ADVANCED GENERAL CHEMISTRYEDIT



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Advanced General Chemistry

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1.1: Introduction

Lung diseases and lung cancers are among the world's most devastating illnesses partly due to delayed detection and diagnosis. Most noninvasive screening procedures aren't reliable, and patients often resist more accurate methods due to discomfort with the procedures or with the potential danger that the procedures cause. But what if you could be accurately diagnosed through a simple breath test?

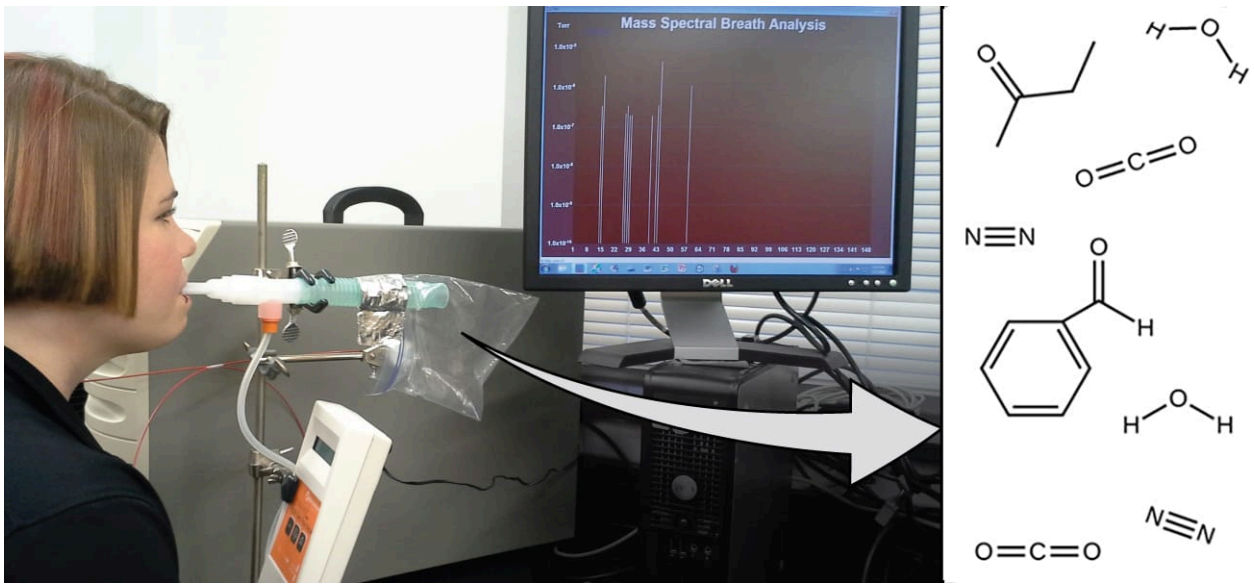


Figure 1.1.1: Analysis of molecules in an exhaled breath can provide valuable information, leading to early diagnosis of diseases or detection of environmental exposure to harmful substances. (credit: modification of work by Paul Flowers)

Early detection of biomarkers, substances that indicate an organism's disease or physiological state, could allow diagnosis and treatment before a condition becomes serious or irreversible. Recent studies have shown that your exhaled breath can contain molecules that may be biomarkers for recent exposure to environmental contaminants or for pathological conditions ranging from asthma to lung cancer. Scientists are working to develop biomarker "fingerprints" that could be used to diagnose a specific disease based on the amounts and identities of certain molecules in a patient's exhaled breath. In Sangeeta Bhatia's lab at MIT, a team used substances that react specifically inside diseased lung tissue; the products of the reactions will be present as biomarkers that can be identified through mass spectrometry (an analytical method discussed later in the chapter). A potential application would allow patients with early symptoms to inhale or ingest a "sensor" substance, and, minutes later, to breathe into a detector for diagnosis. Similar research by scientists such as Laura López-Sánchez has provided similar processes for lung cancer. 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: 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 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 1.2.1). A macroscopic sample of an element contains an incredibly large number of atoms, all of which have identical chemical properties.

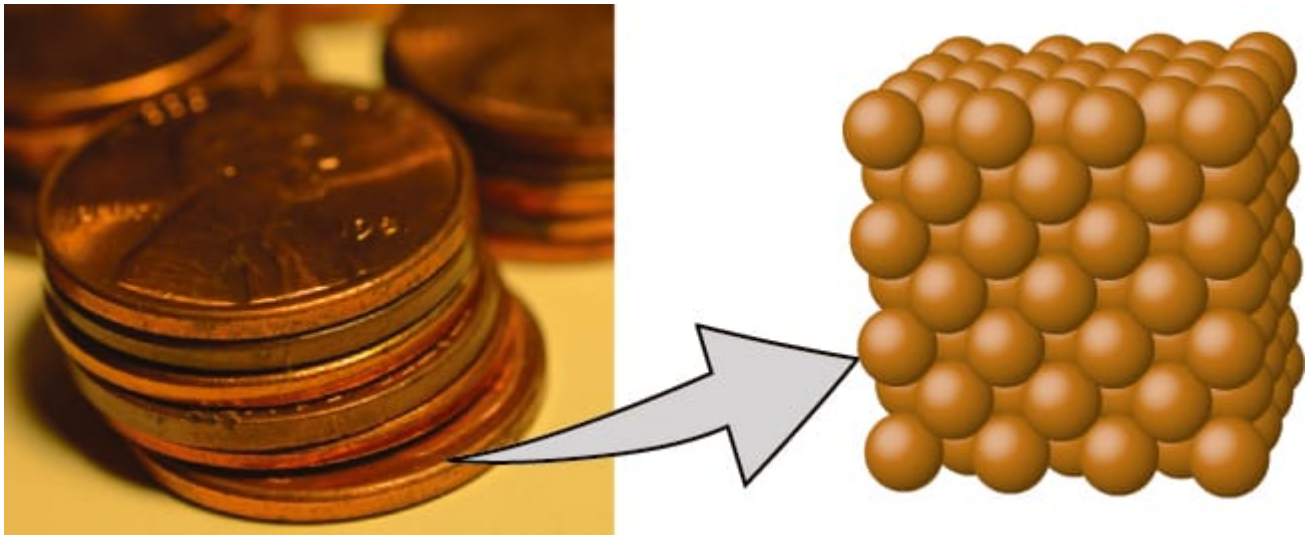


Figure 1.2.1: A pre-1982 copper penny (left) contains approximately 3×10^{22} copper atoms (several dozen are represented as brown spheres at the right), each of which has the same chemical properties. (credit: modification of work by "slgckgc"/Flickr)

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).

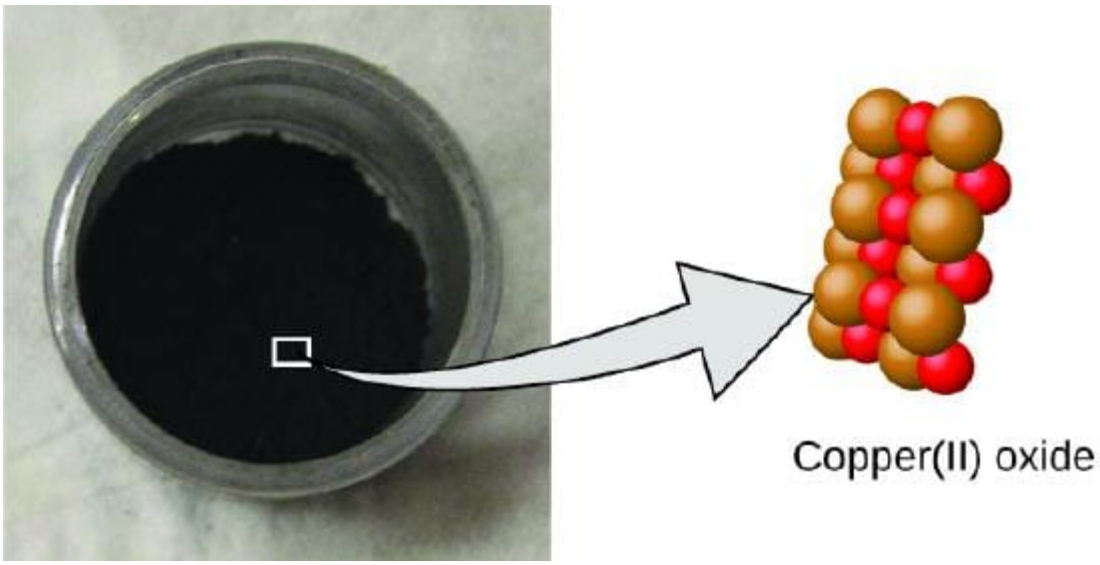


Figure 1.2.2: Copper(II) oxide, a powdery, black compound, results from the combination of two types of atoms—copper (brown spheres) and oxygen (red spheres)—in a 1:1 ratio. (credit: modification of work by "Chemicalinterest"/Wikimedia Commons)

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 1.2.3).

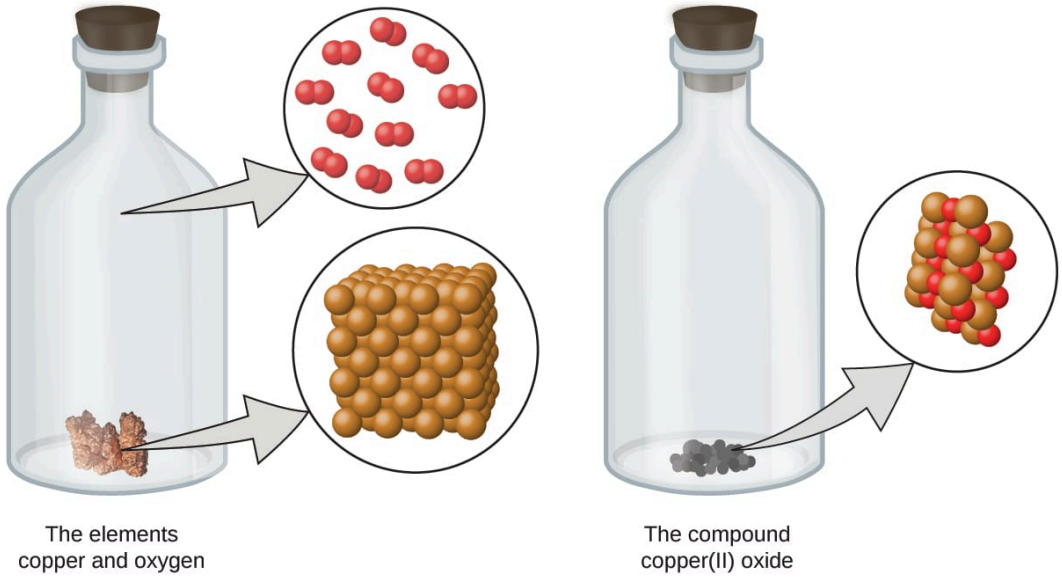


Figure 1.2.3: When the elements copper (a shiny, red-brown solid, shown here as brown spheres) and oxygen (a clear and colorless gas, shown here as red spheres) react, their atoms rearrange to form a compound containing copper and oxygen (a powdery, black solid). (credit copper: modification of work by http://images-of-elements.com/copper.php)

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 1.2.1: 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?



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 1.2.1

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?



Answer available at the end of this section.

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 1.1.

Table 1.1: Constant Composition of Isooctane

Sample	Carbon	Hydrogen	Mass Ratio
A	14.82 g	2.78 g	
B	22.33 g	4.19 g	
C	19.40 g	3.64 g	

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.

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 1.2.4).

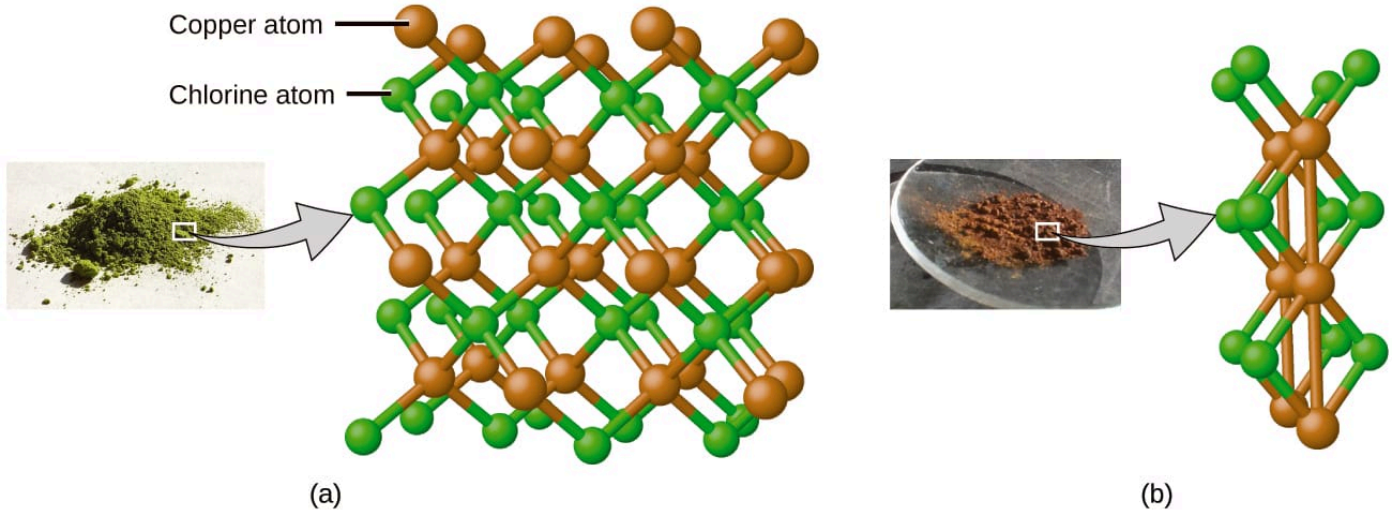


Figure 1.2.4: Compared to the copper chlorine compound in (a), where copper is represented by brown spheres and chlorine by green spheres, the copper chlorine compound in (b) has twice as many chlorine atoms per copper atom. (credit a: modification of work by "Benjah-bmm27"/Wikimedia Commons; credit b: modification of work by "Walkerma"/Wikimedia Commons)

Example 1.2.2: 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 oxygen to carbon is:

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

The ratio of these ratios is:

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

Exercise 1.2.1

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 available at the end of this section.

Answers

Exercise 1.2.1

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.

Exercise 1.2.1

In compound X, the mass ratio of carbon to hydrogen is In compound Y, the mass ratio of carbon to hydrogen is The ratio of these ratios is This small, whole-number ratio supports the law of multiple proportions. This means that X and Y are different compounds.

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1.3: Evolution of Atomic Theory

Learning Objectives

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

- 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
- Define isotopes and give examples for several elements

If matter is composed of atoms, what are atoms composed of? Are they the smallest particles, or is 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 1.3.1).

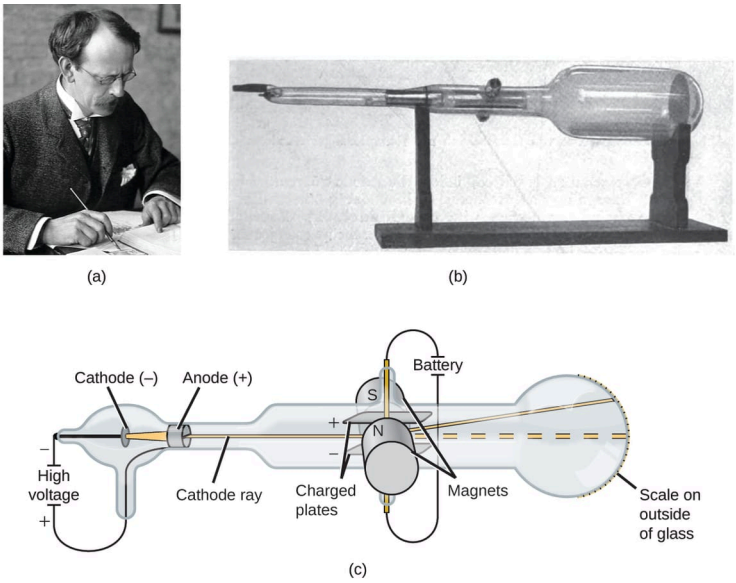


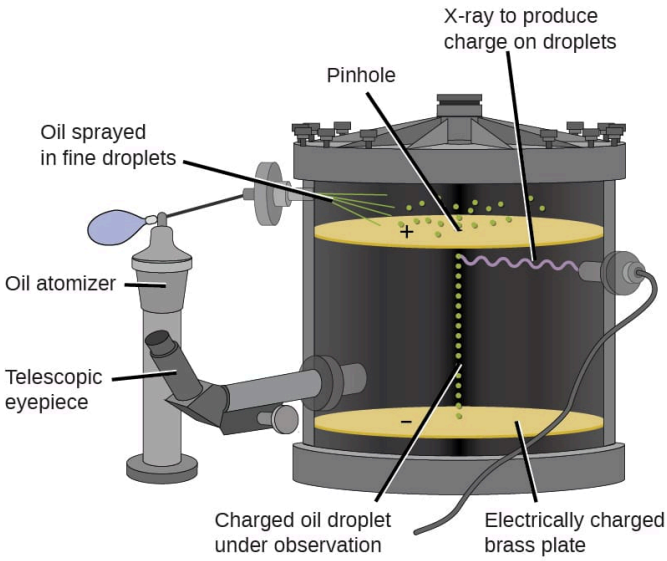
Figure 1.3.1: (a) J. J. Thomson produced a visible beam in a cathode ray tube. (b) This is an early cathode ray tube, invented in 1897 by Ferdinand Braun. (c) In the cathode ray, the beam (shown in yellow) comes from the cathode and is accelerated past the anode toward a fluorescent scale at the end 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*."

Link to Learning

Click here to hear Thomson describe his discovery in his own voice.

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 1.3.2).



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 1.3.2: 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.

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 1.3.3).

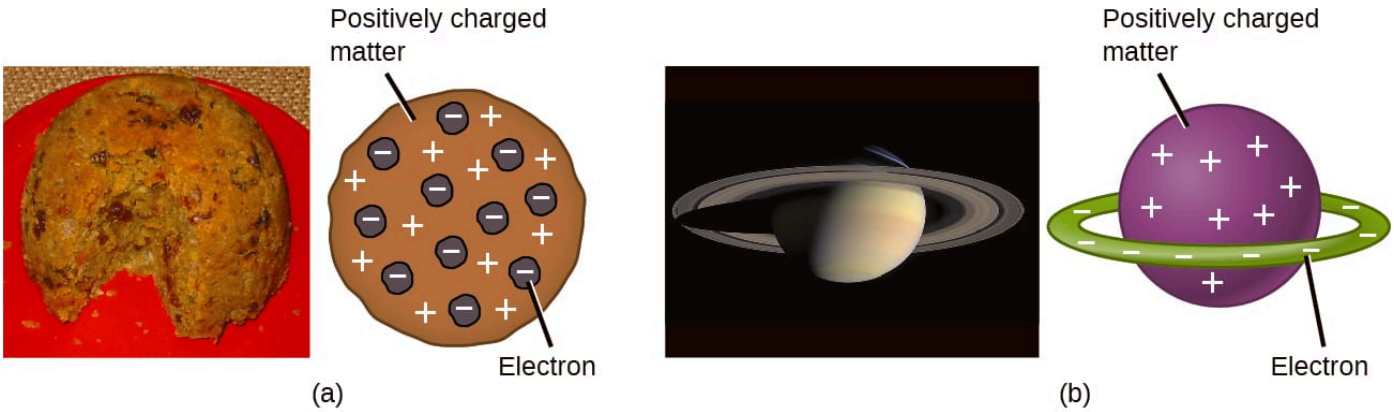


Figure 1.3.3: (a) Thomson suggested that atoms resembled plum pudding, an English dessert consisting of moist cake with embedded raisins ("plums"). (b) Nagaoka proposed that atoms resembled the planet Saturn, with a ring of electrons surrounding a positive "planet." (credit a: modification of work by "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 1.3.4). 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]

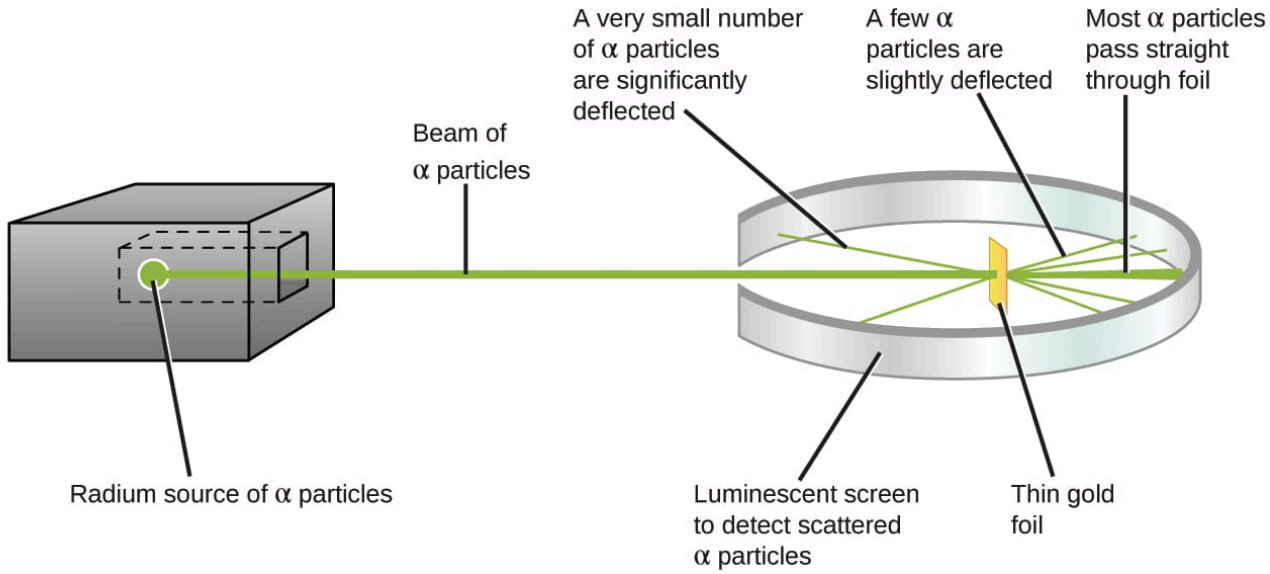


Figure 1.3.4: Geiger and Rutherford fired α particles at a piece of gold foil and detected where those particles went, as shown in this schematic diagram of their experiment. Most of the particles passed straight through the foil, but a few were deflected slightly and a very small number were significantly 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.

Link to Learning

View this simulation of the Rutherford gold foil experiment. Adjust the slit width to produce a narrower or broader beam of α particles to see how that affects the scattering pattern.

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 1.3.5). 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.

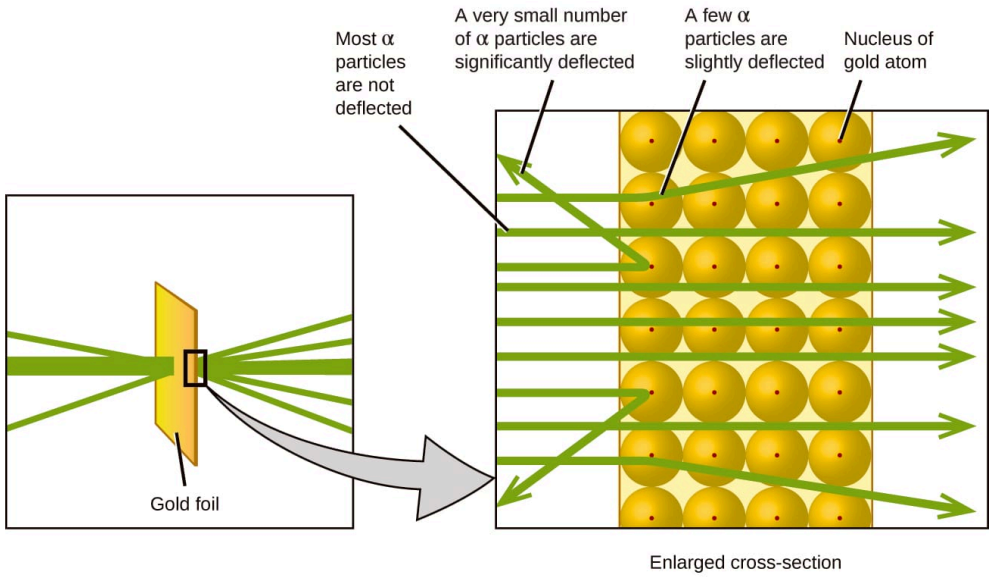


Figure 1.3.5: The α particles are deflected only when they collide with or pass close to the much heavier, positively charged gold nucleus. Because the nucleus is very small compared to the size of an atom, very few α particles are deflected. Most pass through the relatively large region occupied by electrons, which are too light to deflect the rapidly moving particles.

Link to Learning

The Rutherford Scattering simulation allows you to investigate the differences between a "plum pudding" atom and a Rutherford atom by firing α particles at each type of atom.

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.

Footnotes

- 1Ernest 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.

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1.4: 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 1.4.1).

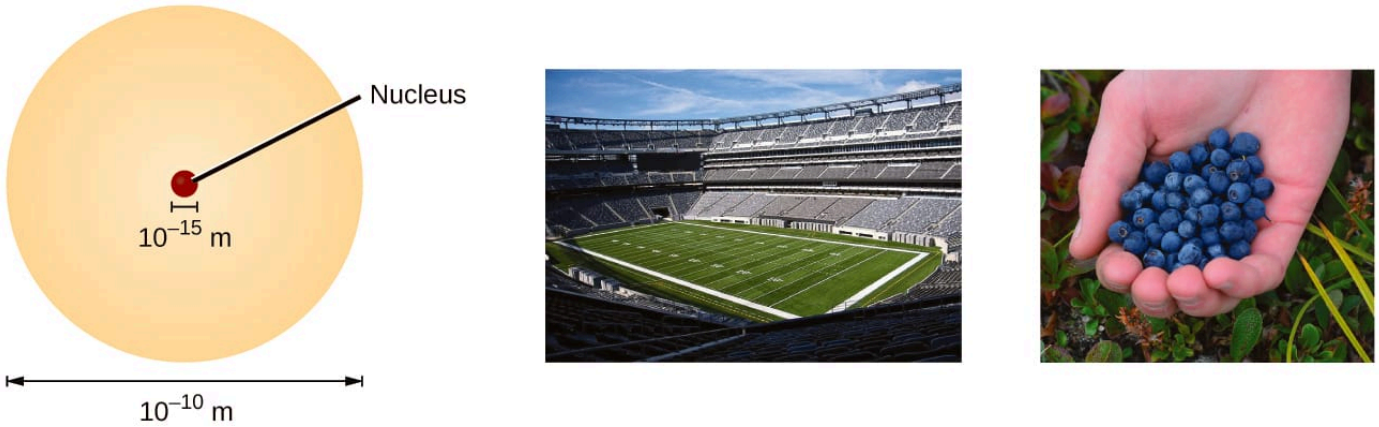


Figure 1.4.1: If an atom could be expanded to the size of a football stadium, the nucleus would be the size of a single blueberry. (credit middle: modification of work by "babyknight"/Wikimedia Commons; credit right: modification of work by Paxson Woelber).

