangle around a central atom with 120° angles between each pair and the central atom

Triple bond | bond in which three pairs of electrons are shared between two atoms

Triple point | temperature and pressure at which the vapor, liquid, and solid phases of a substance are in equilibrium

Triprotic acid | acid that contains three ionizable hydrogen atoms per molecule; ionization of triprotic acids occurs in three steps

Tyndall effect | scattering of visible light by a colloidal dispersion

Uncertainty | estimate of amount by which measurement differs from true value

Unified atomic mass unit (u) | alternative unit equivalent to the atomic mass unit

Unit | standard of comparison for measurements

Unit cell | smallest portion of a space lattice that is repeated in three dimensions to form the entire lattice

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

Unsaturated | of concentration less than solubility

Vacancy | defect that occurs when a position that should contain an atom or ion is vacant

Valence bond theory | description of bonding that involves atomic orbitals overlapping to form σ or π bonds, within which pairs of electrons are shared

Valence electrons | electrons in the outermost or valence shell (highest value of n) of a ground-state atom; determine how an element reacts

Valence shell | outermost shell of electrons in a ground-state atom; for main group elements, the orbitals with the highest n level (s and p subshells) are in the valence shell, while for transition metals, the highest energy s and d subshells make up the valence shell and for inner transition elements, the highest s, d, and f subshells are included

Valence shell electron-pair repulsion theory (VSEPR) | theory used to predict the bond angles in a molecule based on positioning regions of high electron density as far apart as possible to minimize electrostatic repulsion

Van der Waals equation | modified version of the ideal gas equation containing additional terms to account for non-ideal gas behavior

Van der Waals force | attractive or repulsive force between molecules, including dipole-dipole, dipole-induced dipole, and London dispersion forces; does not include forces due to covalent or ionic bonding, or the attraction between ions and molecules

Van't Hoff factor (i) | the ratio of the number of moles of particles in a solution to the number of moles of formula units dissolved in the solution

Vapor pressure | (also, equilibrium vapor pressure) pressure exerted by a vapor in equilibrium with a solid or a liquid at a given temperature

Vaporization | change from liquid state to gaseous state

Vector | quantity having magnitude and direction

Viscosity | measure of a liquid's resistance to flow

Voltaic cell | another name for a galvanic cell

Volume | amount of space occupied by an object

Volume percentage | ratio of solute-to-solution volume expressed as a percentage

Wave | oscillation that can transport energy from one point to another in space

Wave-particle duality | term used to describe the fact that elementary particles including matter exhibit properties of both particles (including localized position, momentum) and waves (including nonlocalization, wavelength, frequency)

Wavefunction (ψ) | mathematical description of an atomic orbital that describes the shape of the orbital; it can be used to calculate the probability of finding the electron at any given location in the orbital, as well as dynamical variables such as the energy and the angular momentum

Wavelength (λ) | distance between two consecutive peaks or troughs in a wave

Weak electrolyte | substance that ionizes only partially when dissolved in water

Weak-field ligand | ligand that causes small crystal field splittings

Weight | force that gravity exerts on an object

Work (w) | energy transfer due to changes in external, macroscopic variables such as pressure and volume; or causing matter to move against an opposing force

X-ray crystallography | experimental technique for determining distances between atoms in a crystal by measuring the angles at which X-rays are diffracted when passing through the crystal

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