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 1.4.1. (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 1.4.1: 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}
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 1.4.1: 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 1.4.2).

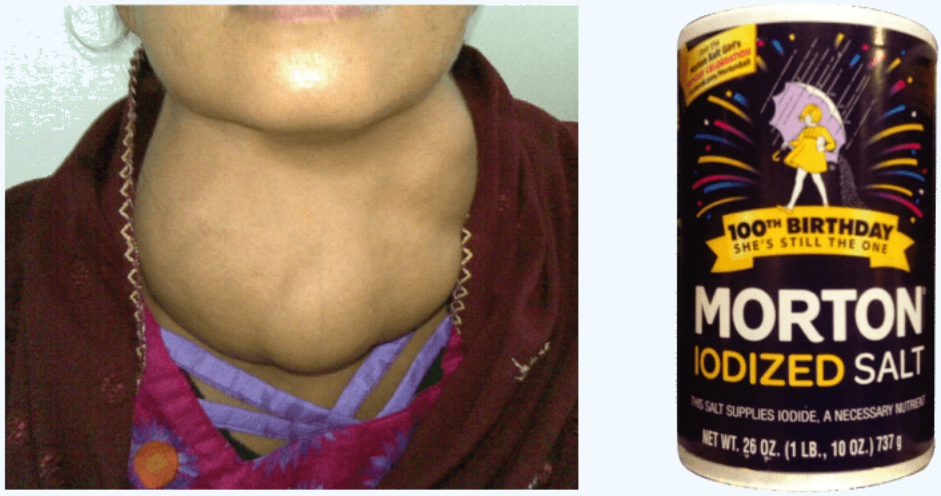


Figure 1.4.2: (a) Insufficient iodine in the diet can cause an enlargement of the thyroid gland called a goiter. (b) The addition of small amounts of iodine to salt, which prevents the formation of goiters, has helped eliminate this concern in the US where salt consumption is high. (credit a: modification 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 1.4.1

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 available at the end of this section.

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 1.4.3). 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).

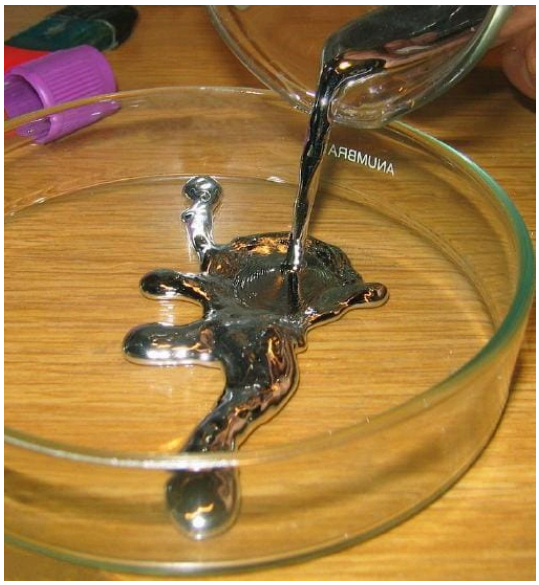


Figure 1.4.3: The symbol Hg represents the element mercury regardless of the amount; it could represent one atom of mercury or a large amount of mercury. from Wikipedia (user: Materialscientist).

The symbols for several common elements and their atoms are listed in Table 1.4.2. 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 1.4.2: 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
cobalt	Co	potassium	K (from *kalium*)
copper	Cu (from *cuprum*)	silicon	Si
fluorine	F	silver	Ag (from *argentum*)
gold	Au (from *aurum*)	sodium	Na (from *natrium*)
helium	He	sulfur	S
hydrogen	H	tin	Sn (from *stannum*)
iodine	I	zinc	Zn

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

Isotopes

The symbol for a specific isotope of any element is written by placing the mass number as a superscript to the left of the element symbol (Figure 1.4.4). 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.

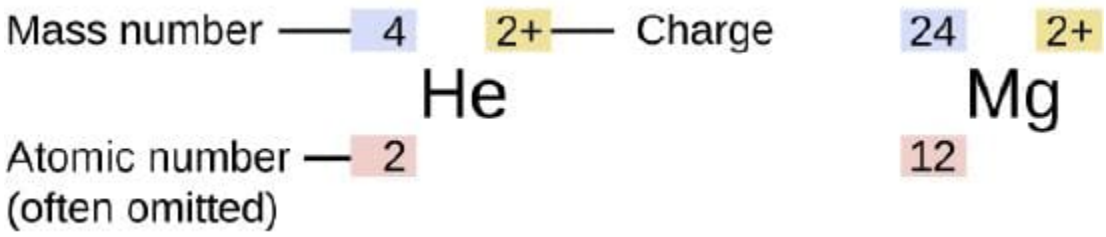


Figure 1.4.4: The symbol for an atom indicates the element via its usual two-letter symbol, the mass number as a left superscript, the atomic number as a left subscript (sometimes omitted), and the charge as a right superscript.

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 1.4.2. 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 1.4.2: 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
	$^{2}_{1}$H (deuterium)	1	1	1	2.0141	0.0115
	$^{3}_{1}$H (tritium)	1	1	2	3.01605	— (trace)
helium	$^{3}_{2}$He	2	2	1	3.01603	0.00013
	$^{4}_{2}$He	2	2	2	4.0026	100
lithium	$^{6}_{3}$Li	3	3	3	6.0151	7.59
	$^{7}_{3}$Li	3	3	4	7.0160	92.41
beryllium	$^{9}_{4}$Be	4	4	5	9.0122	100
boron	$^{10}_{5}$B	5	5	5	10.0129	19.9
	$^{11}_{5}$B	5	5	6	11.0093	80.1
carbon	$^{12}_{6}$C	6	6	6	12.0000	98.89
	$^{13}_{6}$C	6	6	7	13.0034	1.11
	$^{14}_{6}$C	6	6	8	14.0032	— (trace)

Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
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

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 1.4.2: 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 1.4.2

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 available at the end of this section.

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

Example 1.4.3: 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 1.4.3

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 available at the end of this section.

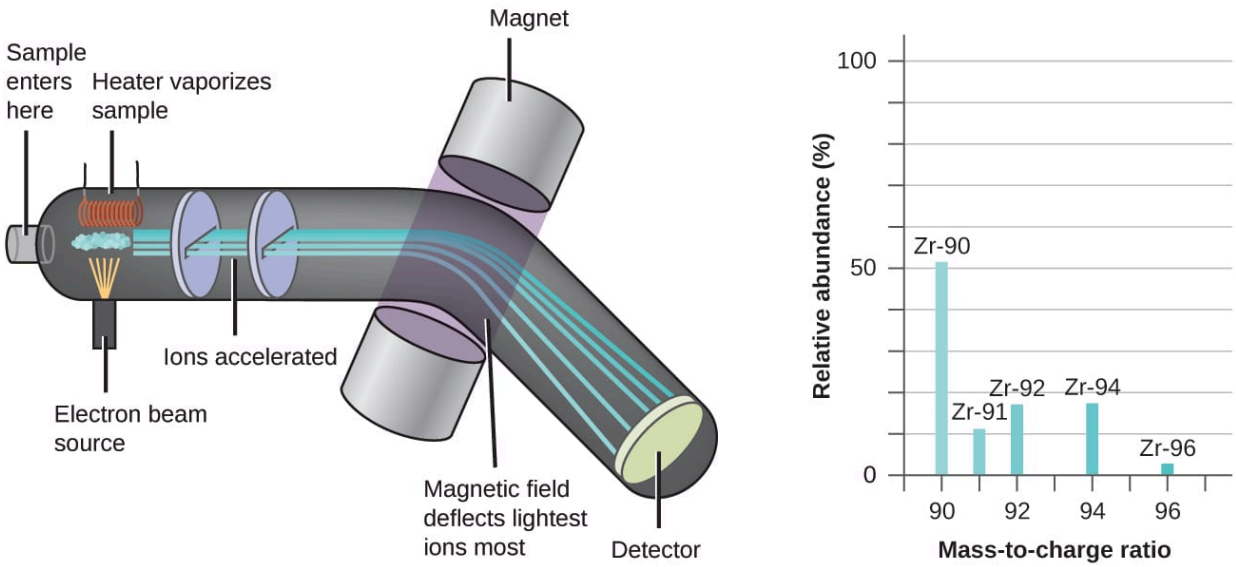


Figure 1.4.5: Analysis of zirconium in a mass spectrometer produces a mass spectrum with peaks showing the different isotopes of Zr. The left diagram shows how a mass spectrometer works. The graph to the right of the spectrometer shows a mass spectrum of zirconium. The relative abundance, as a percentage 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 1.4.5), 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.

YouTube Video

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

View this YouTube Video online

Video 1.4.1*: 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.

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).

Answers

Exercise 1.4.1

78 protons; 117 neutrons; charge is 4+

Exercise 1.4.2

24.31 amu

Exercise 1.4.3

69.15% Cu-63 and 30.85% Cu-65

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1.5: Chemical Formulas

Learning Objectives

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

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

Molecular and Empirical 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 1.16). 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.

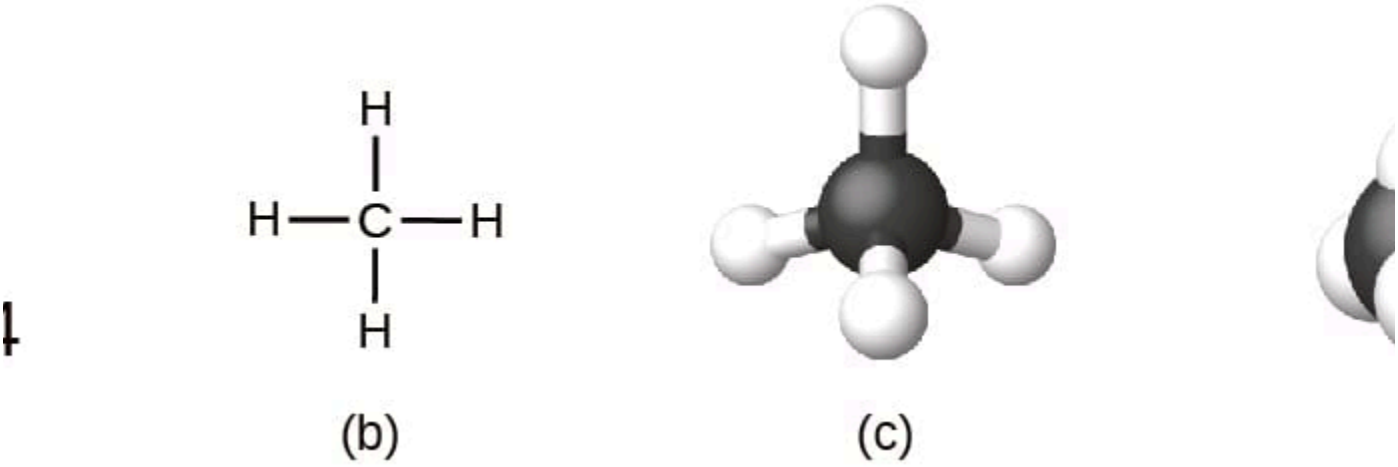


Figure 1.16 A methane molecule can be represented as (a) a molecular formula, (b) a structural formula, (c) a ball-and-stick model, and (d) a space-filling model. Carbon and hydrogen atoms are represented by black and white spheres, respectively.

Although many elements consist of discrete, individual atoms, some exist as molecules made up of two or more atoms of the element chemically bonded together. For example, most samples of the elements hydrogen, oxygen, and nitrogen are composed of molecules that contain two atoms each (called diatomic molecules) and thus have the molecular formulas H_2, O_2, and N_2, respectively. Other elements commonly found as diatomic molecules are fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2). The most common form of the element sulfur is composed of molecules that consist of eight atoms of sulfur; its molecular formula is S_8 (Figure 1.17).

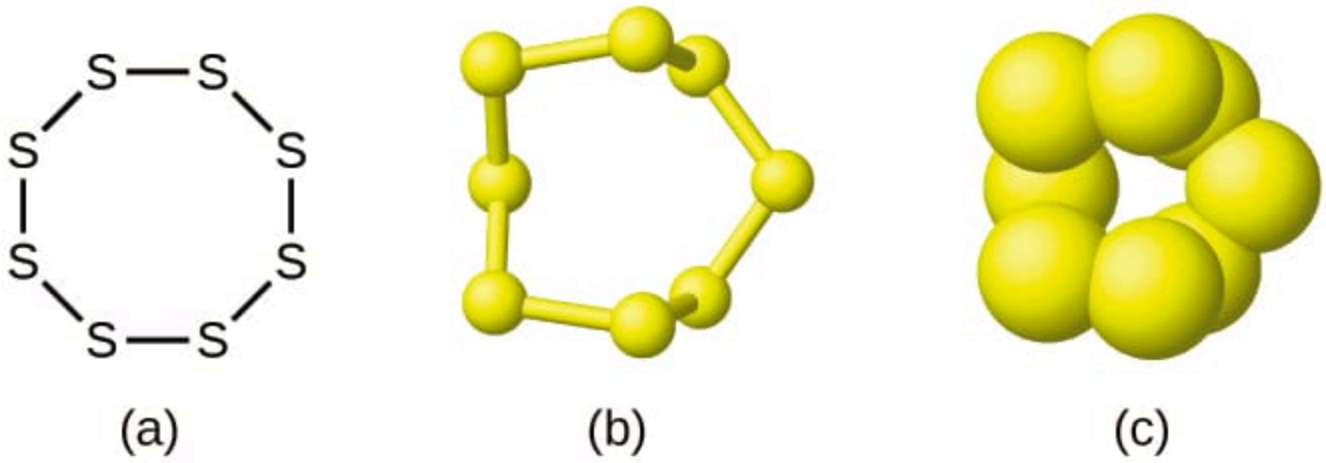


Figure 1.17 A molecule of sulfur is composed of eight sulfur atoms and is therefore written as S_8. It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres.

It is important to note that a subscript following a symbol and a number in front of a symbol do not represent the same thing; for example, H_2 and 2H represent distinctly different species. H_2 is a molecular formula; it represents a diatomic molecule of hydrogen, consisting of two atoms of the element that are chemically bonded together. The expression 2H, on the other hand, indicates two separate hydrogen atoms that are not combined as a unit. The expression $2H_2$ represents two molecules of diatomic hydrogen (Figure 2.18).

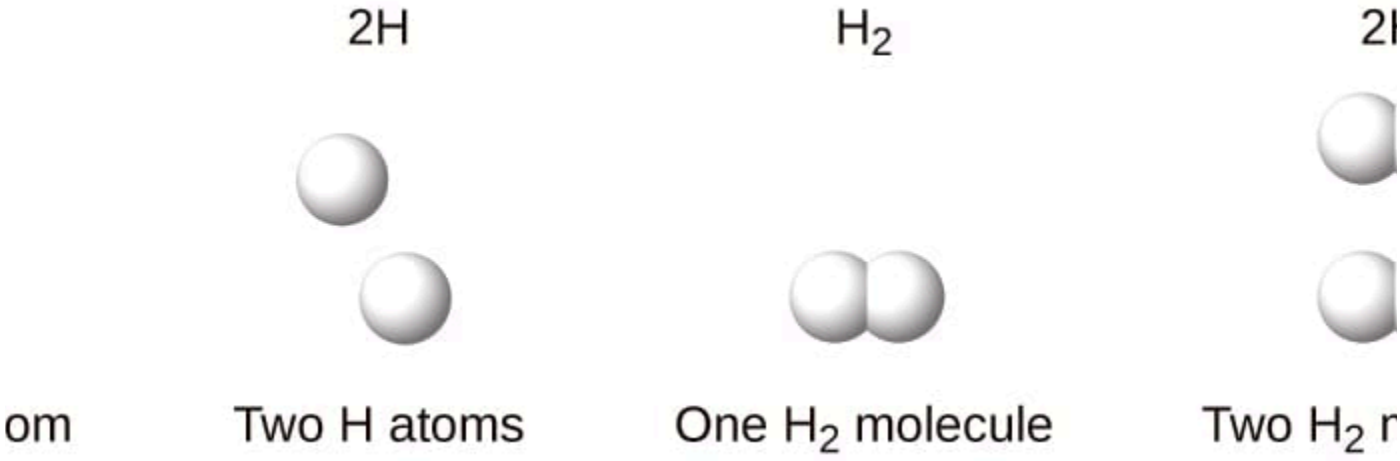
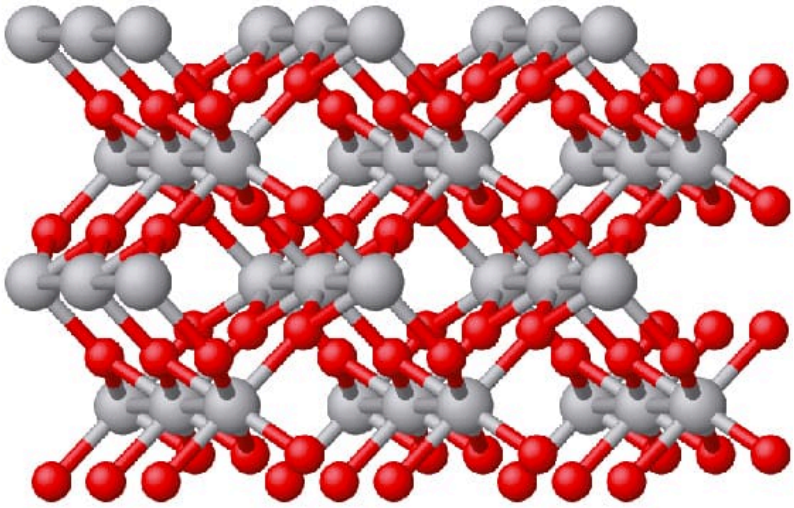


Figure 1.18 The symbols H, 2H, H_2, and $2H_2$ represent very different entities.

Compounds are formed when two or more elements chemically combine, resulting in the formation of bonds. For example, hydrogen and oxygen can react to form water, and sodium and chlorine can react to form table salt. We sometimes describe the composition of these compounds with an empirical formula, which indicates the types of atoms present and *the simplest whole-number ratio of the number of atoms (or ions) in the compound*. For example, titanium dioxide (used as pigment in white paint and in the thick, white, blocking type of sunscreen) has an empirical formula of TiO_2. This identifies the elements titanium (Ti) and oxygen (O) as the constituents of titanium dioxide, and indicates the presence of twice as many atoms of the element oxygen as atoms of the element titanium (Figure 1.19).



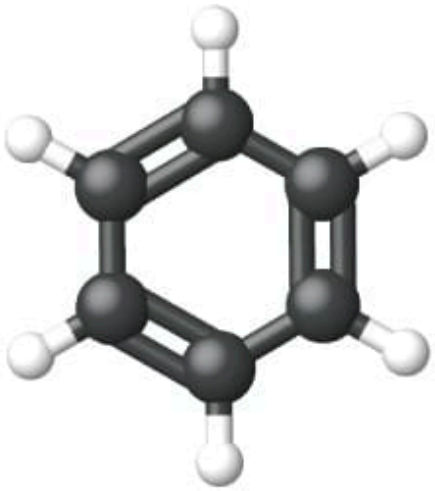
(a)



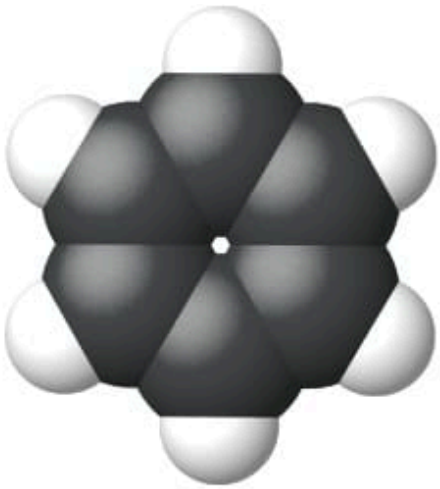
(b)

Figure 1.19 (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)

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 1.20).



(b)



(c)



Figure 1.20 Benzene, C_6H_6, is produced during oil refining and has many industrial uses. A benzene molecule can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. (d) Benzene is a clear liquid. (credit d: modification of work by Sahar Atwa)

If we know a compound’s 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 1.21) 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.

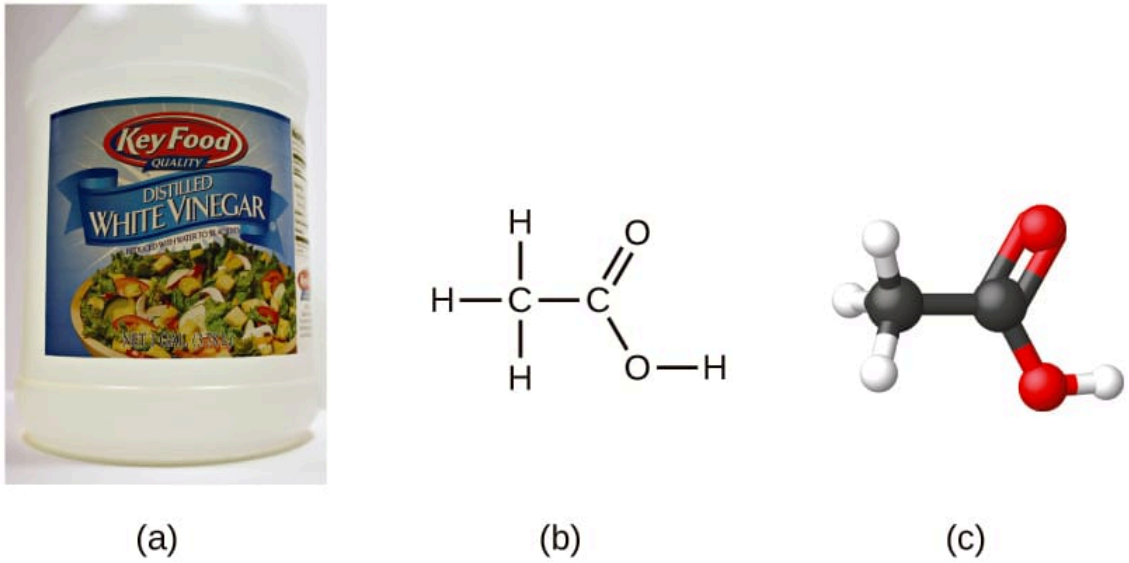


Figure 1.21 (a) Vinegar contains acetic acid, $C_2H_4O_2$, which has an empirical formula of CH_2O. It can be represented as (b) a structural formula and (c) as a ball-and-stick model. (credit a: modification of work by "HomeSpot HQ"/Flickr)

Example 1.6

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.

Check Your Learning

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

Answer:

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

Link to Learning

You can explore molecule building using an online simulation.

Portrait of a Chemist

Paula Hammond

You've learned about the evolution of atomic theory, and you've started to explore different chemical structures. These structures result in molecules attracting or repelling each other, or help them arrange into our cell membranes or lead them to either spread into thin films or clump into solid masses.

What do these structures mean to scientists, and to us? Essentially, everything. It's the structure and makeup of a molecule on a virus surface that allows it to attach to one of our cells, and it's the structure and makeup of antibodies—substances created by our immune system—that block that attachment. Chlorophyll's structure enables it to use the sun's energy to make glucose. Chemists and chemical engineers don't simply observe and understand these structures—they can create new ones.



Figure 1.22 Paula Hammond pioneered new techniques to precisely formulate chemical structures. Hammond's work applies to cancer treatments, wound healing, cataract medicine, and fuel cells. Widely recognized as a leader in the field, she has won numerous awards and has been elected to various prestigious positions and fellowships by her peers and the U.S. government. She chairs the chemical engineering department at MIT, which is usually ranked as one of the best engineering and science institutions in the world. (credit: modification of work by The White House)

Paula Hammond does exactly that to solve challenging problems ranging from cancer to energy consumption. She is the chair of the department of chemical engineering at Massachusetts Institute of Technology, and leads a research team focused on assembling unique molecular structures. They have created cancer drug carriers—nanoparticle-sized coatings that enable medicines to travel into tumors without being affected by its defenses—that can deliver pharmaceuticals directly into cancerous tumors. They build these "stealth" molecules layer by layer; using certain properties of electricity and chemical behavior, they can "tune" the coatings to address particular cancers and other variables. This precision approach is necessary to treat cancers more effectively and with less harm to the patient. The company Hammond founded uses similar technology to release medication into cataract patients' eyes, as well as to improve wound healing.

While Hammond's research team is composed of established and leading experts such as herself, students certainly play a role. College research labs are typically full of PhD, graduate, and even undergraduate students who participate in the work. And thus chemists and chemical engineers who use their knowledge to solve problems are also supporting the next generation of creators and problem-solvers.

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 a 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 1.23). 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.

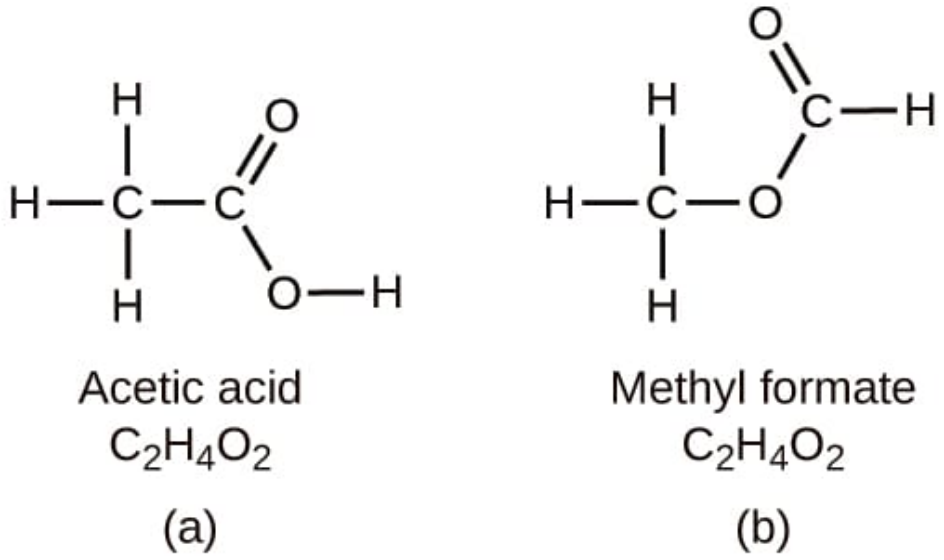


Figure 1.23 Molecules of (a) acetic acid and methyl formate (b) are structural isomers; they have the same formula ($C_2H_4O_2$) but different structures (and therefore different chemical properties).

Many types of isomers exist (Figure 1.24). 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.

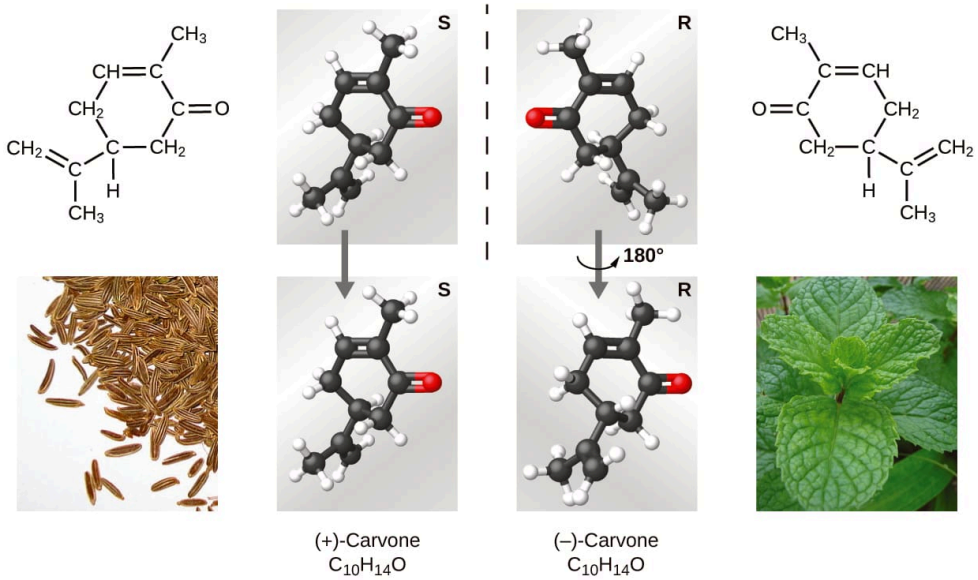


Figure 1.24 Molecules of carvone are spatial isomers; they only differ in the relative orientations of the atoms in space. (credit bottom left: modification of work by "Miansari66"/Wikimedia Commons; credit bottom right: modification of work by Forest & Kim Starr)

Link to Learning

Select this link to view an explanation of isomers, spatial isomers, and why they have different smells (select the video titled "Mirror Molecule: Carvone").

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 sample of matter. One Latin connotation for the word “mole” is “large mass” or “bulk,” which is consistent with its use as the name for this unit. The mole provides a link between an easily measured macroscopic property, bulk mass, and an extremely important fundamental property, number of atoms, molecules, and so forth. A mole of substance is that amount in which there are $6.02214076 \times 10^{23}$ discrete entities (atoms or molecules). This large number is a fundamental constant known as 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 6.022×10^{23}/mol.

Consistent with its definition as an amount unit, 1 mole of any element contains the same number of atoms as 1 mole of any other element. The masses of 1 mole of different elements, however, are different, since the masses of the individual atoms are drastically different. The molar mass of an element (or compound) is the mass in grams of 1 mole of that substance, a property expressed in units of grams per mole (g/mol) (see Figure 1.25).

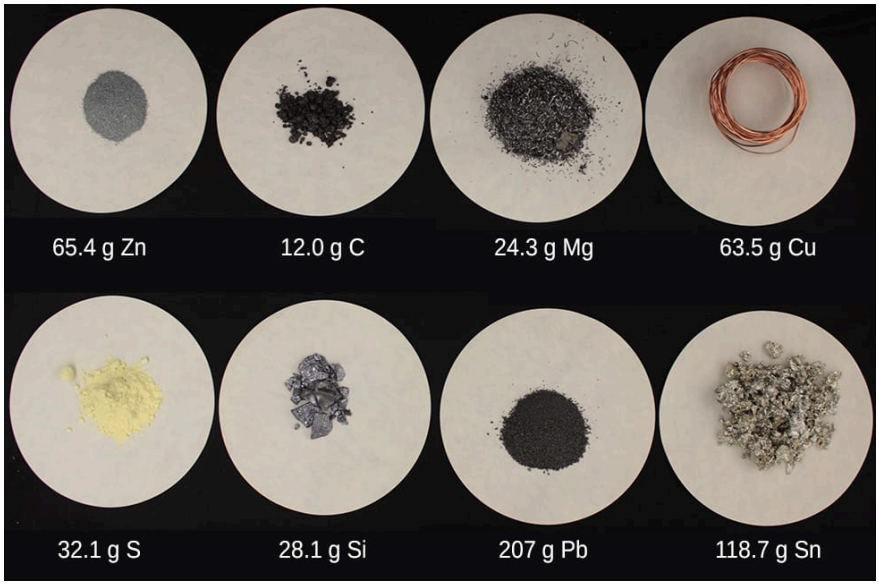


Figure 1.25 Each sample contains 6.022×10^{23} atoms —1.00 mol of atoms. From left to right (top row): 65.4 g zinc, 12.0 g carbon, 24.3 g magnesium, and 63.5 g copper. From left to right (bottom row): 32.1 g sulfur, 28.1 g silicon, 207 g lead, and 118.7 g tin. (credit: modification of work by Mark Ott)

The molar mass of any substance is numerically equivalent to its atomic or formula weight in amu. Per the amu definition, a single ^{12}C atom weighs 12 amu (its atomic mass is 12 amu). A mole of ^{12}C atoms weighs 12 g (its molar mass is 12 g/mol). This relationship holds for all elements, since their atomic masses are measured relative to that of the amu-reference substance, ^{12}C. Extending this principle, the molar mass of a compound in grams is likewise numerically equivalent to its formula mass in amu (Figure 1.26).



Figure 1.26 Each sample contains 6.02×10^{23} molecules or formula units—1.00 mol of the compound or element. Clock-wise from the upper left: 130.2 g of $C_8H_{17}OH$ (1-octanol, formula mass 130.2 amu), 454.4 g of HgI_2 (mercury(II) iodide, formula mass 454.4 amu), 32.0 g of CH_3OH (methanol, formula mass 32.0 amu) and 256.5 g of S_8 (sulfur, formula mass 256.5 amu). (credit: Sahar Atwa)

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	35.45	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 weighing about 0.03 g (see Figure 1.27). Although this represents just a tiny fraction of 1 mole of water (~18 g), it contains more water molecules than can be clearly imagined. If the molecules were distributed equally among the roughly seven billion people on earth, each person would receive more than 100 billion molecules.

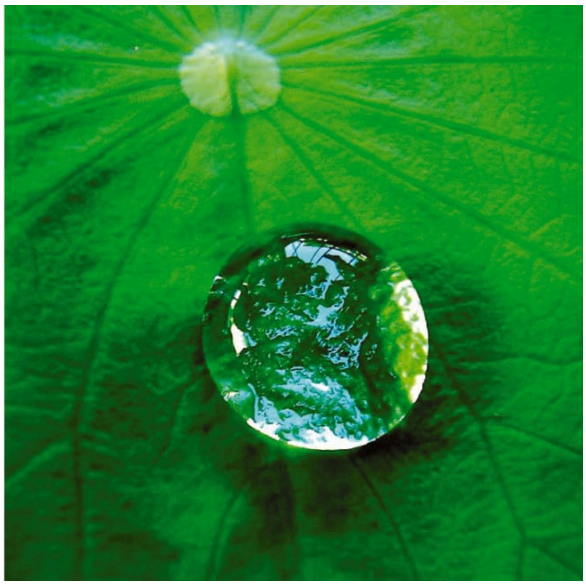


Figure 1.27 The number of molecules in a single droplet of water is roughly 100 billion times greater than the number of people on earth. (credit: "tanakawho"/Wikimedia commons)

Link to Learning

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 1.7

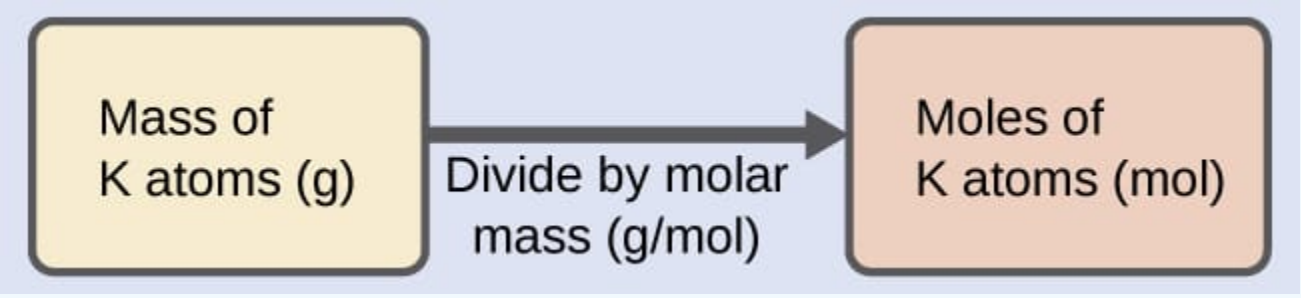
Deriving Moles from Grams for an Element

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:”

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

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

Check Your Learning

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

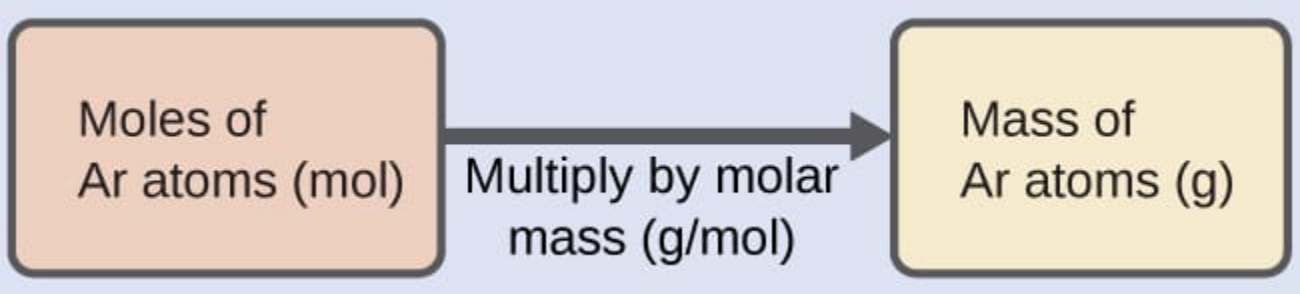
Example 1.8

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):

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

The result is in agreement with our expectations, around 0.04 g Ar.

–

Check Your Learning

What is the mass of 2.561 mol of gold?

Answer:

504.4 g

Example 1.9

Deriving Number of Atoms from Mass for an Element

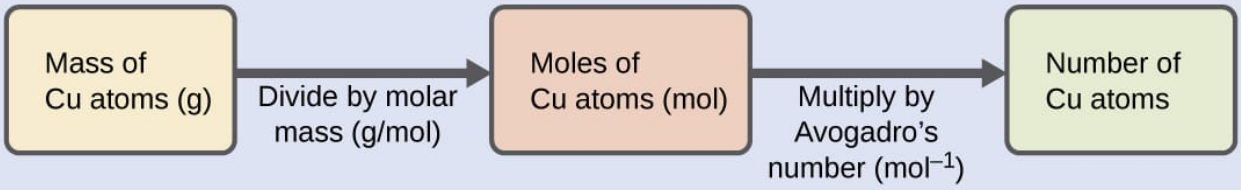
Copper is commonly used to fabricate electrical wire (Figure 1.28). How many copper atoms are in 5.00 g of copper wire?



Figure 1.28 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:

$$5.00\text{gCu}\left(\frac{\text{molCu}^{\text{g}}}{63.55\ \text{gCu}}\right)\left(\frac{6.022\times10^{23}\text{Cu atoms}}{\text{mol Cu}}\right)=4.74\times10^{22}\text{Cu atoms}$$

The factor-label method yields the desired cancellation of units, and the computed result is on the order of 10^{22} as expected

Check Your Learning

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:

4.586×10^{22} Au atoms

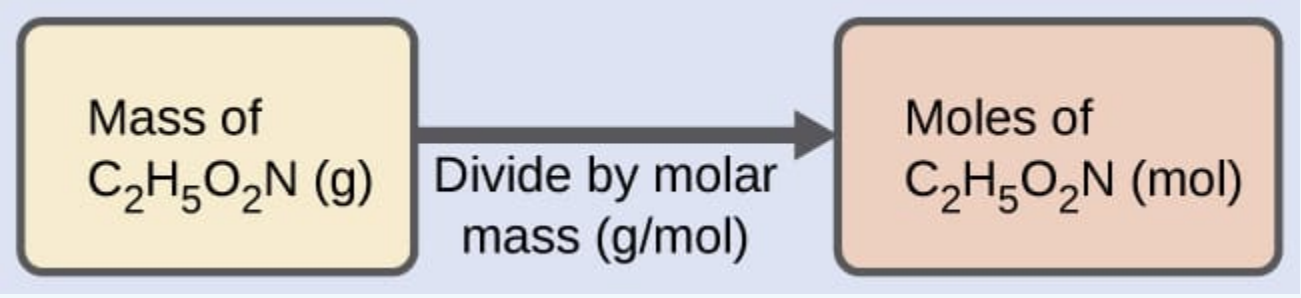
Example 2.10

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?

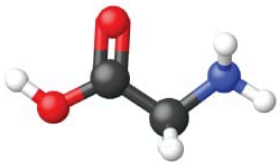
Solution

We can derive the number of moles of a compound from its mass following the same procedure we used for an element in Example 2.7:



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



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:

$$28.35 \text{ g glycine} \left(\frac{\text{mol glycine}}{75.07 \text{ g glyeine}} \right) = 0.3776 \text{ mol glycine}$$

This result is consistent with our rough estimate.

This result is consistent with our rough estimate.

Check Your Learning

How many moles of sucrose, $C_{12}H_{22}O_{11}$, are in a 25-g sample of sucrose?

Answer:

0.073 mol

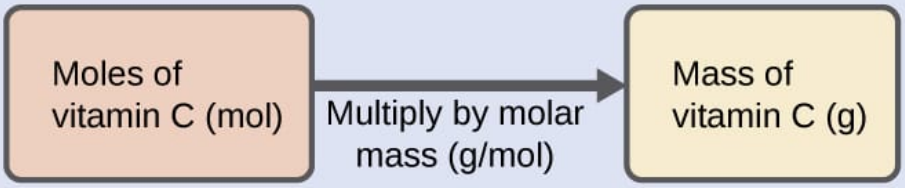
Example 2.11

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:

$$1.42 \times 10^{-4} \text{ mol vitamin C} \left(\frac{176.124 \text{ g vitamin C}}{\text{mol vitamin C}} \right) = 0.0250 \text{ g vitamin C}$$

This is consistent with the anticipated result.

Check Your Learning

What is the mass of 0.443 mol of hydrazine, N_2H_4?

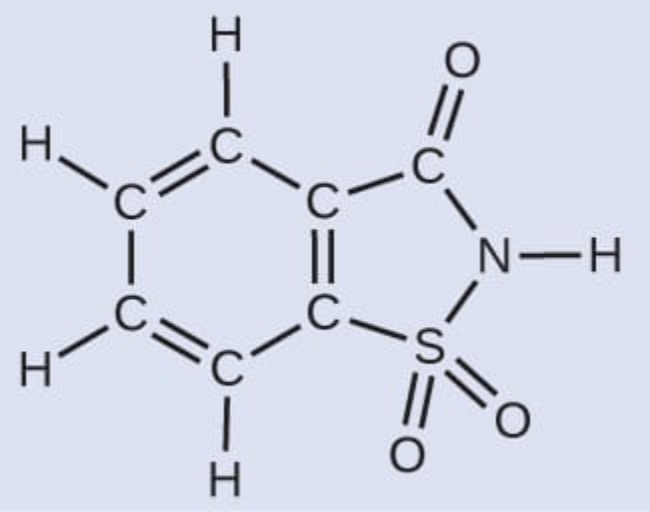
Answer:

14.2 g

Example 2.12

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

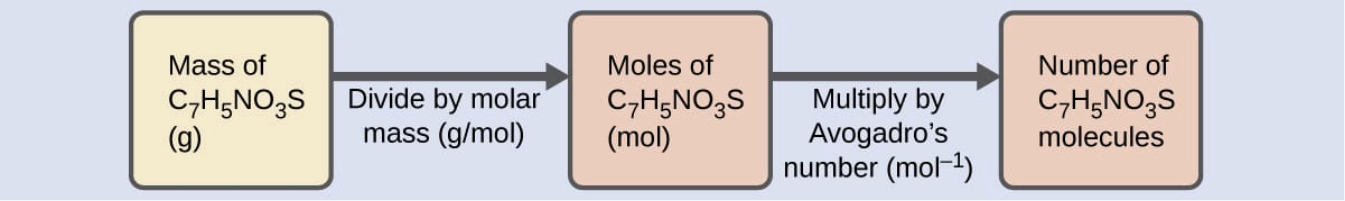
A packet of an artificial sweetener contains 40.0 mg of saccharin ($C_7H_5NO_3S$), which has the structural formula:



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

Solution

The number of molecules in a given mass of compound is computed by first deriving the number of moles, as demonstrated in Example 2.10, and then multiplying by Avogadro's number:



Using the provided mass and molar mass for saccharin yields:

$$0.0400\ \text{g}\,\text{C}_7\text{H}_5\text{NO}_3\ \text{S}\left(\frac{\text{mol}\,\text{G}_7\text{H}_5\text{NO}_3\ \text{S}}{183.18\,\text{G}_7\text{H}_5\text{NO}_3\ \text{S}}\right)\left(\frac{6.022\times10^{23}\,\text{C}_7\text{H}_5\text{NO}_3\ \text{S molecules}}{1\,\text{mol}\,\text{C}_7\text{H}_5\text{NO}_3\ \text{S}}\right)$$
$$=1.31\times10^{20}\,\text{C}_7\text{H}_5\text{NO}_3\ \text{S molecules}$$

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

$$1.31\times10^{20}\,\text{C}_7\text{H}_5\text{NO}_3\ \text{S molecules}\left(\frac{7\text{C atoms}}{1\,\text{C}_7\text{H}_5\text{NO}_3\ \text{S molecule}}\right)=9.17\times10^{20}\,\text{C atoms}$$

Check Your Learning

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

How Sciences Interconnect

Counting Neurotransmitter Molecules in the Brain

The brain is the control center of the central nervous system (Figure 1.29). It sends and receives signals to and from muscles and other internal organs to monitor and control their functions; it processes stimuli detected by sensory organs to guide interactions with the external world; and it houses the complex physiological processes that give rise to our intellect and emotions. The broad field of neuroscience spans all aspects of the structure and function of the central nervous system, including research on the anatomy and physiology of the brain. Great progress has been made in brain research over the past few decades, and the BRAIN Initiative, a federal initiative announced in 2013, aims to accelerate and capitalize on these advances through the concerted efforts of various industrial, academic, and government agencies (see BRAIN Initiative website for details).

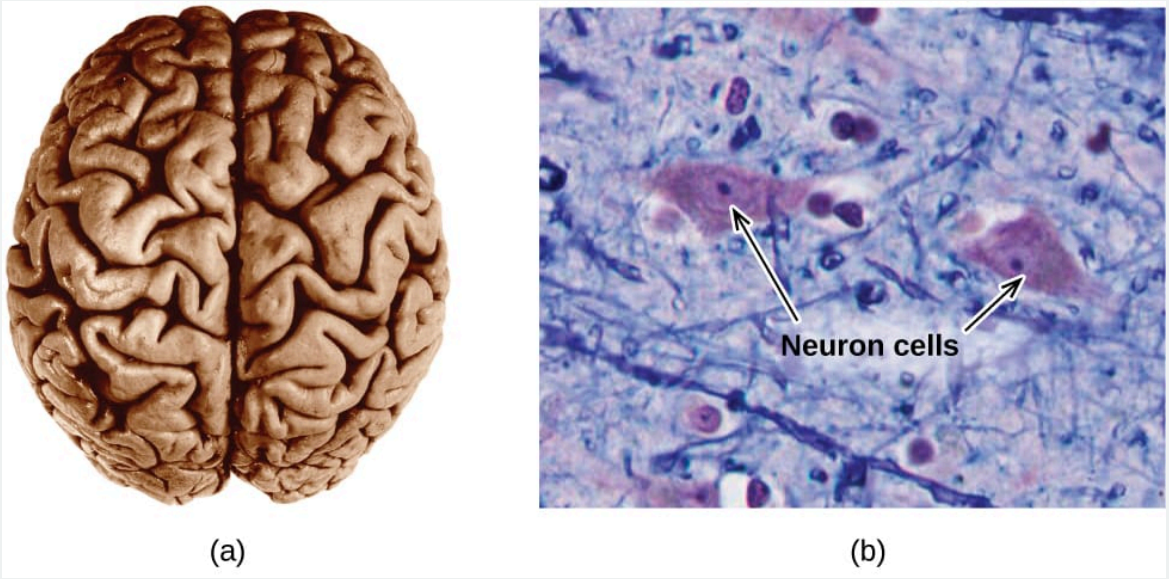


Figure 1.29 (a) A typical human brain weighs about 1.5 kg and occupies a volume of roughly 1.1 L. (b) Information is transmitted in brain tissue and throughout the central nervous system by specialized cells called neurons (micrograph shows cells at 1600× magnification).

Specialized cells called neurons transmit information between different parts of the central nervous system by way of electrical and chemical signals. Chemical signaling occurs at the interface between different neurons when one of the cells releases molecules (called neurotransmitters) that diffuse across the small gap between the cells (called the synapse) and bind to the surface of the other cell. These neurotransmitter molecules are stored in small intracellular structures called vesicles that fuse to the cell membrane and then break open to release their contents when the neuron is appropriately stimulated. This process is called exocytosis (see Figure 1.30). One neurotransmitter that has been very extensively studied is dopamine, $C_8H_{11}NO_2$. Dopamine is involved in various neurological processes that impact a wide variety of human behaviors. Dysfunctions in the dopamine systems of the brain underlie serious neurological diseases such as Parkinson's and schizophrenia.

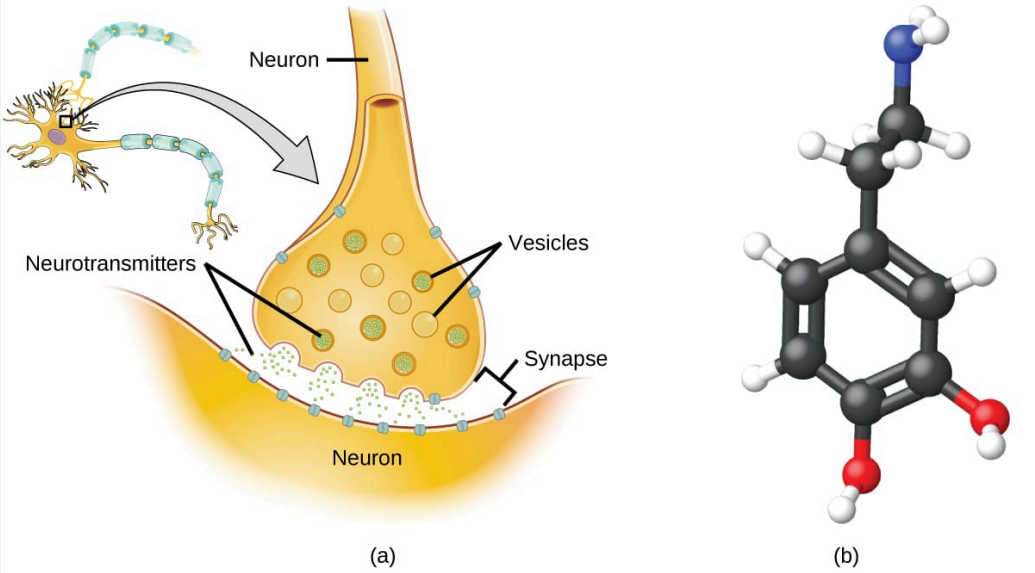


Figure 1.30 (a) Chemical signals are transmitted from neurons to other cells by the release of neurotransmitter molecules into the small gaps (synapses) between the cells. (b) Dopamine, $C_8H_{11}NO_2$, is a neurotransmitter involved in a number of neurological processes.

One important aspect of the complex processes related to dopamine signaling is the number of neurotransmitter molecules released during exocytosis. Since this number is a central factor in determining neurological response (and subsequent human thought and action), it is important to know how this number changes with certain controlled stimulations, such as the administration of drugs. It is also important to understand the mechanism responsible for any changes in the number of neurotransmitter molecules released—for example, some dysfunction in exocytosis, a change in the number of vesicles in the neuron, or a change in the number of neurotransmitter molecules in each vesicle.

Significant progress has been made recently in directly measuring the number of dopamine molecules stored in individual vesicles and the amount actually released when the vesicle undergoes exocytosis. Using miniaturized probes that can selectively detect dopamine molecules in very small amounts, scientists have determined that the vesicles of a certain type of mouse brain neuron contain an average of 30,000 dopamine molecules per vesicle (about 5×10^{-20}

Footnotes

2 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.

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1.6: Key Terms

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

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 112112 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

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

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

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

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)

isomers
compounds with the same chemical formula but different structures

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

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 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

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

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.

neutron
uncharged, subatomic particle located in the nucleus

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

proton
positively charged, subatomic particle located in the nucleus

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

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

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

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1.7: Key Equations

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

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1.8: 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.

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.

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 $\frac{1}{12}$ 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.

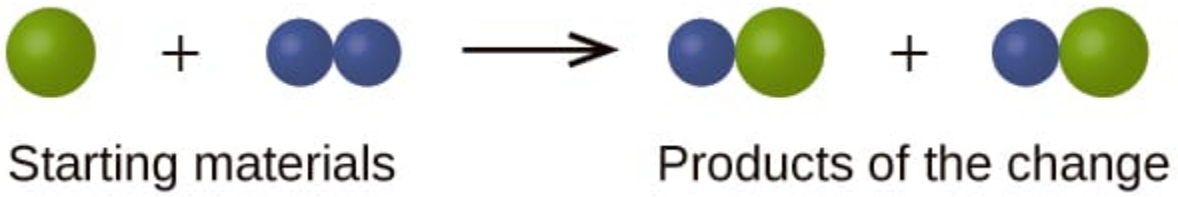
A molecular formula uses chemical symbols and subscripts to indicate the exact numbers of different atoms in a molecule or compound. An empirical formula gives the simplest, whole-number ratio of atoms in a compound. A structural formula indicates the bonding arrangement of the atoms in the molecule. 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. 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.

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1.9: Exercises

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 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?



2.

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.

3.

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.

4.

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?

5.

The existence of isotopes violates one of the original ideas of Dalton's atomic theory. Which one?

6.

How are electrons and protons similar? How are they different?

7.

How are protons and neutrons similar? How are they different?

8.

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.

9.

Predict and test the behavior of α particles fired at a Rutherford atom model.

(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) 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) 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) 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 “2” 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.

10.

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

11.

Write the symbol for each of the following ions:

(a) the ion with a 1+ charge, atomic number 55, and mass number 133

(b) the ion with 54 electrons, 53 protons, and 74 neutrons

(c) the ion with atomic number 15, mass number 31, and a 3– charge

(d) the ion with 24 electrons, 30 neutrons, and a 3+ charge

12.

Write the symbol for each of the following ions:

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

(b) the ion with 36 electrons, 35 protons, and 45 neutrons

(c) the ion with 86 electrons, 142 neutrons, and a 4+ charge

(d) the ion with a 2+ charge, atomic number 38, and mass number 87

13.

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

(a) Pick any one of the first 10 elements that you would like to build and state its symbol.

(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.

(c) Click on “Net Charge” and “Mass Number,” check your answers to (b), and correct, if needed.

(d) Predict whether your atom will be stable or unstable. State your reasoning.

(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.

14.

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.

15.

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.

16.

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).

17.

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–

18.

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

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

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

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

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

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

19.

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

20.

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.

21.

Repeat Exercise 2.20 using an element that has three naturally occurring isotopes.

22.

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.

23.

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, respectively) and abundances (50.69% and 49.31%, respectively) were determined in earlier experiments. Calculate the average atomic mass of bromine based on these experiments.

24.

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.

25.

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, 11.00931 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.

26.

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?

27.

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

28.

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

29.

Write the molecular and empirical formulas of the following compounds:

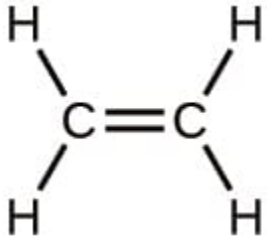
(a)



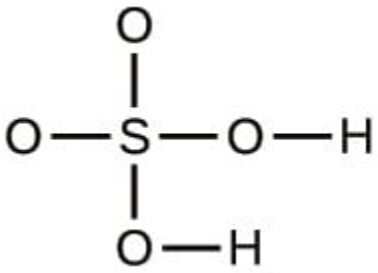
(b)



(c)



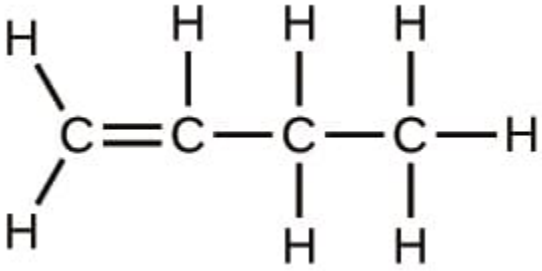
(d)



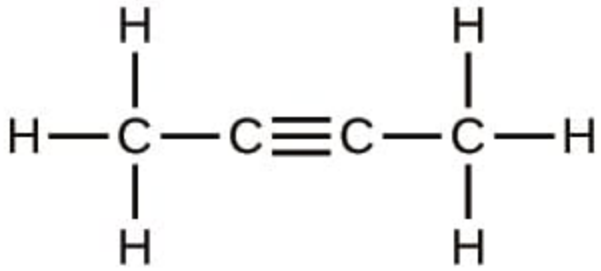
30.

Write the molecular and empirical formulas of the following compounds:

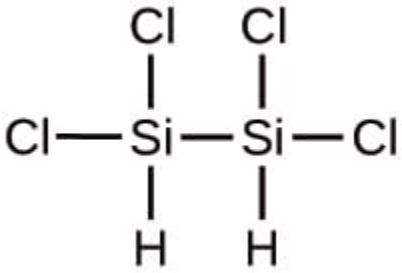
(a)



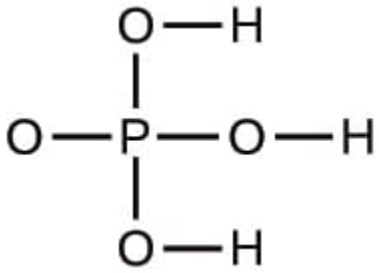
(b)



(c)



(d)



31.

Determine the empirical formulas for the following compounds:

(a) caffeine, $C_8H_{10}N_4O_2$

(b) sucrose, $C_{12}H_{22}O_{11}$

(c) hydrogen peroxide, H_2O_2

(d) glucose, $C_6H_{12}O_6$

(e) ascorbic acid (vitamin C), $C_6H_8O_6$

32.

Determine the empirical formulas for the following compounds:

(a) acetic acid, $C_2H_4O_2$

(b) citric acid, $C_6H_8O_7$

(c) hydrazine, N_2H_4

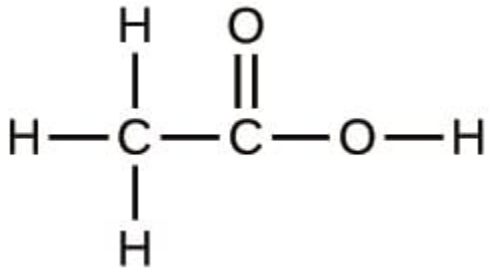
(d) nicotine, $C_{10}H_{14}N_2$

(e) butane, C_4H_{10}

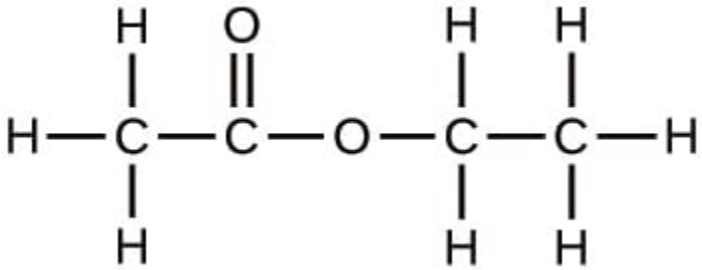
33.

Write the empirical formulas for the following compounds:

(a)



(b)



34.

Open the Build a Molecule simulation and select the “Larger Molecules” tab. Select an appropriate atom's “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.

(a) Draw the structural formula of this molecule and state its name.

(b) Can you arrange these atoms in any way to make a different compound?

35.

Use the Build a Molecule simulation to repeat Exercise 2.34, but build a molecule with two carbons, six hydrogens, and one oxygen.

(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)?

36.

Use the Build a Molecule simulation to repeat Exercise 2.34, 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)?

37.

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.

38.

Compare 1 mole of H_2, 1 mole of O_2, and 1 mole of F_2.

(a) Which has the largest number of molecules? Explain why.

(b) Which has the greatest mass? Explain why.

39.

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.

40.

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.

41.

How are the molecular mass and the molar mass of a compound similar and how are they different?

42.

Calculate the molar mass of each of the following compounds:

(a) hydrogen fluoride, HF

(b) ammonia, NH_3

(c) nitric acid, HNO_3

(d) silver sulfate, Ag_2SO_4

(e) boric acid, $B(OH)_3$

43.

Calculate the molar mass of each of the following:

(a) S_8

(b) C_5H_{12}

(c) $Sc_2(SO_4)_3$

(d) CH_3COCH_3 (acetone)

(e) $C_6H_{12}O_6$ (glucose)

44.

Calculate the empirical or molecular formula mass and the molar mass of each of the following minerals:

(a) limestone, $CaCO_3$

(b) halite, NaCl

(c) beryl, $Be_3Al_2Si_6O_{18}$

(d) malachite, $Cu_2(OH)_2CO_3$

(e) turquoise, $CuAl_6(PO_4)_4(OH)_8(H_2O)_4$

45.

Calculate the molar mass of each of the following:

(a) the anesthetic halothane, $C_2HBrClF_3$

(b) the herbicide paraquat, $C_{12}H_{14}N_2Cl_2$

(c) caffeine, $C_8H_{10}N_4O_2$

(d) urea, $CO(NH_2)_2$

(e) a typical soap, $C_{17}H_{35}CO_2Na$

46.

Determine the number of moles of compound and the number of moles of each type of atom in each of the following:

(a) 25.0 g of propylene, C_3H_6

(b) 3.06×10^{-3} g of the amino acid glycine, $C_2H_5NO_2$

(c) 25 lb of the herbicide Treflan, $C_{13}H_{16}N_2O_4F$ (1 lb = 454 g)

(d) 0.125 kg of the insecticide Paris Green, $Cu_4(AsO_3)_2(CH_3CO_2)_2$

(e) 325 mg of aspirin, $C_6H_4(CO_2H)(CO_2CH_3)$

47.

Determine the mass of each of the following:

(a) 0.0146 mol KOH

(b) 10.2 mol ethane, C_2H_6

(c) 1.6×10^{-3} mol $Na_2 SO_4$

(d) 6.854×10^{3} mol glucose, $C_6 H_{12} O_6$

(e) 2.86 mol $Co(NH_3)_6Cl_3$

48.

Determine the number of moles of the compound and determine the number of moles of each type of atom in each of the following:

(a) 2.12 g of potassium bromide, KBr

(b) 0.1488 g of phosphoric acid, H_3PO_4

(c) 23 kg of calcium carbonate, $CaCO_3$

(d) 78.452 g of aluminum sulfate, $Al_2(SO_4)_3$

(e) 0.1250 mg of caffeine, $C_8H_{10}N_4O_2$

49.

Determine the mass of each of the following:

(a) 2.345 mol LiCl

(b) 0.0872 mol acetylene, C_2H_2

(c) 3.3×10^{-2} mol $Na_2 CO_3$

(d) 1.23×10^{3} mol fructose, $C_6 H_{12} O_6$

(e) 0.5758 mol $FeSO_4(H_2O)_7$

50.

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?

51.

Determine the mass in grams of each of the following:

(a) 0.600 mol of oxygen atoms

(b) 0.600 mol of oxygen molecules, O_2

(c) 0.600 mol of ozone molecules, O_3

52.

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?

53.

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.

54.

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.

55.

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.

56.

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?

57.

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?

58.

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?

59.

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?

60.

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?

61.

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 C_3H_6 (42.08 g/mol)

(d) 100.0 g of N_2O (44.02 g/mol)

(e) 84.0 g of HF (20.01 g/mol)

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2: ELECTRONIC STRUCTURE AND PERIODIC PROPERTIES

2.1: Introduction

2.2: Electromagnetic Energy

2.3: The Bohr Model

2.4: Development of Quantum Theory

2.5: Electronic Structure of Atoms (Electron Configurations)

2.6: Periodic Variations in Element Properties

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2.8: Ionic and Molecular Compounds

2.9: Key Terms

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2.1: Introduction

In 1054, Chinese astronomers recorded the appearance of a “guest star” in the sky, visible even during the day, which then disappeared slowly over the next two years. The sudden appearance was due to a supernova explosion, which was much brighter than the original star. Even though this supernova was observed almost a millennium ago, the remaining Crab Nebula (Figure 2.1.1) continues to release energy today. It emits not only visible light but also infrared light, X-rays, and other forms of electromagnetic radiation. The nebula emits both continuous spectra (the blue-white glow) and atomic emission spectra (the colored filaments). In this chapter, we will discuss light and other forms of electromagnetic radiation and how they are related to the electronic structure of atoms. We will also see how this radiation can be used to identify elements, even from thousands of light years away.

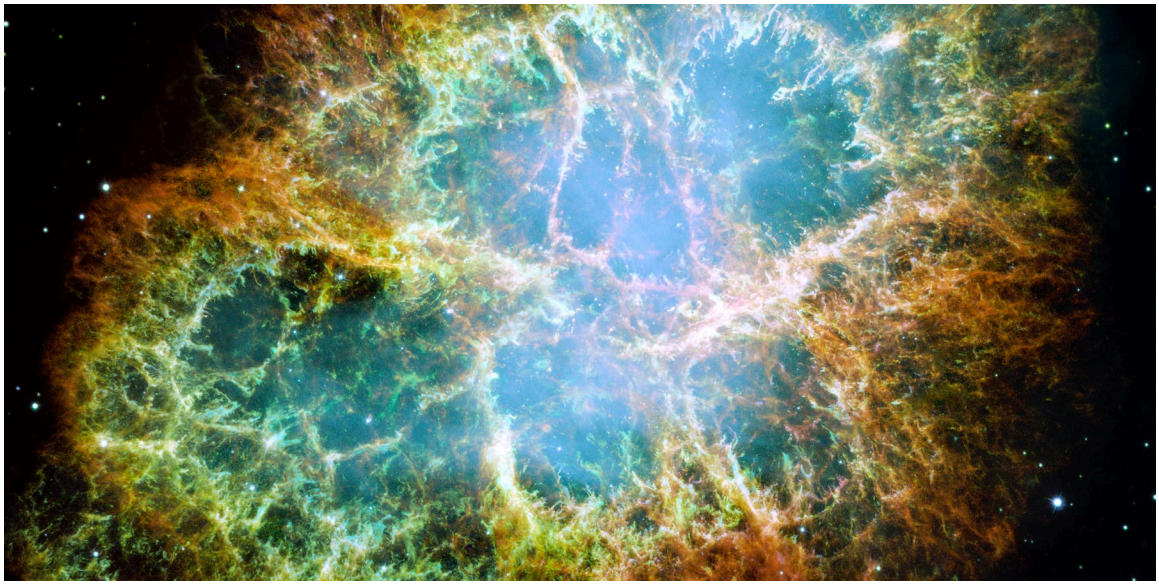


Figure 2.1.1: The Crab Nebula consists of remnants of a supernova (the explosion of a star). NASA’s Hubble Space Telescope produced this composite image. Measurements of the emitted light wavelengths enabled astronomers to identify the elements in the nebula, determining that it contains specific ions including S^{+} (green filaments) and O^{2+} (red filaments). (credit: modification of work by NASA and ESA)

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2.2: Electromagnetic Energy

Learning Objectives

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

- Explain the basic behavior of waves, including travelling waves and standing waves
- Describe the wave nature of light
- Use appropriate equations to calculate related light-wave properties such as frequency, wavelength, and energy
- Distinguish between line and continuous emission spectra
- Describe the particle nature of light

The nature of light has been a subject of inquiry since antiquity. In the seventeenth century, Isaac Newton performed experiments with lenses and prisms and was able to demonstrate that white light consists of the individual colors of the rainbow combined together. Newton explained his optics findings in terms of a "corpuscular" view of light, in which light was composed of streams of extremely tiny particles travelling at high speeds according to Newton's laws of motion. Others in the seventeenth century, such as Christiaan Huygens, had shown that optical phenomena such as reflection and refraction could be equally well explained in terms of light as waves travelling at high speed through a medium called "luminiferous aether" that was thought to permeate all space. Early in the nineteenth century, Thomas Young demonstrated that light passing through narrow, closely spaced slits produced interference patterns that could not be explained in terms of Newtonian particles but could be easily explained in terms of waves. Later in the nineteenth century, after James Clerk Maxwell developed his theory of electromagnetic radiation and showed that light was the visible part of a vast spectrum of electromagnetic waves, the particle view of light became thoroughly discredited. By the end of the nineteenth century, scientists viewed the physical universe as roughly comprising two separate domains: matter composed of particles moving according to Newton's laws of motion, and electromagnetic radiation consisting of waves governed by Maxwell's equations. Today, these domains are referred to as classical mechanics and classical electrodynamics (or classical electromagnetism). Although there were a few physical phenomena that could not be explained within this framework, scientists at that time were so confident of the overall soundness of this framework that they viewed these aberrations as puzzling paradoxes that would ultimately be resolved somehow within this framework. As we shall see, these paradoxes led to a contemporary framework that intimately connects particles and waves at a fundamental level called wave-particle duality, which has superseded the classical view.

Visible light and other forms of electromagnetic radiation play important roles in chemistry, since they can be used to infer the energies of electrons within atoms and molecules. Much of modern technology is based on electromagnetic radiation. For example, radio waves from a mobile phone, X-rays used by dentists, the energy used to cook food in your microwave, the radiant heat from red-hot objects, and the light from your television screen are forms of electromagnetic radiation that all exhibit wavelike behavior.

Waves

A **wave** is an oscillation or periodic movement that can transport energy from one point in space to another. Common examples of waves are all around us. Shaking the end of a rope transfers energy from your hand to the other end of the rope, dropping a pebble into a pond causes waves to ripple outward along the water's surface, and the expansion of air that accompanies a lightning strike generates sound waves (thunder) that can travel outward for several miles. In each of these cases, kinetic energy is transferred through matter (the rope, water, or air) while the matter remains essentially in place. An insightful example of a wave occurs in sports stadiums when fans in a narrow region of seats rise simultaneously and stand with their arms raised up for a few seconds before sitting down again while the fans in neighboring sections likewise stand up and sit down in sequence. While this wave can quickly encircle a large stadium in a few seconds, none of the fans actually travel with the wave-they all stay in or above their seats.

Waves need not be restricted to travel through matter. As Maxwell showed, electromagnetic waves consist of an electric field oscillating in step with a perpendicular magnetic field, both of which are perpendicular to the direction of travel. These waves can travel through a vacuum at a constant speed of 2.998 108 m/s, the speed of light (denoted by c).

All waves, including forms of electromagnetic radiation, are characterized by, a **wavelength** (denoted by λ, the lowercase Greek

letter lambda), a **frequency** (denoted by ν, the lowercase Greek letter nu), and an **amplitude**. As can be seen in Figure $2.2.1$, the wavelength is the distance between two consecutive peaks or troughs in a wave (measured in meters in the SI system). Electromagnetic waves have wavelengths that fall within an enormous range-wavelengths of kilometers (10^{3} m) to picometers (10^{-12} m) have been observed. The frequency is the number of wave cycles that pass a specified point in space in a specified amount of time (in the SI system, this is measured in seconds). A cycle corresponds to one complete wavelength. The unit for frequency, expressed as cycles per second [s^{-1}], is the **hertz** (Hz). Common multiples of this unit are megahertz, ($1\ \mathrm{MHz} = 1 \times 10^{6}\ \mathrm{Hz}$) and gigahertz ($1\ \mathrm{GHz} = 1 \times 10^{9}\ \mathrm{Hz}$). The amplitude corresponds to the magnitude of the wave's displacement and so, in Figure $2.2.1$, this corresponds to one-half the height between the peaks and troughs. The amplitude is related to the intensity of the wave, which for light is the brightness, and for sound is the loudness.

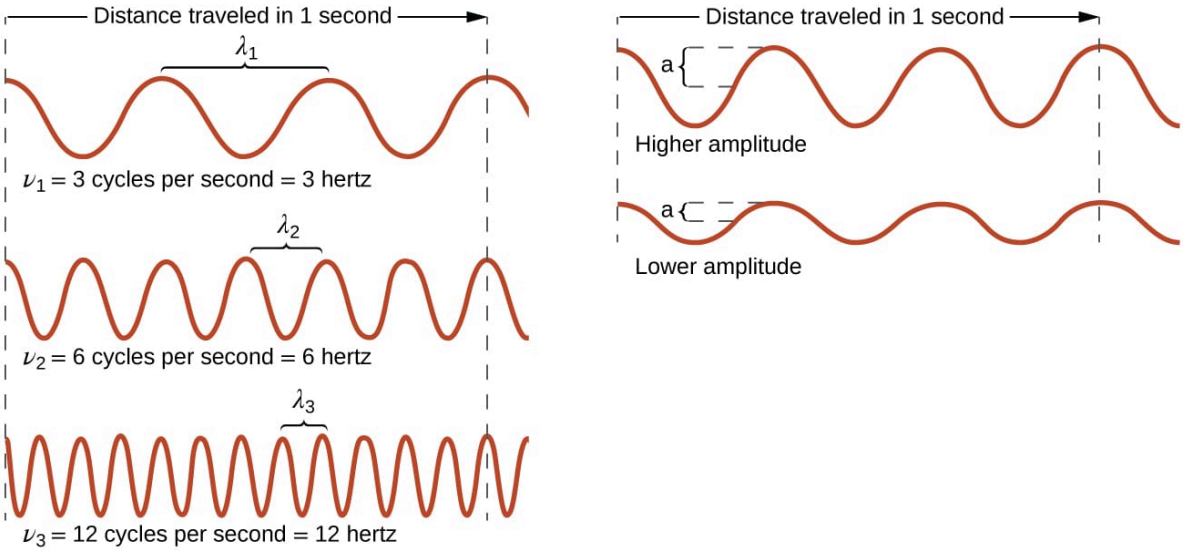


Figure $2.2.1$: One-dimensional sinusoidal waves show the relationship among wavelength, frequency, and speed. The wave with the shortest wavelength has the highest frequency. Amplitude is one-half the height of the wave from peak to trough.

The product of a wave's wavelength (λ) and its frequency (ν), $\lambda\nu$, is the speed of the wave. Thus, for electromagnetic radiation in a vacuum, speed is equal to the fundamental constant, c:

$$c = 2.998 \times 10^{8} m s^{-1} = \lambda\nu$$

Wavelength and frequency are inversely proportional: As the wavelength increases, the frequency decreases. The inverse proportionality is illustrated in Figure $2.2.2$. This figure also shows the electromagnetic spectrum, the range of all types of electromagnetic radiation. Each of the various colors of visible light has specific frequencies and wavelengths associated with them, and you can see that visible light makes up only a small portion of the electromagnetic spectrum. Because the technologies developed to work in various parts of the electromagnetic spectrum are different, for reasons of convenience and historical legacies, different units are typically used for different parts of the spectrum. For example, radio waves are usually specified as frequencies (typically in units of MHz), while the visible region is usually specified in wavelengths (typically in units of nm or angstroms).

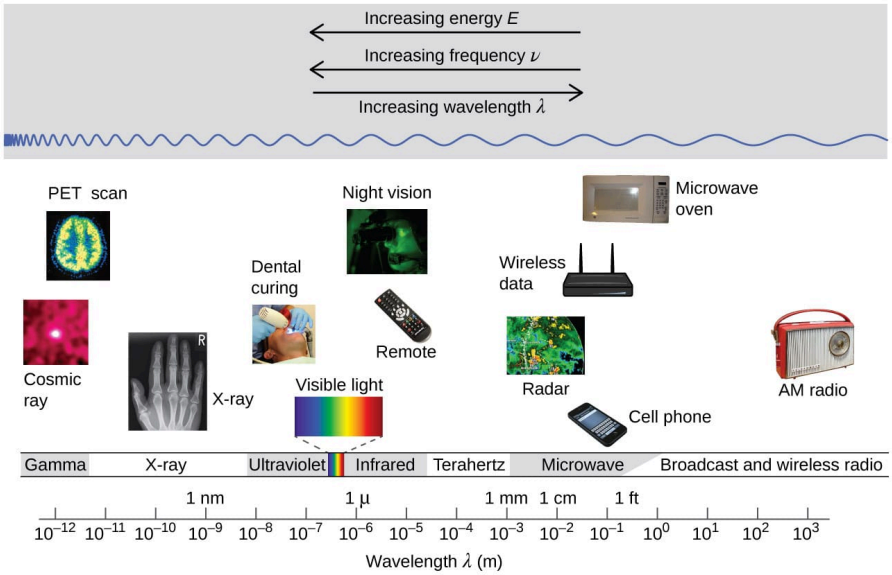


Figure 2.2.2: Portions of the electromagnetic spectrum are shown in order of decreasing frequency and increasing wavelength. (credit “Cosmic ray": modification of work by NASA; credit “PET scan": modification of work by the National Institute of Health; credit “X-ray": modification of work by Dr. Jochen Lengerke; credit “Dental curing": modification of work by the Department of the Navy; credit “Night vision": modification of work by the Department of the Army; credit “Remote": modification of work by Emilian Robert Vicol; credit “Cell phone": modification of work by Brett Jordan; credit “Microwave oven": modification of work by Billy Mabray; credit “Ultrasound": modification of work by Jane Whitney; credit “AM radio": modification of work by Dave Clausen)

Example 2.2.1: Determining the Frequency and Wavelength of Radiation

A sodium streetlight gives off yellow light that has a wavelength of 589 nm (1 nm = 1×10^{-9} m). What is the frequency of this light?

Solution

We can rearrange the Equation $c = \lambda\nu$ to solve for the frequency:

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

Since c is expressed in meters per second, we must also convert 589 nm to meters.

$$\nu = \left(\frac{2.998 \times 10^{8} ms^{-1}}{589 nm}\right)\left(\frac{1 \times 10^{9} nm}{1 m}\right) = 5.09 \times 10^{14} s^{-1}$$

Exercise 2.2.1

One of the frequencies used to transmit and receive cellular telephone signals in the United States is 850 MHz. What is the wavelength in meters of these radio waves?

Answer available at the end of this section.

Chemistry in Everyday Life: Wireless Communication



Figure 2.2.3: Radio and cell towers are typically used to transmit long-wavelength electromagnetic radiation. Increasingly, cell towers are designed to blend in with the landscape, as with the Tucson, Arizona, cell tower (right) disguised as a palm tree. (credit left: modification of work by Sir Mildred Pierce; credit middle: modification of work by M.O. Stevens)

Many valuable technologies operate in the radio (3 kHz-300 GHz) frequency region of the electromagnetic spectrum. At the low frequency (low energy, long wavelength) end of this region are AM (amplitude modulation) radio signals (540-2830 kHz) that can travel long distances. FM (frequency modulation) radio signals are used at higher frequencies (87.5-108.0 MHz). In AM radio, the information is transmitted by varying the amplitude of the wave (Figure 2.2.4). In FM radio, by contrast, the amplitude is constant and the instantaneous frequency varies.

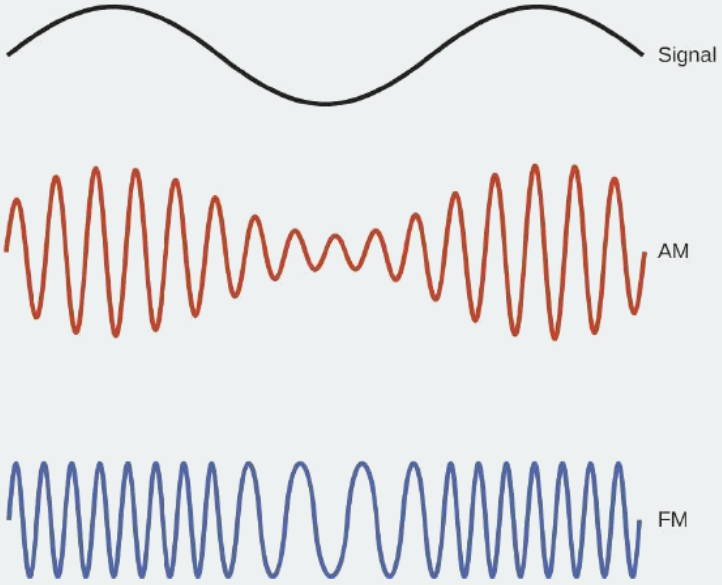


Figure 2.2.4: This schematic depicts how amplitude modulation (AM) and frequency modulation (FM) can be used to transmit a radio wave.

Other technologies also operate in the radio-wave portion of the electromagnetic spectrum. For example, 4G cellular telephone signals are approximately 880 MHz, while Global Positioning System (GPS) signals operate at 1.228 and 1.575 GHz, local area wireless technology (Wi-Fi) networks operate at 2.4 to 5 GHz, and highway toll sensors operate at 5.8 GHz. The frequencies associated with these applications are convenient because such waves tend not to be absorbed much by common building materials.

One particularly characteristic phenomenon of waves results when two or more waves come into contact: They interfere with each other. Figure 2.2.5 shows the interference patterns that arise when light passes through narrow slits closely spaced about a wavelength apart. The fringe patterns produced depend on the wavelength, with the fringes being more closely spaced for shorter wavelength light passing through a given set of slits. When the light passes through the two slits, each slit effectively acts as a new source, resulting in two closely spaced waves coming into contact at the detector (the camera in this case). The dark regions in Figure 2.2.5 correspond to regions where the peaks for the wave from one slit happen to coincide with the troughs for the wave from the other slit (destructive interference), while the brightest regions correspond to the regions where the peaks for the two waves (or their two troughs) happen to coincide (constructive interference). Likewise, when two stones are tossed close together into a pond, interference patterns are visible in the interactions between the waves produced by the stones. Such interference patterns cannot be explained by particles moving according to the laws of classical mechanics.



Figure 2.2.5: Interference fringe patterns are shown for light passing through two closely spaced, narrow slits. The spacing of the fringes depends on the wavelength, with the fringes being more closely spaced for the shorter-wavelength blue light. (credit: PASCO)

Portrait of a Chemist: Dorothy Crowfoot Hodgkin

X-rays exhibit wavelengths of approximately 0.01–10 nm. Since these wavelengths are comparable to the spaces between atoms in a crystalline solid, X-rays are scattered when they pass through crystals. The scattered rays undergo constructive and destructive interference that creates a specific diffraction pattern that may be measured and used to precisely determine the positions of atoms within the crystal. This phenomenon of X-ray diffraction is the basis for very powerful techniques enabling the determination of molecular structure. One of the pioneers who applied this powerful technology to important biochemical substances was Dorothy Crowfoot Hodgkin.

Born in Cairo, Egypt, in 1910 to British parents, Dorothy's fascination with chemistry was fostered early in her life. At age 11 she was enrolled in a prestigious English grammar school where she was one of just two girls allowed to study chemistry. On her 16th birthday, her mother, Molly, gifted her a book on X-ray crystallography, which had a profound impact on the trajectory of her career. She studied chemistry at Oxford University, graduating with first-class honors in 1932 and directly entering Cambridge University to pursue a doctoral degree. At Cambridge, Dorothy recognized the promise of X-ray crystallography for protein structure determinations, conducting research that earned her a PhD in 1937. Over the course of a very productive career, Dr. Hodgkin was credited with determining structures for several important biomolecules, including cholesterol iodide, penicillin, and vitamin B12. In recognition of her achievements in the use of X-ray techniques to elucidate the structures of biochemical substances, she was awarded the 1964 Nobel Prize in Chemistry. In 1969, she led a team of scientists who deduced the structure of insulin, facilitating the mass production of this hormone and greatly advancing the treatment of diabetic patients worldwide. Dr. Hodgkin continued working with the international scientific community, earning numerous distinctions and awards prior to her death in 1993.

Not all waves are travelling waves. Standing waves (also known as stationary waves) remain constrained within some region of space. As we shall see, standing waves play an important role in our understanding of the electronic structure of atoms and molecules. The simplest example of a standing wave is a one-dimensional wave associated with a vibrating string that is held fixed at its two end points. Figure 2.2.6 shows the four lowest-energy standing waves (the fundamental wave and the lowest three harmonics) for a vibrating string at a particular amplitude. Although the string's motion lies mostly within a plane, the wave itself is considered to be one dimensional, since it lies along the length of the string. The motion of string segments in a direction perpendicular to the string length generates the waves and so the amplitude of the waves is visible as the maximum displacement of the curves seen in Figure 2.2.6. The key observation from the figure is *that only those waves having an integer number, n, of half-wavelengths between the end points can form*. A system with fixed end points such as this restricts the number and type of the possible waveforms. This is an example of **quantization**, in which only discrete values from a more general set of continuous values of some property are observed. Another important observation is that the harmonic waves (those waves displaying more than one-half wavelength) all have one or more points between the two end points that are not in motion. These special points are **nodes**. The energies of the standing waves with a given amplitude in a vibrating string increase with the number of half-

wavelengths n. Since the number of nodes is $n–1$, the energy can also be said to depend on the number of nodes, generally increasing as the number of nodes increases.

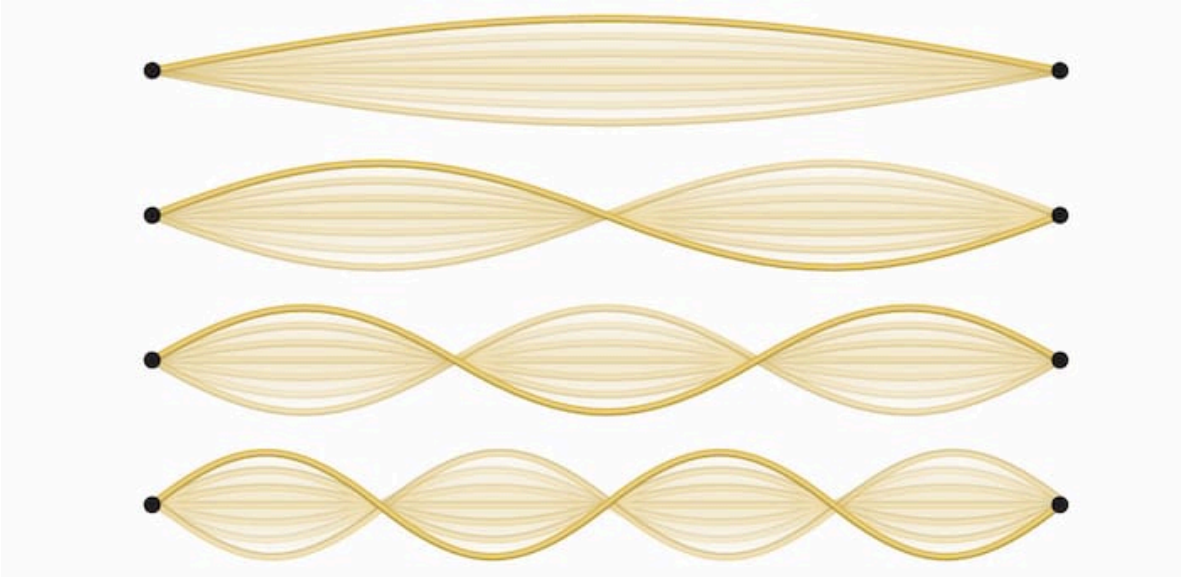


Figure 2.2.6: A vibrating string shows some one-dimensional standing waves. Since the two end points of the string are held fixed, only waves having an integer number of half-wavelengths can form. The points on the string between the end points that are not moving are called the nodes.

An example of two-dimensional standing waves is shown in Figure 2.2.7, which shows the vibrational patterns on a flat surface. Although the vibrational amplitudes cannot be seen like they could in the vibrating string, the nodes have been made visible by sprinkling the drum surface with a powder that collects on the areas of the surface that have minimal displacement. For one-dimensional standing waves, the nodes were points on the line, but for two-dimensional standing waves, the nodes are lines on the surface (for three-dimensional standing waves, the nodes are two-dimensional surfaces within the three-dimensional volume).

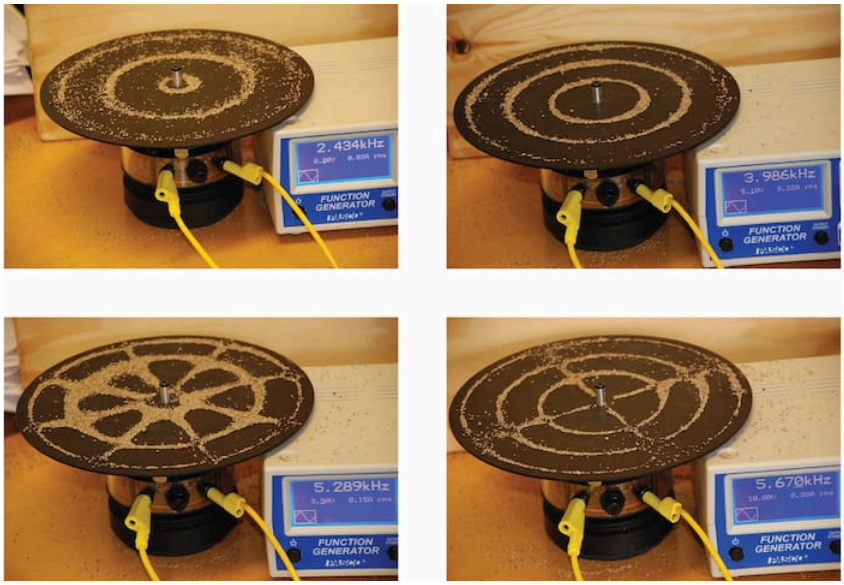


Figure 2.2.7: Two-dimensional standing waves can be visualized on a vibrating surface. The surface has been sprinkled with a powder that collects near the nodal lines. There are two types of nodes visible: radial nodes (circles) and angular nodes (radii).

Link to Learning

You can watch the formation of various radial nodes here as singer Imogen Heap projects her voice across a kettle drum.

Blackbody Radiation and the Ultraviolet Catastrophe

The last few decades of the nineteenth century witnessed intense research activity in commercializing newly discovered electric lighting. This required obtaining a better understanding of the distributions of light emitted from various sources being considered. Artificial lighting is usually designed to mimic natural sunlight within the limitations of the underlying technology. Such lighting consists of a range of broadly distributed frequencies that form a **continuous spectrum**. Figure 2.2.8 shows the wavelength distribution for sunlight. The most intense radiation is in the visible region, with the intensity dropping off rapidly for shorter wavelength ultraviolet (UV) light, and more slowly for longer wavelength infrared (IR) light.

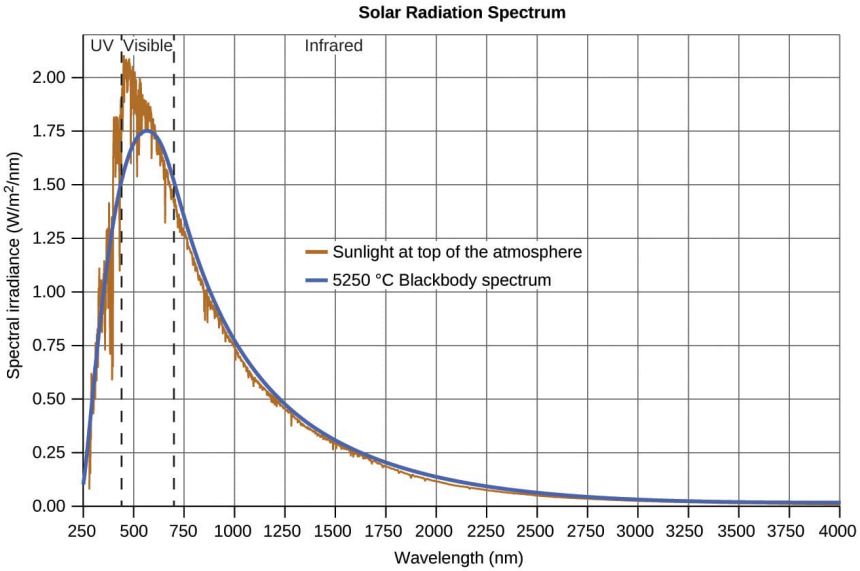


Figure 2.2.8: The spectral distribution (light intensity vs. wavelength) of sunlight reaches the Earth's atmosphere as UV light, visible light, and IR light. The unabsorbed sunlight at the top of the atmosphere has a distribution that approximately matches the theoretical distribution of a blackbody at 5250 °C, represented by the blue curve. (credit: modification of work by American Society for Testing and Materials (ASTM) Terrestrial Reference Spectra for Photovoltaic Performance Evaluation)

In Figure 2.2.8, the solar distribution is compared to a representative distribution, called a **blackbody spectrum**, that corresponds to a temperature of 5250 °C. The blackbody spectrum matches the solar spectrum quite well. A blackbody is a convenient, ideal emitter that approximates the behavior of many materials when heated. It is “ideal” in the same sense that an ideal gas is a convenient, simple representation of real gases that works well, provided that the pressure is not too high nor the temperature too low. A good approximation of a blackbody that can be used to observe blackbody radiation is a metal oven that can be heated to very high temperatures. The oven has a small hole allowing for the light being emitted within the oven to be observed with a spectrometer so that the wavelengths and their intensities can be measured. Figure 2.2.9 shows the resulting curves for some representative temperatures. Each distribution depends only on a single parameter: the temperature. The maxima in the blackbody curves, λ_{max}, shift to shorter wavelengths as the temperature increases, reflecting the observation that metals being heated to high temperatures begin to glow a darker red that becomes brighter as the temperature increases, eventually becoming white hot at very high temperatures as the intensities of all of the visible wavelengths become appreciable. This common observation was at the heart of the first paradox that showed the fundamental limitations of classical physics that we will examine.Physicists derived mathematical expressions for the blackbody curves using well-accepted concepts from the theories of classical mechanics and classical electromagnetism. The theoretical expressions as functions of temperature fit the observed experimental blackbody curves well at longer wavelengths, but showed significant discrepancies at shorter wavelengths. Not only did the theoretical curves not show a peak, they absurdly showed the intensity becoming infinitely large as the wavelength became smaller, which would imply that everyday objects at room temperature should be emitting large amounts of UV light. This became known as the “ultraviolet catastrophe” because no one could find any problems with the theoretical treatment that could lead to such unrealistic short-wavelength behavior. Finally, around 1900, Max Planck derived a theoretical expression for blackbody radiation that fit the experimental observations exactly (within experimental error). Planck developed his theoretical treatment by extending the earlier work that had been based on the premise that the atoms composing the oven vibrated at increasing frequencies (or decreasing wavelengths) as the temperature increased, with these vibrations being the source of the emitted electromagnetic radiation. But where the earlier treatments had allowed the vibrating atoms to have any energy values obtained from a continuous set of energies (perfectly reasonable, according to classical physics), Planck found that by restricting the vibrational energies to discrete values for each frequency, he could derive an expression for blackbody radiation that correctly

had the intensity dropping rapidly for the short wavelengths in the UV region.

$$E = nh\nu, n = 1, 2, 3, ... \tag{2.2.1}$$

The quantity h is a constant now known as **Planck's constant**, in his honor. Although Planck was pleased he had resolved the blackbody radiation paradox, he was disturbed that to do so, he needed to assume the vibrating atoms required quantized energies, which he was unable to explain. The value of Planck's constant is very small, 6.626 10^{-34} joule seconds (J s), which helps explain why energy quantization had not been observed previously in macroscopic phenomena.

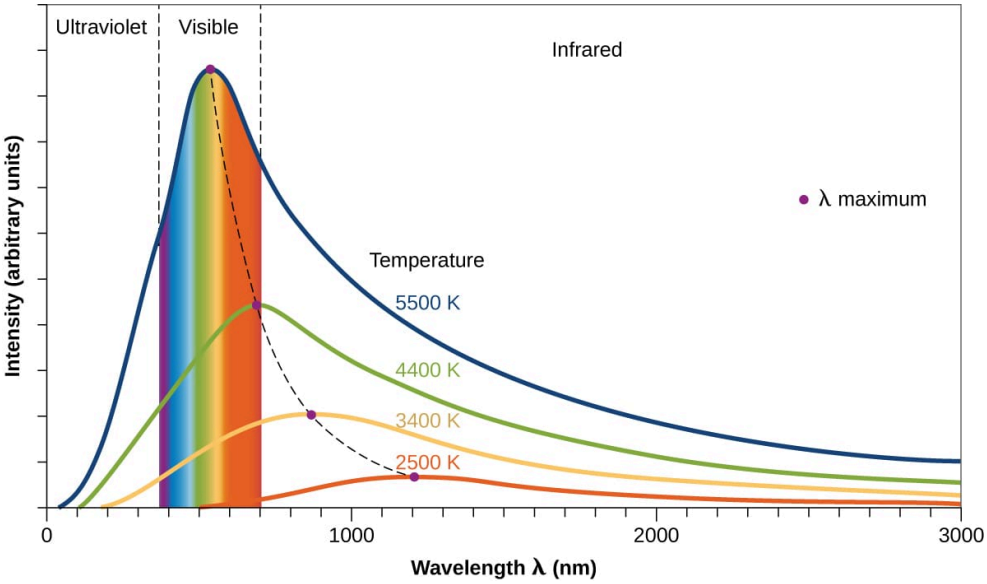


Figure 2.2.9: Blackbody spectral distribution curves are shown for some representative temperatures.

The Photoelectric Effect

The next paradox in the classical theory to be resolved concerned the photoelectric effect (Figure 2.2.10). It had been observed that electrons could be ejected from the clean surface of a metal when light having a frequency greater than some threshold frequency was shone on it. Surprisingly, the kinetic energy of the ejected electrons did not depend on the brightness of the light, but increased with increasing frequency of the light. Since the electrons in the metal had a certain amount of binding energy keeping them there, the incident light needed to have more energy to free the electrons. According to classical wave theory, a wave's energy depends on its intensity (which depends on its amplitude), not its frequency. One part of these observations was that the number of electrons ejected within in a given time period was seen to increase as the brightness increased. In 1905, Albert Einstein was able to resolve the paradox by incorporating Planck's quantization findings into the discredited particle view of light (Einstein actually won his Nobel prize for this work, and not for his theories of relativity for which he is most famous).

Einstein argued that the quantized energies that Planck had postulated in his treatment of blackbody radiation could be applied to the light in the photoelectric effect so that the light striking the metal surface should not be viewed as a wave, but instead as a stream of particles (later called **photons**) whose energy depended on their frequency, according to Planck's formula (Equation 2.2.1), $E = h\nu$ (or, in terms of wavelength using $c = \nu\lambda$, $E = \frac{hc}{\lambda}$). Electrons were ejected when hit by photons having sufficient energy (a frequency greater than the threshold). The greater the frequency, the greater the kinetic energy imparted to the escaping electrons by the collisions. Einstein also argued that the light intensity did not depend on the amplitude of the incoming wave, but instead corresponded to the number of photons striking the surface within a given time period. This explains why the number of ejected electrons increased with increasing brightness, since the greater the number of incoming photons, the greater the likelihood that they would collide with some of the electrons.

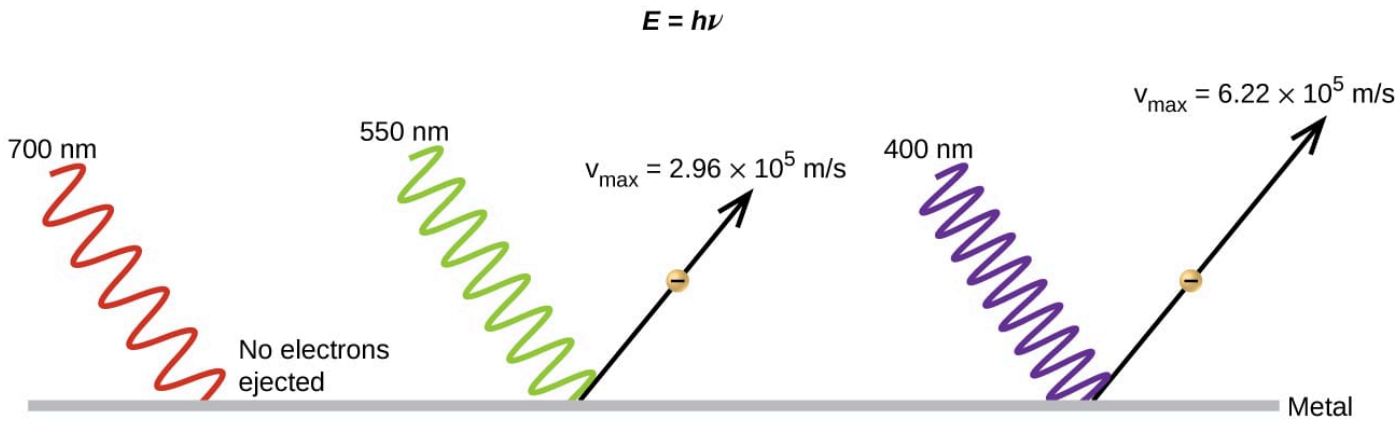


Figure 2.2.10: Photons with low frequencies do not have enough energy to cause electrons to be ejected via the photoelectric effect. For any frequency of light above the threshold frequency, the kinetic energy of an ejected electron will increase linearly with the energy of the incoming photon.

With Einstein's findings, the nature of light took on a new air of mystery. Although many light phenomena could be explained either in terms of waves or particles, certain phenomena, such as the interference patterns obtained when light passed through a double slit, were completely contrary to a particle view of light, while other phenomena, such as the photoelectric effect, were completely contrary to a wave view of light. Somehow, at a deep fundamental level still not fully understood, light is both wavelike and particle-like. This is known as **wave-particle duality**.

Example 2.2.2: Calculating the Energy of Radiation

When we see light from a neon sign, we are observing radiation from excited neon atoms. If this radiation has a wavelength of 640 nm, what is the energy of the photon being emitted?

Solution

We use the part of Planck's equation that includes the wavelength, λ, and convert units of nanometers to meters so that the units of λ and c are the same.

$$\begin{aligned} E &= \frac{hc}{\lambda} \\ &= \frac{\left(6.626 \times 10^{-34}\ \text{J}\cdot\cancel{\text{s}}\right)\left(2.998 \times 10^{8}\ \cancel{\text{m}}\ \cancel{\text{s}}^{-1}\right)}{\left(640\ \cancel{\text{nm}}\right)\left(\frac{1\ \cancel{\text{m}}}{10^{9}\ \cancel{\text{nm}}}\right)} \\ &= 3.10 \times 10^{-19} J \end{aligned}$$

Exercise 2.2.2

The microwaves in an oven are of a specific frequency that will heat the water molecules contained in food. (This is why most plastics and glass do not become hot in a microwave oven-they do not contain water molecules.) This frequency is about 3 10^9 Hz. What is the energy of one photon in these microwaves?

Answer available at the end of this section.

Link to Learning

Use this simulation program to experiment with the photoelectric effect to see how intensity, frequency, type of metal, and other factors influence the ejected photons.

Example 2.2.3: Photoelectric Effect

Identify which of the following statements are false and, where necessary, change the italicized word or phrase to make them true, consistent with Einstein's explanation of the photoelectric effect.

a. Increasing the brightness of incoming light *increases* the kinetic energy of the ejected electrons.
b. Increasing the *wavelength* of incoming light increases the kinetic energy of the ejected electrons.
c. Increasing the brightness of incoming light *increases* the number of ejected electrons.
d. Increasing the *frequency* of incoming light can increase the number of ejected electrons.

Solution

a. False. Increasing the brightness of incoming light *has no effect* on the kinetic energy of the ejected electrons. Only energy, not the number or amplitude, of the photons influences the kinetic energy of the electrons.
b. False. Increasing the *frequency* of incoming light increases the kinetic energy of the ejected electrons. Frequency is proportional to energy and inversely proportional to wavelength. Frequencies above the threshold value transfer the excess energy into the kinetic energy of the electrons.
c. True. Because the number of collisions with photons increases with brighter light, the number of ejected electrons increases.
d. True with regard to the threshold energy binding the electrons to the metal. Below this threshold, electrons are not emitted and above it they are. Once over the threshold value, further increasing the frequency does not increase the number of ejected electrons

Exercise 2.2.3

Calculate the threshold energy in kJ/mol of electrons in aluminum, given that the lowest frequency photon for which the photoelectric effect is observed is $9.87\ 10^{14}$ Hz.

Answer available at the end of this section.

Line Spectra

Another paradox within the classical electromagnetic theory that scientists in the late nineteenth century struggled with concerned the light emitted from atoms and molecules. When solids, liquids, or condensed gases are heated sufficiently, they radiate some of the excess energy as light. Photons produced in this manner have a range of energies, and thereby produce a continuous spectrum in which an unbroken series of wavelengths is present. Most of the light generated from stars (including our sun) is produced in this fashion. You can see all the visible wavelengths of light present in sunlight by using a prism to separate them. As can be seen in Figure 2.2.8: , sunlight also contains UV light (shorter wavelengths) and IR light (longer wavelengths) that can be detected using instruments but that are invisible to the human eye. Incandescent (glowing) solids such as tungsten filaments in incandescent lights also give off light that contains all wavelengths of visible light. These continuous spectra can often be approximated by blackbody radiation curves at some appropriate temperature, such as those shown in Figure 2.2.9.

In contrast to continuous spectra, light can also occur as discrete or **line spectra** having very narrow line widths interspersed throughout the spectral regions such as those shown in Figure 2.2.12. Exciting a gas at low partial pressure using an electrical current, or heating it, will produce line spectra. Fluorescent light bulbs and neon signs operate in this way (Figure 2.2.11). Each element displays its own characteristic set of lines, as do molecules, although their spectra are generally much more complicated.



Figure 2.2.11: Neon signs operate by exciting a gas at low partial pressure using an electrical current. This sign shows the elaborate artistic effects that can be achieved. (credit: Dave Shaver)

Each emission line consists of a single wavelength of light, which implies that the light emitted by a gas consists of a set of discrete energies. For example, when an electric discharge passes through a tube containing hydrogen gas at low pressure, the H_2 molecules are broken apart into separate H atoms and we see a blue-pink color. Passing the light through a prism produces a line spectrum, indicating that this light is composed of photons of four visible wavelengths, as shown in Figure 2.2.12.

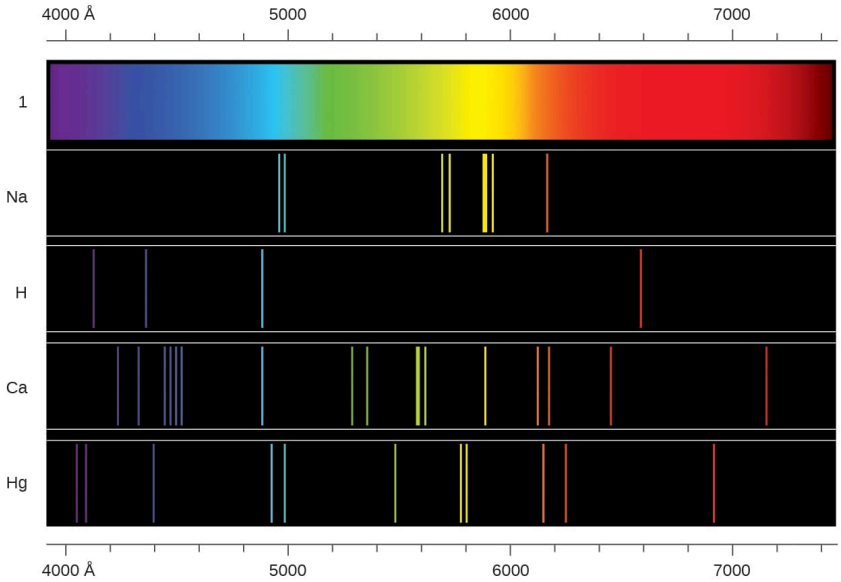


Figure 2.2.12: Compare the two types of emission spectra: continuous spectrum of white light (top) and the line spectra of the light from excited sodium, hydrogen, calcium, and mercury atoms.

The origin of discrete spectra in atoms and molecules was extremely puzzling to scientists in the late nineteenth century, since according to classical electromagnetic theory, only continuous spectra should be observed. Even more puzzling, in 1885, Johann Balmer was able to derive an empirical equation that related the four visible wavelengths of light emitted by hydrogen atoms to whole integers. That equation is the following one, in which *k* is a constant:

$$\frac{1}{\lambda} = k\left(\frac{1}{4} - \frac{1}{n^2}\right), \quad n = 3, 4, 5, 6$$

Other discrete lines for the hydrogen atom were found in the UV and IR regions. Johannes Rydberg generalized Balmer's work and developed an empirical formula that predicted all of hydrogen's emission lines, not just those restricted to the visible range,

where n_1 and n_2 are integers, $n_1 < n_2$, and R_∞ is the **Rydberg constant** (1.097×10^7 m^{-1}).

$$\frac{1}{\lambda} = R_\infty \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Even in the late nineteenth century, spectroscopy was a very precise science, and so the wavelengths of hydrogen were measured to very high accuracy, which implied that the Rydberg constant could be determined very precisely as well. That such a simple formula as the Rydberg formula could account for such precise measurements seemed astounding at the time, but it was the eventual explanation for emission spectra by Neils Bohr in 1913 that ultimately convinced scientists to abandon classical physics and spurred the development of modern quantum mechanics.

Answers

Exercise 2.2.1

0.353 m = 35.3 cm

Exercise 2.2.2

2×10^{-24} J

Exercise 2.2.3

394 kJ/mol

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2.3: The Bohr Model

Learning Objectives

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

- Describe the Bohr model of the hydrogen atom
- Use the Rydberg equation to calculate energies of light emitted or absorbed by hydrogen atoms

Following the work of Ernest Rutherford and his colleagues in the early twentieth century, the picture of atoms consisting of tiny dense nuclei surrounded by lighter and even tinier electrons continually moving about the nucleus was well established. This picture was called the planetary model, since it pictured the atom as a miniature "solar system" with the electrons orbiting the nucleus like planets orbiting the sun. The simplest atom is hydrogen, consisting of a single proton as the nucleus about which a single electron moves. The electrostatic force attracting the electron to the proton depends only on the distance between the two particles. This classical mechanics description of the atom is incomplete, however, since an electron moving in an elliptical orbit would be accelerating (by changing direction) and, according to classical electromagnetism, it should continuously emit electromagnetic radiation. This loss in orbital energy should result in the electron's orbit getting continually smaller until it spirals into the nucleus, implying that atoms are inherently unstable.

In 1913, Niels Bohr attempted to resolve the atomic paradox by ignoring classical electromagnetism's prediction that the orbiting electron in hydrogen would continuously emit light. Instead, he incorporated into the classical mechanics description of the atom Planck's ideas of quantization and Einstein's finding that light consists of photons whose energy is proportional to their frequency. Bohr assumed that the electron orbiting the nucleus would not normally emit any radiation (the stationary state hypothesis), but it would emit or absorb a photon if it moved to a different orbit. The energy absorbed or emitted would reflect differences in the orbital energies according to this equation:

$$|\Delta E| = |E_f - E_i| = h\nu = \frac{hc}{\lambda}$$

In this equation, h is Planck's constant and E_i and E_f are the initial and final orbital energies, respectively. The absolute value of the energy difference is used, since frequencies and wavelengths are always positive. Instead of allowing for continuous values of energy, Bohr assumed the energies of these electron orbitals were quantized:

$$E_n = -\frac{k}{n^2}, n = 1, 2, 3, ...$$

In this expression, *k* is a constant comprising fundamental constants such as the electron mass and charge and Planck's constant. Inserting the expression for the orbit energies into the equation for ΔE gives

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

or

$$\frac{1}{\lambda} = \frac{k}{hc}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

which is identical to the Rydberg equation in which

$$R_\infty = \frac{k}{hc}$$

When Bohr calculated his theoretical value for the Rydberg constant, R_∞, and compared it with the experimentally accepted value, he got excellent agreement. Since the Rydberg constant was one of the most precisely measured constants at that time, this level of agreement was astonishing and meant that Bohr's model was taken seriously, despite the many assumptions that Bohr needed to derive it.

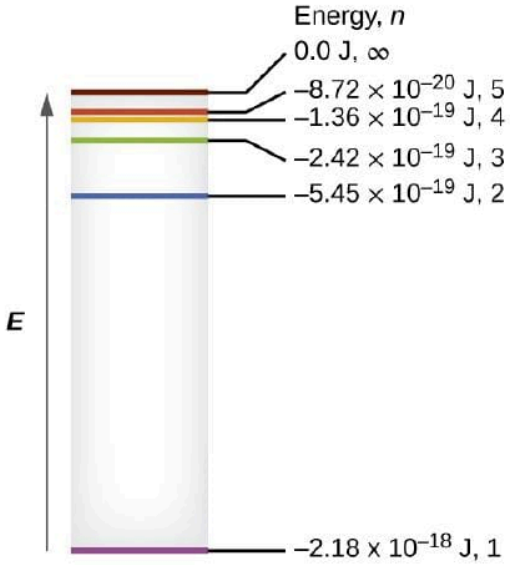


Figure 2.3.1: Quantum numbers and energy levels in a hydrogen atom. The more negative the calculated value, the lower the energy.

The lowest few energy levels are shown in Figure 2.3.1. One of the fundamental laws of physics is that matter is most stable with the lowest possible energy. Thus, the electron in a hydrogen atom usually moves in the n = 1 orbit, the orbit in which it has the lowest energy. When the electron is in this lowest energy orbit, the atom is said to be in its ground electronic state (or simply ground state). If the atom receives energy from an outside source, it is possible for the electron to move to an orbit with a higher n value and the atom is now in an excited electronic state (or simply an excited state) with a higher energy. When an electron transitions from an excited state (higher energy orbit) to a less excited state, or ground state, the difference in energy is emitted as a photon. Similarly, if a photon is absorbed by an atom, the energy of the photon moves an electron from a lower energy orbit up to a more excited one. We can relate the energy of electrons in atoms to what we learned previously about energy. The law of conservation of energy says that we can neither create nor destroy energy. Thus, if a certain amount of external energy is required to excite an electron from one energy level to another, that same amount of energy will be liberated when the electron returns to its initial state (Figure 2.3.2).

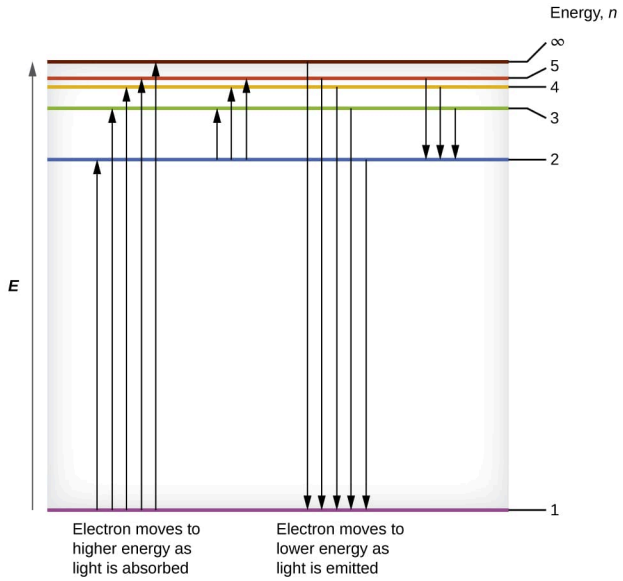


Figure 2.3.2: The horizontal lines show the relative energy of orbits in the Bohr model of the hydrogen atom, and the vertical arrows depict the energy of photons absorbed (left) or emitted (right) as electrons move between these orbits.

Since Bohr's model involved only a single electron, it could also be applied to the single electron ions He^{+}, Li^{2+}, Be^{3+}, and so forth, which differ from hydrogen only in their nuclear charges, and so one-electron atoms and ions are collectively referred to as hydrogen-like atoms. The energy expression for hydrogen-like atoms is a generalization of the hydrogen atom energy, in which Z

is the nuclear charge (+1 for hydrogen, +2 for He, +3 for Li, and so on) and *k* has a value of 2.179 10^{-18} J.

$$E_n = -\frac{kZ^2}{n^2} \tag{2.3.1}$$

The sizes of the circular orbits for hydrogen-like atoms are given in terms of their radii by the following expression, in which r is a constant called the **Bohr radius**, with a value of 5.292 10^{-11} m:

$$r = \frac{n^2}{Z} a_0$$

The equation also shows us that as the electron's energy increases (as n increases), the electron is found at greater distances from the nucleus. This is implied by the inverse dependence of electrostatic attraction on distance, since, as the electron moves away from the nucleus, the electrostatic attraction between it and the nucleus decreases and it is held less tightly in the atom. Note that as n gets larger and the orbits get larger, their energies get closer to zero, and so the limits $n \rightarrow \infty$ and $r \rightarrow \longrightarrow \infty$ imply that $E = 0$ corresponds to the ionization limit where the electron is completely removed from the nucleus. Thus, for hydrogen in the ground state n = 1, the ionization energy would be:

$$\Delta E = E_{n \longrightarrow \infty} - E_1 = 0 + k = k$$

With three extremely puzzling paradoxes now solved (blackbody radiation, the photoelectric effect, and the hydrogen atom), and all involving Planck's constant in a fundamental manner, it became clear to most physicists at that time that the classical theories that worked so well in the macroscopic world were fundamentally flawed and could not be extended down into the microscopic domain of atoms and molecules. Unfortunately, despite Bohr's remarkable achievement in deriving a theoretical expression for the Rydberg constant, he was unable to extend his theory to the next simplest atom, He, which only has two electrons. Bohr's model was severely flawed, since it was still based on the classical mechanics notion of precise orbits, a concept that was later found to be untenable in the microscopic domain, when a proper model of quantum mechanics was developed to supersede classical mechanics.

Example 2.3.1: Calculating the Energy of an Electron in a Bohr Orbit

Early researchers were very excited when they were able to predict the energy of an electron at a particular distance from the nucleus in a hydrogen atom. If a spark promotes the electron in a hydrogen atom into an orbit with *n* = 3, what is the calculated energy, in joules, of the electron?

Solution

The energy of the electron is given by Equation 2.3.1:

$$E = \frac{-kZ^2}{n^2}$$

The atomic number, Z, of hydrogen is 1; *k* = 2.179 10^{-18} J; and the electron is characterized by an n value of 3. Thus,

$$E = \frac{-\left(2.179 \times 10^{-18} J\right) \times (1)^2}{(3)^2} = -2.421 \times 10^{-19} J$$

Exercise 2.3.1

The electron in Figure 2.3.2 is promoted even further to an orbit with $n = 6$. What is its new energy?

Answer available at the end of this section.

Example 2.3.2: Calculating the Energy and Wavelength of Electron Transitions in a One-electron (Bohr) System

What is the energy (in joules) and the wavelength (in meters) of the line in the spectrum of hydrogen that represents the movement of an electron from Bohr orbit with $n = 4$ to the orbit with $n = 6$? In what part of the electromagnetic spectrum do we find this radiation?

Solution

In this case, the electron starts out with $n = 4$, so $n_1 = 4$. It comes to rest in the $n = 6$ orbit, so $n_2 = 6$. The difference in energy between the two states is given by this expression:

$$\begin{aligned}\Delta E &= E_1 - E_2 \\ &= 2.179 \times 10^{-18}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \\ &= 2.179 \times 10^{-18}\left(\frac{1}{4^2} - \frac{1}{6^2}\right) J \\ &= 2.179 \times 10^{-18}\left(\frac{1}{16} - \frac{1}{36}\right) J \\ &= 7.566 \times 10^{-20} J\end{aligned}$$

This energy difference is positive, indicating a photon enters the system (is absorbed) to excite the electron from the *n* = 4 orbit up to the *n* = 6 orbit. The wavelength of a photon with this energy is found by the expression $E = \frac{hc}{\lambda}$. Rearrangement gives:

$$\begin{aligned}\lambda &= \frac{hc}{E} \\ &= \left(6.626 \times 10^{-34}\ \cancel{\text{J} \cdot \text{s}}\right) \times \frac{2.998 \times 10^{8}\ \text{m}\ \cancel{s^{-1}}}{7.566 \times 10^{-20}\ \cancel{J}} \\ &= 2.626 \times 10^{-6}\ \text{m}\end{aligned}$$

From the illustration of the electromagnetic spectrum in Electromagnetic Energy, we can see that this wavelength is found in the infrared portion of the electromagnetic spectrum.

Exercise 2.3.2

What is the energy in joules and the wavelength in meters of the photon produced when an electron falls from the *n* = 5 to the *n* = 3 level in a He^+ ion (*Z* = 2 for He^+)?

Answer available at the end of this section.

Bohr's model of the hydrogen atom provides insight into the behavior of matter at the microscopic level, but it does not account for electron–electron interactions in atoms with more than one electron. It does introduce several important features of all models used to describe the distribution of electrons in an atom. These features include the following:

- The energies of electrons (energy levels) in an atom are quantized, described by quantum numbers: integer numbers having only specific allowed value and used to characterize the arrangement of electrons in an atom.
- An electron's energy increases with increasing distance from the nucleus.
- The discrete energies (lines) in the spectra of the elements result from quantized electronic energies.

Of these features, the most important is the postulate of quantized energy levels for an electron in an atom. As a consequence, the model laid the foundation for the quantum mechanical model of the atom. Bohr won a Nobel Prize in Physics for his contributions to our understanding of the structure of atoms and how that is related to line spectra emissions.

Answers

Exercise 2.3.1

$-6.053\ 10^{-20}$ J

Exercise 2.3.2

$6.198\ 10^{-19}$ J; $3.205\ 10^{-7}$ m

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2.4: Development of Quantum Theory

Learning Objectives

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

- Extend the concept of wave–particle duality that was observed in electromagnetic radiation to matter as well
- Understand the general idea of the quantum mechanical description of electrons in an atom, and that it uses the notion of three-dimensional wave functions, or orbitals, that define the distribution of probability to find an electron in a particular part of space
- List and describe traits of the four quantum numbers that form the basis for completely specifying the state of an electron in an atom

Bohr's model explained the experimental data for the hydrogen atom and was widely accepted, but it also raised many questions. Why did electrons orbit at only fixed distances defined by a single quantum number n = 1, 2, 3, and so on, but never in between? Why did the model work so well describing hydrogen and one-electron ions, but could not correctly predict the emission spectrum for helium or any larger atoms? To answer these questions, scientists needed to completely revise the way they thought about matter.

Behavior in the Microscopic World

We know how matter behaves in the macroscopic world—objects that are large enough to be seen by the naked eye follow the rules of classical physics. A billiard ball moving on a table will behave like a particle: It will continue in a straight line unless it collides with another ball or the table cushion, or is acted on by some other force (such as friction). The ball has a well-defined position and velocity (or a well-defined momentum, $p = mv$, defined by mass m and velocity v) at any given moment. In other words, the ball is moving in a classical trajectory. This is the typical behavior of a classical object.

When waves interact with each other, they show interference patterns that are not displayed by macroscopic particles such as the billiard ball. For example, interacting waves on the surface of water can produce interference patterns similar to those shown on Figure 2.4.1. This is a case of wave behavior on the macroscopic scale, and it is clear that particles and waves are very different phenomena in the macroscopic realm.

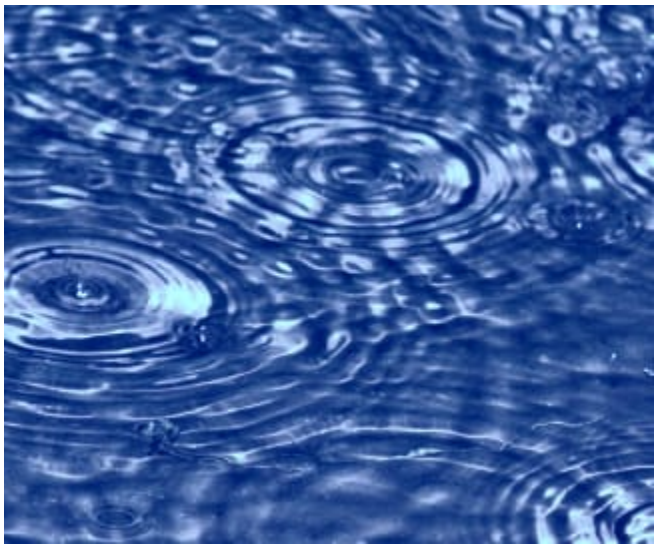


Figure 2.4.1: An interference pattern on the water surface is formed by interacting waves. The waves are caused by reflection of water from the rocks. (credit: modification of work by Sukanto Debnath)

As technological improvements allowed scientists to probe the microscopic world in greater detail, it became increasingly clear

by the 1920s that very small pieces of matter follow a different set of rules from those we observe for large objects. The unquestionable separation of waves and particles was no longer the case for the microscopic world.

One of the first people to pay attention to the special behavior of the microscopic world was Louis de Broglie. He asked the question: If electromagnetic radiation can have particle-like character, can electrons and other submicroscopic particles exhibit wavelike character? In his 1925 doctoral dissertation, de Broglie extended the wave–particle duality of light that Einstein used to resolve the photoelectric-effect paradox to material particles. He predicted that a particle with mass m and velocity v (that is, with linear momentum p) should also exhibit the behavior of a wave with a wavelength value λ, given by this expression in which h is the familiar Planck's constant:

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

This is called the **de Broglie wavelength**. Unlike the other values of λ discussed in this chapter, the de Broglie wavelength is a characteristic of particles and other bodies, not electromagnetic radiation (note that this equation involves velocity [v, m/s], not frequency [ν, Hz]. Although these two symbols appear nearly identical, they mean very different things). Where Bohr had postulated the electron as being a particle orbiting the nucleus in quantized orbits, de Broglie argued that Bohr's assumption of quantization can be explained if the electron is considered not as a particle, but rather as a circular standing wave such that only an integer number of wavelengths could fit exactly within the orbit (Figure 2.4.2).

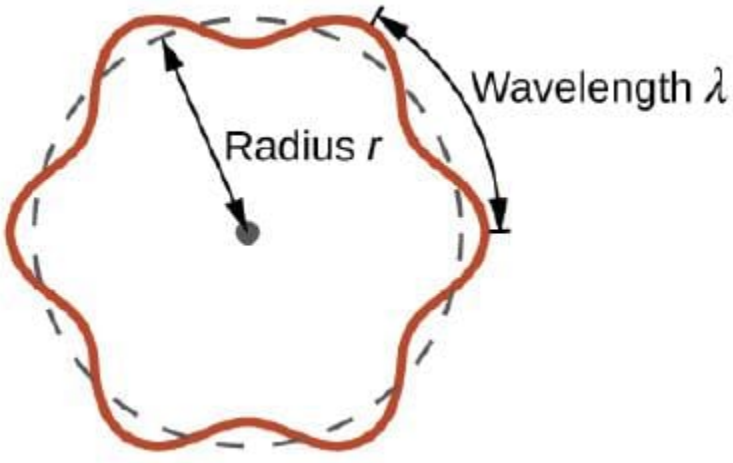


Figure 2.4.2: If an electron is viewed as a wave circling around the nucleus, an integer number of wavelengths must fit into the orbit for this standing wave behavior to be possible.

For a circular orbit of radius r, the circumference is $2\pi r$, and so de Broglie's condition is:

$$2\pi r = n\lambda, \qquad n = 1, 2, 3, \ldots$$

Shortly after de Broglie proposed the wave nature of matter, two scientists at Bell Laboratories, C. J. Davisson and L. H. Germer, demonstrated experimentally that electrons can exhibit wavelike behavior by showing an interference pattern for electrons travelling through a regular atomic pattern in a crystal. The regularly spaced atomic layers served as slits, as used in other interference experiments. Since the spacing between the layers serving as slits needs to be similar in size to the wavelength of the tested wave for an interference pattern to form, Davisson and Germer used a crystalline nickel target for their "slits," since the spacing of the atoms within the lattice was approximately the same as the de Broglie wavelengths of the electrons that they used. Figure 2.4.3 shows an interference pattern. It is strikingly similar to the interference patterns for light shown in Electromagnetic Energy for light passing through two closely spaced, narrow slits. The wave–particle duality of matter can be seen in Figure 2.4.3 by observing what happens if electron collisions are recorded over a long period of time. Initially, when only a few electrons have been recorded, they show clear particle-like behavior, having arrived in small localized packets that appear to be random. As more and more electrons arrived and were recorded, a clear interference pattern that is the hallmark of wavelike behavior emerged. Thus, it appears that while electrons are small localized particles, their motion does not follow the equations of motion implied by classical mechanics, but instead it is governed by some type of a wave equation. Thus the wave–particle duality first observed with photons is actually a fundamental behavior intrinsic to all quantum particles.

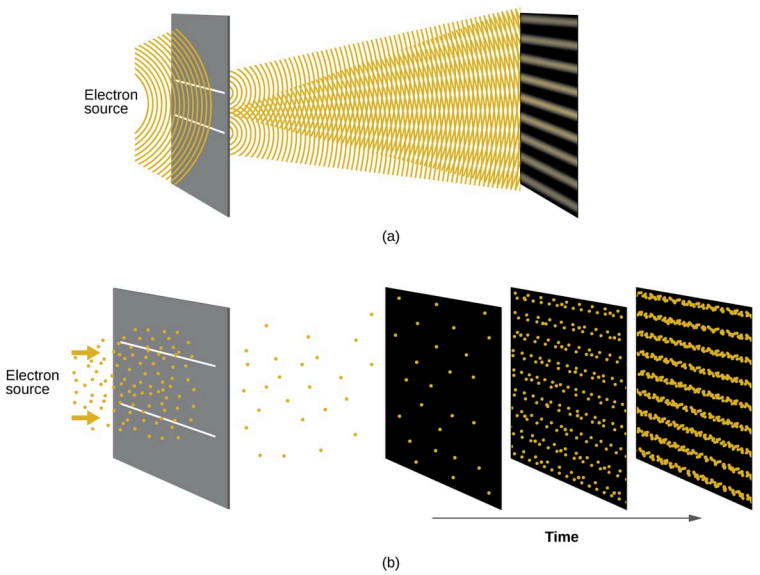


Figure 2.4.3: (a) The interference pattern for electrons passing through very closely spaced slits demonstrates that quantum particles such as electrons can exhibit wavelike behavior. (b) The experimental results illustrated here demonstrate the wave–particle duality in electrons.

Link to Learning

View the Dr. Quantum – Double Slit Experiment cartoon for an easy-to-understand description of wave–particle duality and the associated experiments.

Example 2.4.1: Calculating the Wavelength of a Particle

If an electron travels at a velocity of $1.000 \times 10^7\ \text{m s}^{-1}$ and has a mass of $9.109 \times 10^{-28}\ \text{g}$, what is its wavelength?

Solution

We can use de Broglie's equation to solve this problem, but we first must do a unit conversion of Planck's constant. You learned earlier that $1\ \text{J} = 1\text{kg m}^2/\text{s}^2$. Thus, we can write $h = 6.626 \times 10^{-34}\ \text{J} \cdot \text{s}$ as $6.626 \times 10^{-34}\ \text{kg m}^2/\text{s}$.

$$\begin{aligned}\lambda &= \frac{h}{mv} \\ &= \frac{6.626 \times 10^{-34}\,\text{kg m}^2/\text{s}}{\left(9.109 \times 10^{-31}\,\text{kg}\right)\left(1.000 \times 10^7\,\text{m/s}\right)} \\ &= 7.274 \times 10^{-11} m\end{aligned}$$

This is a small value, but it is significantly larger than the size of an electron in the classical (particle) view. This size is the same order of magnitude as the size of an atom. This means that electron wavelike behavior is going to be noticeable in an atom.

Exercise 2.4.1

Calculate the wavelength of a softball with a mass of 100 g traveling at a velocity of 35 m s^{-1}, assuming that it can be modeled as a single particle.

Answer available at the end of this section.

Werner Heisenberg considered the limits of how accurately we can measure properties of an electron or other microscopic

particles. He determined that there is a fundamental limit to how accurately one can measure both a particle's position and its momentum simultaneously. The more accurately we measure the momentum of a particle, the less accurately we can determine its position at that time, and vice versa. This is summed up in what we now call the Heisenberg uncertainty principle: *It is fundamentally impossible to determine simultaneously and exactly both the momentum and the position of a particle*. For a particle of mass \(*m*\) moving with velocity v_x in the x direction (or equivalently with momentum p_x), the product of the uncertainty in the position, Δx, and the uncertainty in the momentum, Δp_x, must be greater than or equal to $\hbar/2$ (where $\hbar = h/2$, the value of Planck's constant divided by 2π).

$$\Delta x \times \Delta p_x = (\Delta x)(m\Delta v) \geq \frac{\hbar}{2}$$

This equation allows us to calculate the limit to how precisely we can know both the simultaneous position of an object and its momentum. For example, if we improve our measurement of an electron's position so that the uncertainty in the position (Δx) has a value of, say, 1 pm (10^{-12} m, about 1% of the diameter of a hydrogen atom), then our determination of its momentum must have an uncertainty with a value of at least

$$\left[\Delta p = m\Delta v = \frac{\hbar}{(2\Delta x)}\right] = \frac{\left(1.055 \times 10^{-34}\,\mathrm{kg\,m^2/s}\right)}{\left(2 \times 1 \times 10^{-12}\,\mathrm{m}\right)} = 5 \times 10^{-23}\,\mathrm{kg\,m/s}$$

The value of $\hbar$ is not large, so the uncertainty in the position or momentum of a macroscopic object like a baseball is too insignificant to observe. However, the mass of a microscopic object such as an electron is small enough that the uncertainty can be large and significant.

It should be noted that Heisenberg's uncertainty principle is not just limited to uncertainties in position and momentum, but it also links other dynamical variables. For example, when an atom absorbs a photon and makes a transition from one energy state to another, the uncertainty in the energy and the uncertainty in the time required for the transition are similarly related, as:

$$\Delta E \Delta t \geq \frac{\hbar}{2}$$

Heisenberg's principle imposes ultimate limits on what is knowable in science. The uncertainty principle can be shown to be a consequence of wave–particle duality, which lies at the heart of what distinguishes modern quantum theory from classical mechanics.

Link to Learning

Read this article that describes a recent macroscopic demonstration of the uncertainty principle applied to microscopic objects.

The Quantum-Mechanical Model of an Atom

Shortly after de Broglie published his ideas that the electron in a hydrogen atom could be better thought of as being a circular standing wave instead of a particle moving in quantized circular orbits, Erwin Schrödinger extended de Broglie's work by deriving what is today known as the Schrödinger equation. When Schrödinger applied his equation to hydrogen-like atoms, he was able to reproduce Bohr's expression for the energy and, thus, the Rydberg formula governing hydrogen spectra. Schrödinger described electrons as three-dimensional stationary waves, or **wavefunctions**, represented by the Greek letter psi, ψ. A few years later, Max Born proposed an interpretation of the wavefunction ψ that is still accepted today: Electrons are still particles, and so the waves represented by ψ are not physical waves but, instead, are complex probability amplitudes. The square of the magnitude of a wavefunction $|\psi|^2$ describes the probability of the quantum particle being present near a certain location in space. This means that wavefunctions can be used to determine the distribution of the electron's density with respect to the nucleus in an atom. In the most general form, the Schrödinger equation can be written as:

$$\hat{H}\psi = E\psi$$

$\hat{H}$ is the Hamiltonian operator, a set of mathematical operations representing the total energy of the quantum particle (such as an electron in an atom), ψ is the wavefunction of this particle that can be used to find the special distribution of the probability of finding the particle, and E is the actual value of the total energy of the particle.

Schrödinger's work, as well as that of Heisenberg and many other scientists following in their footsteps, is generally referred to as **quantum mechanics**.

Link to Learning

You may also have heard of Schrödinger because of his famous thought experiment. This story explains the concepts of superposition and entanglement as related to a cat in a box with poison.

Understanding Quantum Theory of Electrons in Atoms

The goal of this section is to understand the electron orbitals (location of electrons in atoms), their different energies, and other properties. The use of quantum theory provides the best understanding to these topics. This knowledge is a precursor to chemical bonding.

As was described previously, electrons in atoms can exist only on discrete energy levels but not between them. It is said that the energy of an electron in an atom is quantized, that is, it can be equal only to certain specific values and can jump from one energy level to another but not transition smoothly or stay between these levels.

The energy levels are labeled with an n value, where $n = 1, 2, 3, \ldots$. Generally speaking, the energy of an electron in an atom is greater for greater values of n. This number, *n*, is referred to as the principal quantum number. The principal quantum number defines the location of the energy level. It is essentially the same concept as the *n* in the Bohr atom description. Another name for the principal quantum number is the shell number. The shells of an atom can be thought of concentric circles radiating out from the nucleus. The electrons that belong to a specific shell are most likely to be found within the corresponding circular area. The further we proceed from the nucleus, the higher the shell number, and so the higher the energy level (Figure $2.4.4$). The positively charged protons in the nucleus stabilize the electronic orbitals by electrostatic attraction between the positive charges of the protons and the negative charges of the electrons. So the further away the electron is from the nucleus, the greater the energy it has.

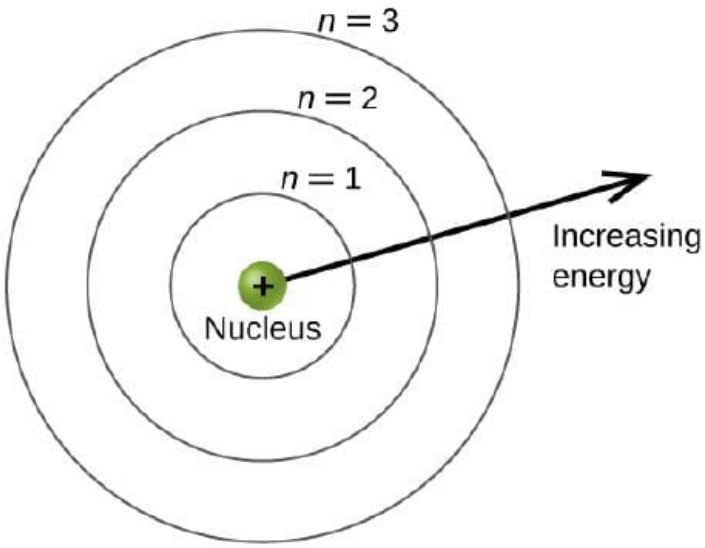


Figure $2.4.4$: Different shells are numbered by principal quantum numbers.

This quantum mechanical model for where electrons reside in an atom can be used to look at electronic transitions, the events when an electron moves from one energy level to another. If the transition is to a higher energy level, energy is absorbed, and the energy change has a positive value. To obtain the amount of energy necessary for the transition to a higher energy level, a photon is absorbed by the atom. A transition to a lower energy level involves a release of energy, and the energy change is negative. This process is accompanied by emission of a photon by the atom. The following equation summarizes these relationships and is based on the hydrogen atom:

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$
$$= -2.18 \times 10^{-18} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) J$$

The values n_f and n_i are the final and initial energy states of the electron.

The principal quantum number is one of three quantum numbers used to characterize an orbital. An **atomic orbital** is a general region in an atom within which an electron is most probable to reside. The quantum mechanical model specifies the probability of finding an electron in the three-dimensional space around the nucleus and is based on solutions of the Schrödinger equation. In addition, the principal quantum number defines the energy of an electron in a hydrogen or hydrogen-like atom or an ion (an atom or an ion with only one electron) and the general region in which discrete energy levels of electrons in a multi-electron atoms and ions are located.

Another quantum number is l, the **secondary (angular momentum) quantum number**. It is an integer that may take the values, $l = 0, 1, 2, \ldots, n–1$. This means that an orbital with $n = 1$ can have only one value of l, $l = 0$, whereas $n = 2$ permits $l = 0$ and $l = 1$, and so on. Whereas the principal quantum number, n, defines the general size and energy of the orbital, the secondary quantum number l specifies the shape of the orbital. Orbitals with the same value of l define a **subshell**.

Orbitals with $l = 0$ are called s orbitals and they make up the s subshells. The value $l = 1$ corresponds to the p orbitals. For a given n, p orbitals constitute a p subshell (e.g., 3p if n = 3). The orbitals with $l = 2$ are called the **d orbitals**, followed by the *f-, g-, and h*-orbitals for l = 3, 4, and 5.

There are certain distances from the nucleus at which the probability density of finding an electron located at a particular orbital is zero. In other words, the value of the wavefunction ψ is zero at this distance for this orbital. Such a value of radius r is called a **radial node**. The number of radial nodes in an orbital is $n–l–1$.

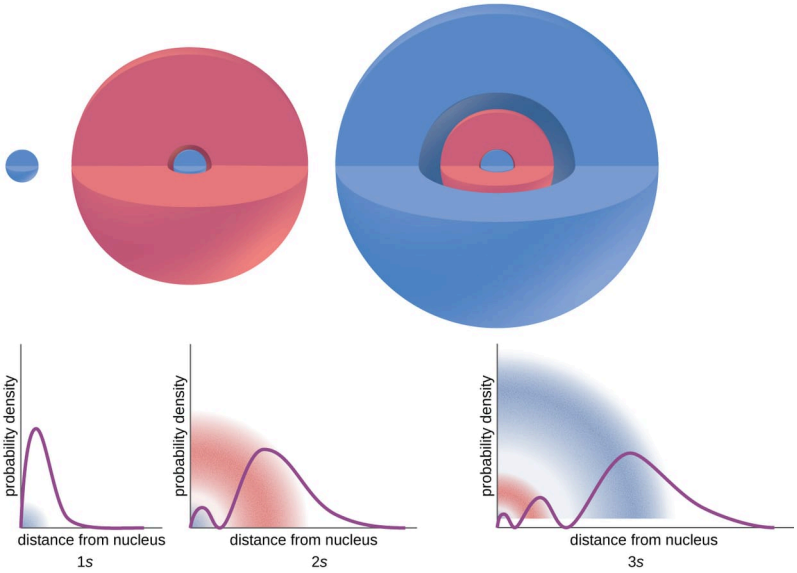


Figure 2.4.5: The graphs show the probability (*y* axis) of finding an electron for the 1s, 2s, 3s orbitals as a function of distance from the nucleus.

Consider the examples in Figure 2.4.5. The orbitals depicted are of the s type, thus $l = 0$ for all of them. It can be seen from the graphs of the probability densities that there are 1 – 0 – 1 = 0 places where the density is zero (nodes) for 1s (*n* = 1), 2 – 0 – 1 = 1 node for 2s, and 3 – 0 – 1 = 2 nodes for the 3s orbitals.

The *s* subshell electron density distribution is spherical and the *p* subshell has a dumbbell shape. The *d* and *f* orbitals are more complex. These shapes represent the three-dimensional regions within which the electron is likely to be found.

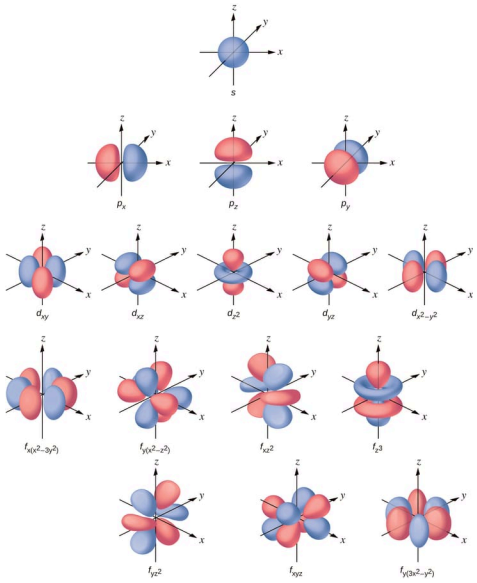


Figure 2.4.6: Shapes of s, *p*, *d*, and *f* orbitals.

The **magnetic quantum number**, m_l, specifies the relative spatial orientation of a particular orbital. Generally speaking, m_l are rangeed from $-l$ to $+l$, i.e.

$$-l, -(l-1), \ldots, 0, \ldots, (l-1), l.$$

The total number of possible orbitals with the same value of l (that is, in the same subshell) is $2l + 1$. Thus, there is one s-orbital in an s subshell ($l = 0$), there are three p-orbitals in a p subshell ($l = 1$), five d-orbitals in a d subshell (l = 2), seven f-orbitals in an f subshell ($l = 3$), and so forth. The principal quantum number defines the general value of the electronic energy. The angular momentum quantum number determines the shape of the orbital. And the magnetic quantum number specifies orientation of the orbital in space, as can be seen in Figure 2.4.6.

Figure 2.4.7 illustrates the energy levels for various orbitals. The number before the orbital name (such as 2*s*, 3*p*, and so forth) stands for the principal quantum number, n. The letter in the orbital name defines the subshell with a specific angular momentum quantum number *l* = 0 for s orbitals, 1 for *p* orbitals, 2 for *d* orbitals. Finally, there are more than one possible orbitals for $l \geq 1$, each corresponding to a specific value of m_l. In the case of a hydrogen atom or a one-electron ion (such as He^+, Li^{2+}, and so on), energies of all the orbitals with the same n are the same. This is called a degeneracy, and the energy levels for the same principal quantum number, n, are called degenerate orbitals. However, in atoms with more than one electron, this degeneracy is eliminated by the electron–electron interactions, and orbitals that belong to different subshells have different energies, as shown on Figure 2.4.7. Orbitals within the same subshell are still degenerate and have the same energy.

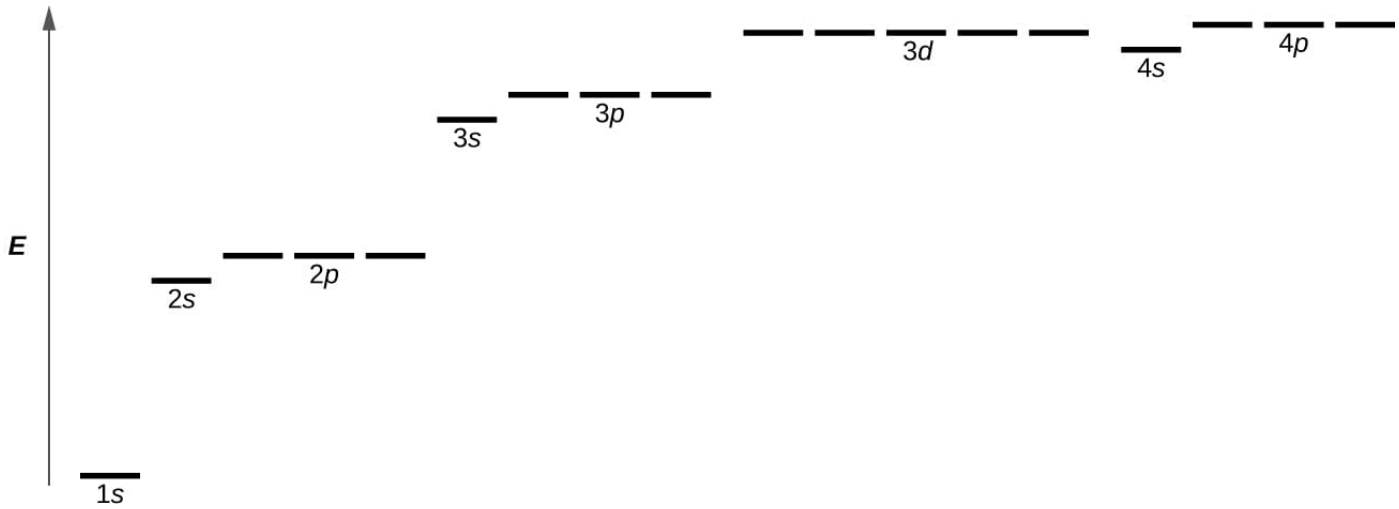


Figure 2.4.7: The chart shows the energies of electron orbitals in a multi-electron atom.

While the three quantum numbers discussed in the previous paragraphs work well for describing electron orbitals, some experiments showed that they were not sufficient to explain all observed results. It was demonstrated in the 1920s that when hydrogen-line spectra are examined at extremely high resolution, some lines are actually not single peaks but, rather, pairs of closely spaced lines. This is the so-called fine structure of the spectrum, and it implies that there are additional small differences in energies of electrons even when they are located in the same orbital. These observations led Samuel Goudsmit and George Uhlenbeck to propose that electrons have a fourth quantum number. They called this the **spin quantum number**, or m_s.

The other three quantum numbers, n, l, and m_l, are properties of specific atomic orbitals that also define in what part of the space an electron is most likely to be located. Orbitals are a result of solving the Schrödinger equation for electrons in atoms. The electron spin is a different kind of property. It is a completely quantum phenomenon with no analogues in the classical realm. In addition, it cannot be derived from solving the Schrödinger equation and is not related to the normal spatial coordinates (such as the Cartesian *x*, *y*, and *z*). Electron spin describes an intrinsic electron "rotation" or "spinning." Each electron acts as a tiny magnet or a tiny rotating object with an angular momentum, or as a loop with an electric current, even though this rotation or current cannot be observed in terms of spatial coordinates.

The magnitude of the overall electron spin can only have one value, and an electron can only “spin” in one of two quantized states. One is termed the α state, with the z component of the spin being in the positive direction of the z axis. This corresponds to the spin quantum number $m_s = +1/2$. The other is called the $\beta state$, with the z component of the spin being negative and $m_s = -1/2$. Any electron, regardless of the atomic orbital it is located in, can only have one of those two values of the spin quantum number. The energies of electrons having $m_s = +1/2$ and $m_s = -1/2$ are different if an external magnetic field is applied.

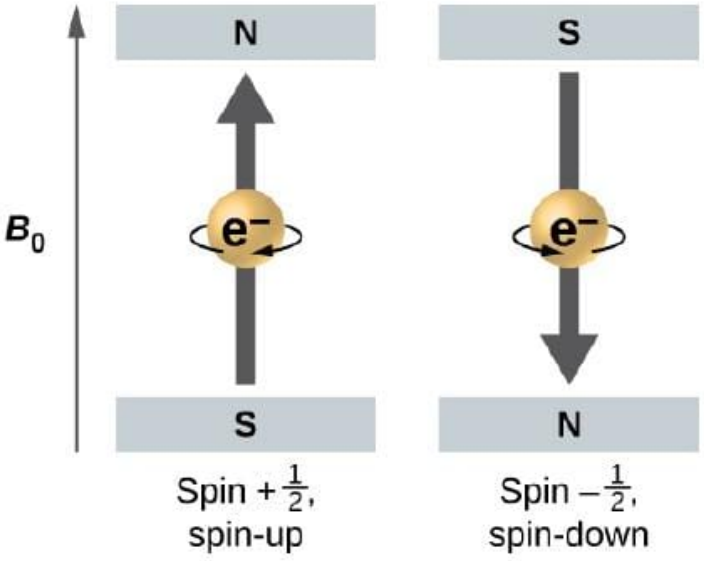


Figure 2.4.8: Electrons with spin values in an external magnetic field.

Figure 2.4.8 illustrates this phenomenon. An electron acts like a tiny magnet. Its moment is directed up (in the positive direction of the *z* axis) for the $m_s = +1/2$ spin quantum number and down (in the negative z direction) for the spin quantum number of $m_s = -1/2$. A magnet has a lower energy if its magnetic moment is aligned with the external magnetic field (the left electron on Figure 2.4.8) and a higher energy for the magnetic moment being opposite to the applied field. This is why an electron with $m_s = +1/2$ has a slightly lower energy in an external field in the positive z direction, and an electron with $m_s = -1/2$ has a slightly higher energy in the same field. This is true even for an electron occupying the same orbital in an atom. A spectral line corresponding to a transition for electrons from the same orbital but with different spin quantum numbers has two possible values of energy; thus, the line in the spectrum will show a fine structure splitting.

The Pauli Exclusion Principle

An electron in an atom is completely described by four quantum numbers: n, l, m_l, and m_s. The first three quantum numbers define the orbital and the fourth quantum number describes the intrinsic electron property called spin. An Austrian physicist Wolfgang Pauli formulated a general principle that gives the last piece of information that we need to understand the general behavior of electrons in atoms. The **Pauli exclusion principle** can be formulated as follows: No two electrons in the same atom can have exactly the same set of all the four quantum numbers. What this means is that two electrons can share the same orbital (the same

set of the quantum numbers *n*, *l*, and m_l) only if their spin quantum numbers m_s have different values. Since the spin quantum number can only have two values no more than two electrons can occupy the same orbital (and if two electrons are located in the same orbital, they must have opposite spins). Therefore, any atomic orbital can be populated by only zero, one, or two electrons. The properties and meaning of the quantum numbers of electrons in atoms are briefly summarized in Table 2.4.1.

Table 2.4.1: Quantum Numbers, Their Properties, and Significance

Name	Symbol	Allowed values	Physical meaning
principal quantum number	n	1, 2, 3, 4, ...	shell, the general region for the value of energy for an electron on the orbital
angular momentum or azimuthal quantum number	l	$0 \leq l \leq n–1$	subshell, the shape of the orbital
magnetic quantum number	m_l	$–l \leq m_l \leq l$	orientation of the orbital
spin quantum number	m_s	$+\frac{1}{2}$ and $-\frac{1}{2}$	direction of the intrinsic quantum “spinning” of the electron

Example 2.4.2: Working with Shells and Subshells

Indicate the number of subshells, the number of orbitals in each subshell, and the values of l and m_l for the orbitals in the $n = 4$ shell of an atom.

Solution

For $n = 4$, l can have values of 0, 1, 2, and 3. Thus, s, p, d, and f subshells are found in the n = 4 shell of an atom. For $l = 0$ (the s subshell), m_l can only be 0. Thus, there is only one 4s orbital. For $l = 1$ (p-type orbitals), m can have values of –1, 0, +1, so we find three 4p orbitals. For l = 2 (d-type orbitals), m_l can have values of –2, –1, 0, +1, +2, so we have five 4d orbitals. When $l = 3$ (f-type orbitals), m_l can have values of –3, –2, –1, 0, +1, +2, +3, and we can have seven 4f orbitals. Thus, we find a total of 16 orbitals in the $n = 4$ shell of an atom.

Exercise 2.4.2

Identify the subshell in which electrons with the following quantum numbers are found:

a. *n* = 3, l = 1
b. n = 5, l = 3
c. n = 2, l = 0

Answer available at the end of this section.

Example 2.4.3: Maximum Number of Electrons

Calculate the maximum number of electrons that can occupy a shell with (a) *n* = 2, (b) *n* = 5, and (c) *n* as a variable. Note you are only looking at the orbitals with the specified *n* value, not those at lower energies.

Solution

a. When $n = 2$, there are four orbitals (a single 2s orbital, and three orbitals labeled 2p). These four orbitals can contain eight electrons.
b. When $n = 2$, there are four orbitals (a single 2s orbital, and three orbitals labeled 2p). These four orbitals can contain eight electrons.
   When $n = 5$, there are five subshells of orbitals that we need to sum:

$$
\begin{aligned}
&1 \text{ orbital labeled 5s} \\
&3 \text{ orbitals labeled 5p} \\
&5 \text{ orbitals labeled 5d} \\
&7 \text{ orbitals labeled 5f} \\
+\ &9 \text{ orbitals labeled 5g} \\
&25 \text{ orbitals total}
\end{aligned}
$$

Again, each orbital holds two electrons, so 50 electrons can fit in this shell.

c. The number of orbitals in any shell n will equal n^2. There can be up to two electrons in each orbital, so the maximum number of electrons will be $2 \times n^2$.

Exercise 2.4.3

If a shell contains a maximum of 32 electrons, what is the principal quantum number, n?

Answer available at the end of this section.

Example 2.4.4: Working with Quantum Numbers

Complete the following table for atomic orbitals:

Orbital	n	l	m_l degeneracy	Radial nodes (#)
4*f*				
	4	1		
	7		7	3
5*d*				

Solution

The table can be completed using the following rules:

- The orbital designation is nl, where $l = 0, 1, 2, 3, 4, 5, \ldots$ is mapped to the letter sequence s, p, d, f, g, h, ...,
- The m_l degeneracy is the number of orbitals within an l subshell, and so is $2l + 1$ (there is one s orbital, three p orbitals, five d orbitals, seven f orbitals, and so forth).
- The number of radial nodes is equal to n–l–1.

Orbital	n	l	m_l degeneracy	Radial nodes (#)
4*f*	4	3	7	0
4*p*	4	1	3	2
7*f*	7	3	7	3
5*d*	5	2	5	2

Exercise 2.4.1

How many orbitals have $l = 2$ and $n = 3$?

Answer available at the end of this section.

Answers

Exercise 2.4.1

1.9 10^{-34} m.

We never think of a thrown softball having a wavelength, since this wavelength is so small it is impossible for our senses or any known instrument to detect (strictly speaking, the wavelength of a real baseball would correspond to the wavelengths of its constituent atoms and molecules, which, while much larger than this value, would still be microscopically tiny). The de Broglie wavelength is only appreciable for matter that has a very small mass and/or a very high velocity.

Exercise 2.4.2

a. 3*p*
b. 5*f*
c. 2s

Exercise 2.4.3

$n = 4$

Exercise 2.4.1

The five degenerate 3*d* orbitals

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2.5: Electronic Structure of Atoms (Electron Configurations)

Learning Objectives

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

- Derive the predicted ground-state electron configurations of atoms
- Identify and explain exceptions to predicted electron configurations for atoms and ions
- Relate electron configurations to element classifications in the periodic table

Having introduced the basics of atomic structure and quantum mechanics, we can use our understanding of quantum numbers to determine how atomic orbitals relate to one another. This allows us to determine which orbitals are occupied by electrons in each atom. The specific arrangement of electrons in orbitals of an atom determines many of the chemical properties of that atom.

Orbital Energies and Atomic Structure

The energy of atomic orbitals increases as the principal quantum number, *n*, increases. In any atom with two or more electrons, the repulsion between the electrons makes energies of subshells with different values of *l* differ so that the energy of the orbitals increases within a shell in the order *s* < *p* < *d* < *f*. Figure 2.5.1: depicts how these two trends in increasing energy relate. The 1*s* orbital at the bottom of the diagram is the orbital with electrons of lowest energy. The energy increases as we move up to the 2*s* and then 2*p*, 3*s*, and 3*p* orbitals, showing that the increasing *n* value has more influence on energy than the increasing *l* value for small atoms. However, this pattern does not hold for larger atoms. The 3*d* orbital is higher in energy than the 4*s* orbital. Such overlaps continue to occur frequently as we move up the chart.

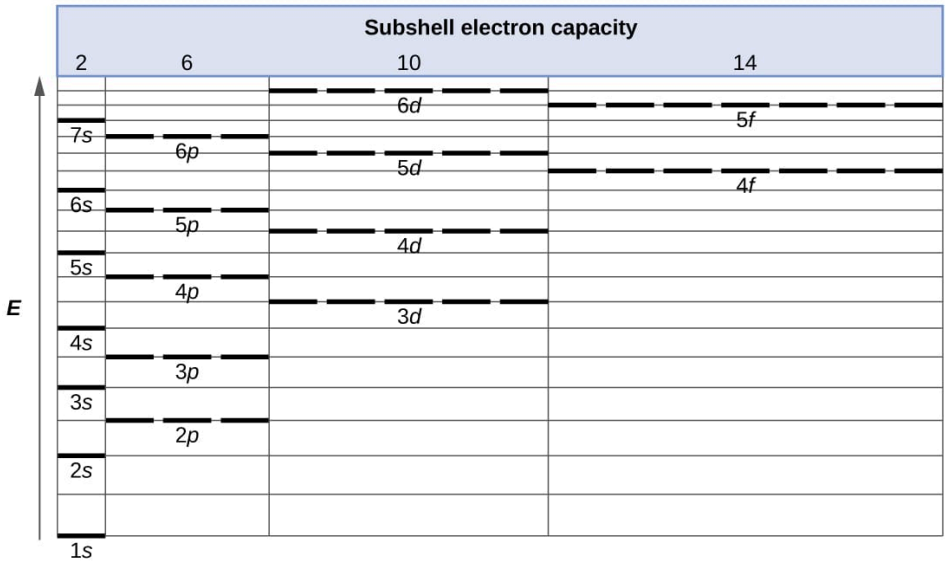


Figure 2.5.1: Generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale).

Electrons in successive atoms on the periodic table tend to fill low-energy orbitals first. Thus, many students find it confusing that, for example, the 5*p* orbitals fill immediately after the 4*d*, and immediately before the 6*s*. The filling order is based on observed experimental results, and has been confirmed by theoretical calculations. As the principal quantum number, *n*, increases, the size of the orbital increases and the electrons spend more time farther from the nucleus. Thus, the attraction to the nucleus is weaker and the energy associated with the orbital is higher (less stabilized). But this is not the only effect we have to take into account. Within each shell, as the value of *l* increases, the electrons are less penetrating (meaning there is less electron density found close to the nucleus), in the order *s* > *p* > *d* > *f*. Electrons that are closer to the nucleus slightly repel electrons that are farther out, offsetting the more dominant electron–nucleus attractions slightly (recall that all electrons have –1 charges, but nuclei have +*Z* charges). This phenomenon is called shielding and will be discussed in more detail in the next section. Electrons in orbitals that

experience more shielding are less stabilized and thus higher in energy. For small orbitals (1s through 3*p*), the increase in energy due to *n* is more significant than the increase due to *l*; however, for larger orbitals the two trends are comparable and cannot be simply predicted. We will discuss methods for remembering the observed order.

The arrangement of electrons in the orbitals of an atom is called the **electron configuration** of the atom. We describe an electron configuration with a symbol that contains three pieces of information (Figure 2.5.2):

1. The number of the principal quantum shell, n,
2. The letter that designates the orbital type (the subshell, l), and
3. A superscript number that designates the number of electrons in that particular subshell.

For example, the notation $2p^4$ (read "two–p–four") indicates four electrons in a *p* subshell ($l = 1$) with a principal quantum number (n) of 2. The notation $3d^8$ (read "three–d–eight") indicates eight electrons in the *d* subshell (i.e., $l = 2$) of the principal shell for which $n = 3$.

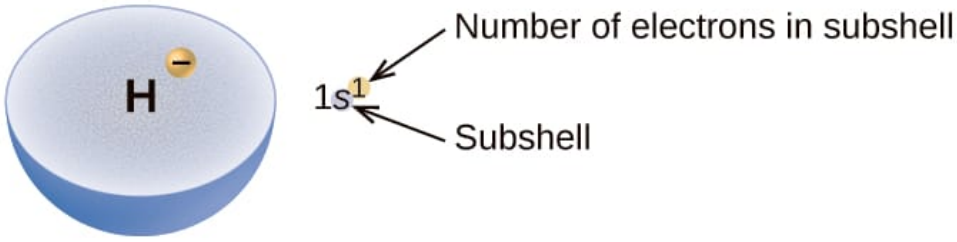


Figure 2.5.2: The diagram of an electron configuration specifies the subshell (*n* and *l* value, with letter symbol) and superscript number of electrons.

The Aufbau Principle

To determine the electron configuration for any particular atom, we can “build” the structures in the order of atomic numbers. Beginning with hydrogen, and continuing across the periods of the periodic table, we add one proton at a time to the nucleus and one electron to the proper subshell until we have described the electron configurations of all the elements. This procedure is called the **Aufbau principle**, from the German word *Aufbau* (“to build up”). Each added electron occupies the subshell of lowest energy available (in the order shown in Figure 2.5.1), subject to the limitations imposed by the allowed quantum numbers according to the Pauli exclusion principle. Electrons enter higher-energy subshells only after lower-energy subshells have been filled to capacity. Figure 2.5.3 illustrates the traditional way to remember the filling order for atomic orbitals.

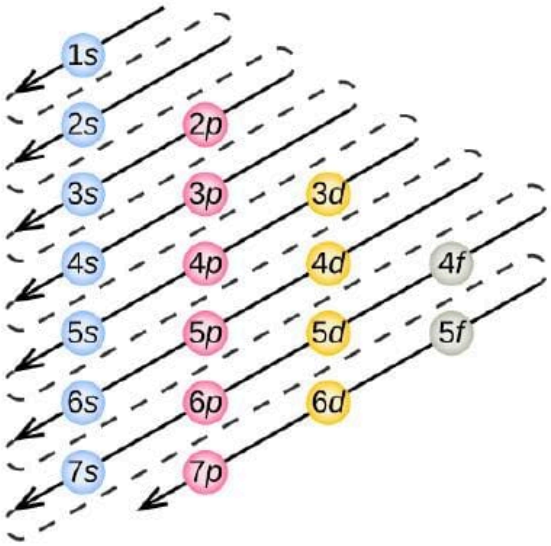


Figure 2.5.3: This diagram depicts the energy order for atomic orbitals and is useful for deriving ground-state electron configurations.

Since the arrangement of the periodic table is based on the electron configurations, Figure 2.5.4 provides an alternative method for determining the electron configuration. The filling order simply begins at hydrogen and includes each subshell as you proceed in increasing *Z* order. For example, after filling the 3*p* block up to Ar, we see the orbital will be 4s (K, Ca), followed by the 3*d* orbitals.

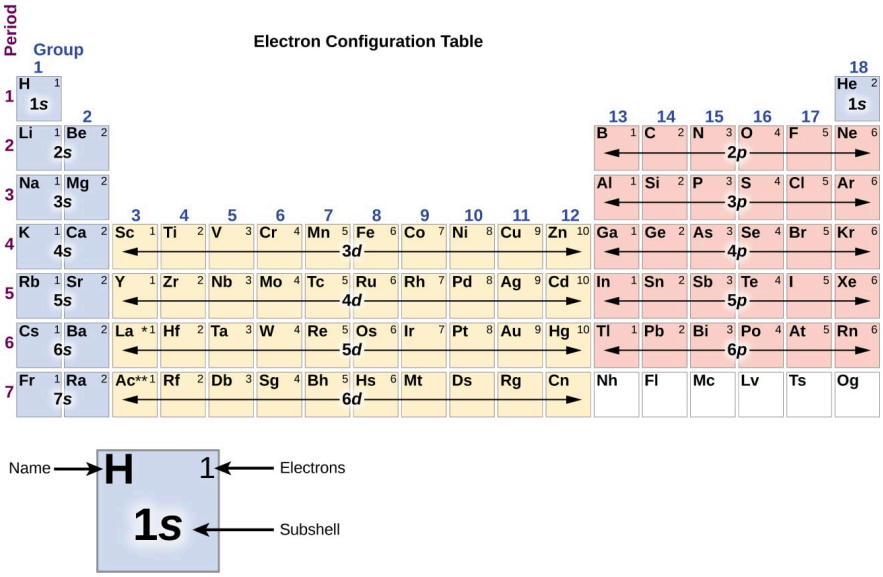
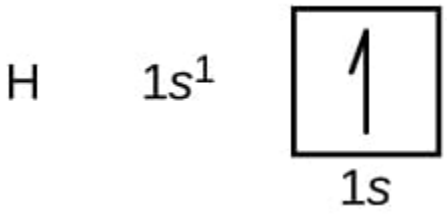
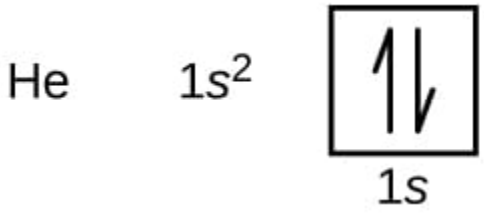


Figure 2.5.4: This partial periodic table shows electron configurations for the valence subshells of atoms. By "building up" from hydrogen, this table can be used to determine the electron configuration for atoms of most elements in the periodic table. (Electron configurations of the lanthanides and actinides are not accurately predicted by this simple approach. See Figure 2.5.6:

We will now construct the ground-state electron configuration and orbital diagram for a selection of atoms in the first and second periods of the periodic table. **Orbital diagrams** are pictorial representations of the electron configuration, showing the individual orbitals and the pairing arrangement of electrons. We start with a single hydrogen atom (atomic number 1), which consists of one proton and one electron. Referring to Figure 2.5.3 or Figure 2.5.4, we would expect to find the electron in the 1s orbital. By convention, the $m_s = +\frac{1}{2}$ value is usually filled first. The electron configuration and the orbital diagram are:

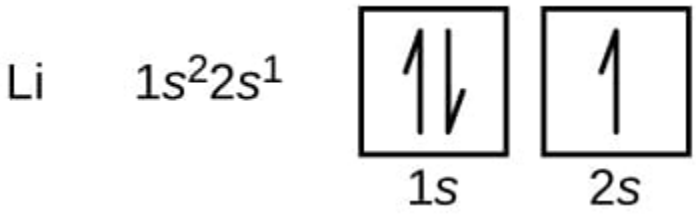


Following hydrogen is the noble gas helium, which has an atomic number of 2. The helium atom contains two protons and two electrons. The first electron has the same four quantum numbers as the hydrogen atom electron ((*n* = 1), (*l* = 0), (m_l = 0), $m_s = +\frac{1}{2}$. The second electron also goes into the 1s orbital and fills that orbital. The second electron has the same n, l, and ml quantum numbers, but must have the opposite spin quantum number, $m_s = -\frac{1}{2}$. This is in accord with the Pauli exclusion principle: No two electrons in the same atom can have the same set of four quantum numbers. For orbital diagrams, this means two arrows go in each box (representing two electrons in each orbital) and the arrows must point in opposite directions (representing paired spins). The electron configuration and orbital diagram of helium are:

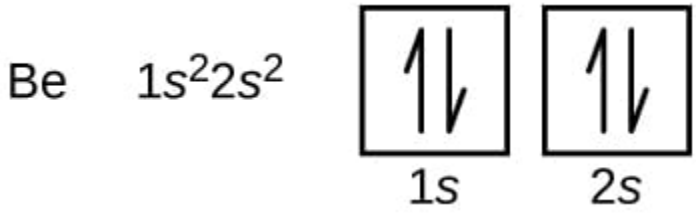


The $n = 1$ shell is completely filled in a helium atom.

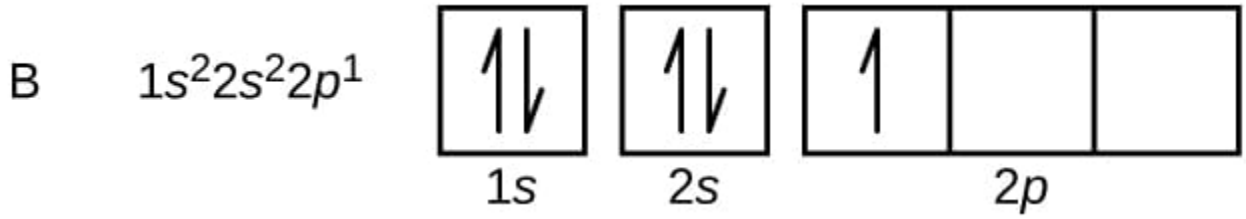
The next atom is the alkali metal lithium with an atomic number of 3. The first two electrons in lithium fill the 1s orbital and have the same sets of four quantum numbers as the two electrons in helium. The remaining electron must occupy the orbital of next lowest energy, the 2s orbital (Figure $2.5.3$ or Figure $2.5.4$). Thus, the electron configuration and orbital diagram of lithium are:



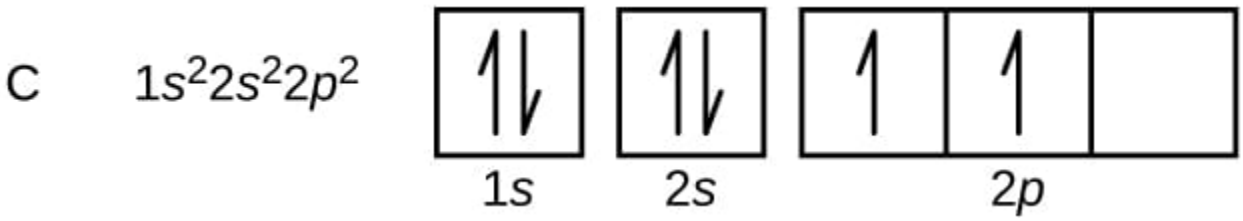
An atom of the alkaline earth metal beryllium, with an atomic number of 4, contains four protons in the nucleus and four electrons surrounding the nucleus. The fourth electron fills the remaining space in the 2s orbital.



An atom of boron (atomic number 5) contains five electrons. The n = 1 shell is filled with two electrons and three electrons will occupy the n = 2 shell. Because any s subshell can contain only two electrons, the fifth electron must occupy the next energy level, which will be a 2*p* orbital. There are three degenerate 2*p* orbitals (m_l = –1, 0, +1) and the electron can occupy any one of these *p* orbitals. When drawing orbital diagrams, we include empty boxes to depict any empty orbitals in the same subshell that we are filling.

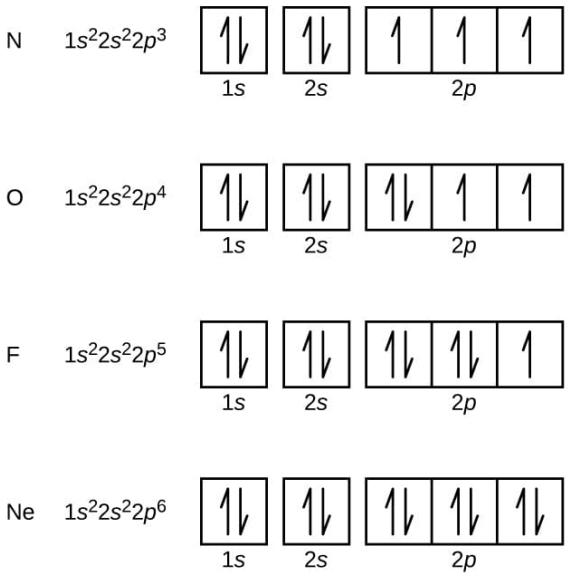


Carbon (atomic number 6) has six electrons. Four of them fill the 1s and 2s orbitals. The remaining two electrons occupy the 2*p* subshell. We now have a choice of filling one of the 2*p* orbitals and pairing the electrons or of leaving the electrons unpaired in two different, but degenerate, *p* orbitals. The orbitals are filled as described by **Hund's rule**: the lowest-energy configuration for an atom with electrons within a set of degenerate orbitals is that having the maximum number of unpaired electrons. Thus, the two electrons in the carbon 2*p* orbitals have identical n, l, and m_s quantum numbers and differ in their m_l quantum number (in accord with the Pauli exclusion principle). The electron configuration and orbital diagram for carbon are:



Nitrogen (atomic number 7) fills the 1s and 2s subshells and has one electron in each of the three 2*p* orbitals, in accordance with Hund's rule. These three electrons have unpaired spins. Oxygen (atomic number 8) has a pair of electrons in any one of the 2*p*

orbitals (the electrons have opposite spins) and a single electron in each of the other two. Fluorine (atomic number 9) has only one 2*p* orbital containing an unpaired electron. All of the electrons in the noble gas neon (atomic number 10) are paired, and all of the orbitals in the *n* = 1 and the *n* = 2 shells are filled. The electron configurations and orbital diagrams of these four elements are:



The alkali metal sodium (atomic number 11) has one more electron than the neon atom. This electron must go into the lowest-energy subshell available, the 3s orbital, giving a $1s^2 2s^2 2p^6 3s^1$ configuration. The electrons occupying the outermost shell orbital(s) (highest value of *n*) are called **valence electrons**, and those occupying the inner shell orbitals are called **core electrons** (Figure 2.5.5). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1s^2 2s^2 2p^6$) and our abbreviated or condensed configuration is $[Ne]3s^1$.

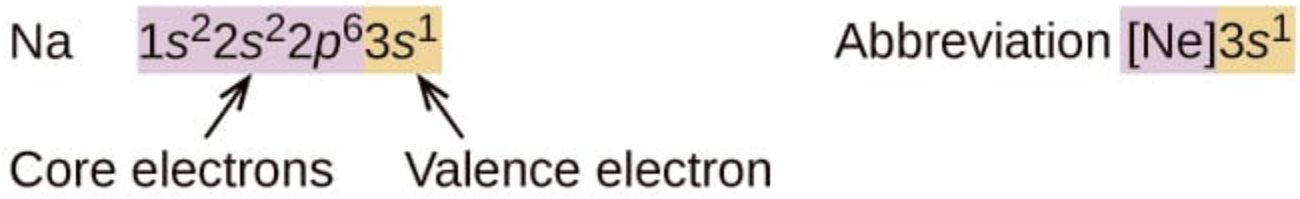


Figure 2.5.5: A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

Similarly, the abbreviated configuration of lithium can be represented as $[He]2s^1$, where [He] represents the configuration of the helium atom, which is identical to that of the filled inner shell of lithium. Writing the configurations in this way emphasizes the similarity of the configurations of lithium and sodium. Both atoms, which are in the alkali metal family, have only one electron in a valence s subshell outside a filled set of inner shells.

$$Li : [He]2s^1$$
$$Na : [Ne]3s^1$$

The alkaline earth metal magnesium (atomic number 12), with its 12 electrons in a $[Ne]3s^2$ configuration, is analogous to its family member beryllium, $[He]2s^2$. Both atoms have a filled s subshell outside their filled inner shells. Aluminum (atomic number 13), with 13 electrons and the electron configuration $[Ne]3s^2 3p^1$, is analogous to its family member boron, $[He]2s^2 2p^1$.

The electron configurations of silicon (14 electrons), phosphorus (15 electrons), sulfur (16 electrons), chlorine (17 electrons), and

argon (18 electrons) are analogous in the electron configurations of their outer shells to their corresponding family members carbon, nitrogen, oxygen, fluorine, and neon, respectively, except that the principal quantum number of the outer shell of the heavier elements has increased by one to $n = 3$. Figure 2.5.6: shows the lowest energy, or ground-state, electron configuration for these elements as well as that for atoms of each of the known elements.

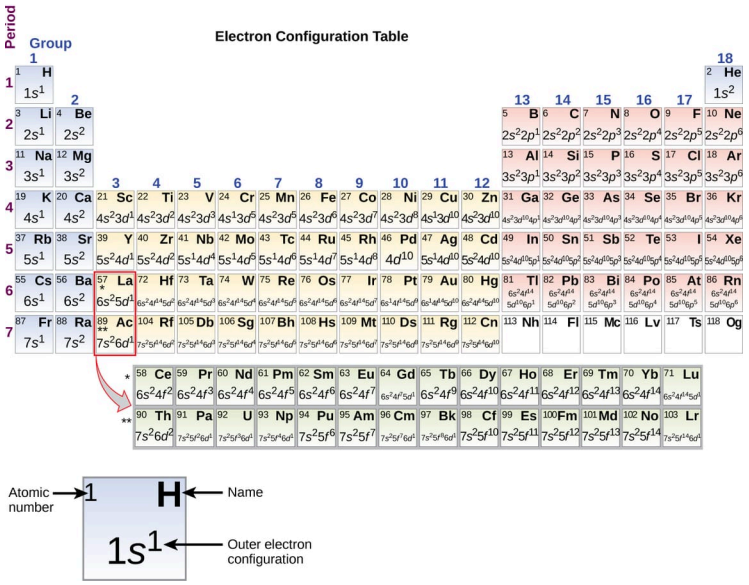


Figure 2.5.6: This version of the periodic table shows the outer-shell electron configuration of each element. Note that down each group, the configuration is often similar.

When we come to the next element in the periodic table, the alkali metal potassium (atomic number 19), we might expect that we would begin to add electrons to the 3*d* subshell. However, all available chemical and physical evidence indicates that potassium is like lithium and sodium, and that the next electron is not added to the 3*d* level but is, instead, added to the 4*s* level (Figure 2.5.6). As discussed previously, the 3*d* orbital with no radial nodes is higher in energy because it is less penetrating and more shielded from the nucleus than the 4s, which has three radial nodes. Thus, potassium has an electron configuration of $[Ar]4s^1$. Hence, potassium corresponds to Li and Na in its valence shell configuration. The next electron is added to complete the 4*s* subshell and calcium has an electron configuration of $[Ar]4s^2$. This gives calcium an outer-shell electron configuration corresponding to that of beryllium and magnesium.

Beginning with the transition metal scandium (atomic number 21), additional electrons are added successively to the 3*d* subshell. This subshell is filled to its capacity with 10 electrons (remember that for $l = 2$ [*d* orbitals], there are $2l + 1 = 5$ values of m_l, meaning that there are five *d* orbitals that have a combined capacity of 10 electrons). The 4*p* subshell fills next. Note that for three series of elements, scandium (Sc) through copper (Cu), yttrium (Y) through silver (Ag), and lutetium (Lu) through gold (Au), a total of 10 *d* electrons are successively added to the $(n - 1)$ shell next to the *n* shell to bring that $(n - 1)$ shell from 8 to 18 electrons. For two series, lanthanum (La) through lutetium (Lu) and actinium (Ac) through lawrencium (Lr), 14 *f* electrons ($l = 3$, $2l + 1 = 7$ m_l values; thus, seven orbitals with a combined capacity of 14 electrons) are successively added to the $(n - 2)$ shell to bring that shell from 18 electrons to a total of 32 electrons.

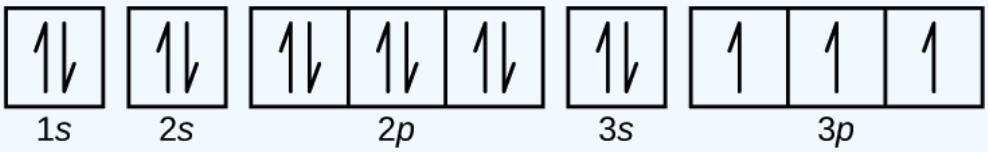
Example 2.5.1: Quantum Numbers and Electron Configurations

What is the electron configuration and orbital diagram for a phosphorus atom? What are the four quantum numbers for the last electron added?

Solution

The atomic number of phosphorus is 15. Thus, a phosphorus atom contains 15 electrons. The order of filling of the energy levels is 1s, 2s, 2*p*, 3s, 3*p*, 4s, . . . The 15 electrons of the phosphorus atom will fill up to the 3*p* orbital, which will contain three electrons:

P $1s^2 2s^2 2p^6 3s^2 3p^3$



The last electron added is a 3*p* electron. Therefore, $n = 3$ and, for a *p*-type orbital, $l = 1$. The m_l value could be –1, 0, or +1. The three *p* orbitals are degenerate, so any of these m_l values is correct. For unpaired electrons, convention assigns the value of $+\frac{1}{2}$ for the spin quantum number; thus, $m_s = +\frac{1}{2}$

Exercise 2.5.1

Identify the atoms from the electron configurations given:

a. $[Ar]4s^2 3d^5$
b. $[Kr]5s^2 4d^{10} 5p^6$

Answer available at the end of this section.

The periodic table can be a powerful tool in predicting the electron configuration of an element. However, we do find exceptions to the order of filling of orbitals that are shown in Figure 2.5.3: or Figure 2.5.4. For instance, the electron configurations (shown in Figure 2.5.6) of the transition metals chromium (Cr; atomic number 24) and copper (Cu; atomic number 29), among others, are not those we would expect. In general, such exceptions involve subshells with very similar energy, and small effects can lead to changes in the order of filling.

In the case of Cr and Cu, we find that half-filled and completely filled subshells apparently represent conditions of preferred stability. This stability is such that an electron shifts from the 4s into the 3*d* orbital to gain the extra stability of a half-filled 3*d* subshell (in Cr) or a filled 3*d* subshell (in Cu). Other exceptions also occur. For example, niobium (Nb, atomic number 41) is predicted to have the electron configuration $[Kr]5s^2 4d^3$. Experimentally, we observe that its ground-state electron configuration is actually $[Kr]5s^1 4d^4$. We can rationalize this observation by saying that the electron–electron repulsions experienced by pairing the electrons in the 5s orbital are larger than the gap in energy between the 5s and 4*d* orbitals. There is no simple method to predict the exceptions for atoms where the magnitude of the repulsions between electrons is greater than the small differences in energy between subshells.

Electron Configurations and the Periodic Table

As described earlier, the periodic table arranges atoms based on increasing atomic number so that elements with the same chemical properties recur periodically. When their electron configurations are added to the table (Figure 2.5.6), we also see a periodic recurrence of similar electron configurations in the outer shells of these elements. Because they are in the outer shells of an atom, valence electrons play the most important role in chemical reactions. The outer electrons have the highest energy of the electrons in an atom and are more easily lost or shared than the core electrons. Valence electrons are also the determining factor in some physical properties of the elements.

Elements in any one group (or column) have the same number of valence electrons; the alkali metals lithium and sodium each have only one valence electron, the alkaline earth metals beryllium and magnesium each have two, and the halogens fluorine and chlorine each have seven valence electrons. The similarity in chemical properties among elements of the same group occurs because they have the same number of valence electrons. It is the loss, gain, or sharing of valence electrons that defines how elements react.

It is important to remember that the periodic table was developed on the basis of the chemical behavior of the elements, well before any idea of their atomic structure was available. Now we can understand why the periodic table has the arrangement it has—the arrangement puts elements whose atoms have the same number of valence electrons in the same group. This arrangement is emphasized in Figure 2.5.6: , which shows in periodic-table form the electron configuration of the last subshell to be filled by the Aufbau principle. The colored sections of Figure 2.5.6: show the three categories of elements classified by

the orbitals being filled: main group, transition, and inner transition elements. These classifications determine which orbitals are counted in the **valence shell**, or highest energy level orbitals of an atom.

1. **Main group elements** (sometimes called **representative elements**) are those in which the last electron added enters an s or a *p* orbital in the outermost shell, shown in blue and red in Figure 2.5.6. This category includes all the nonmetallic elements, as well as many metals and the metalloids. The valence electrons for main group elements are those with the highest *n* level. For example, gallium (Ga, atomic number 31) has the electron configuration [Ar]$\underline{4s^2}3d^{10}\underline{4p^1}$, which contains three valence electrons (underlined). The completely filled *d* orbitals count as core, not valence, electrons.
2. **Transition elements or transition metals**. These are metallic elements in which the last electron added enters a *d* orbital. The valence electrons (those added after the last noble gas configuration) in these elements include the *ns* and (*n* – 1) *d* electrons. The official IUPAC definition of transition elements specifies those with partially filled *d* orbitals. Thus, the elements with completely filled orbitals (Zn, Cd, Hg, as well as Cu, Ag, and Au in Figure 2.5.6) are not technically transition elements. However, the term is frequently used to refer to the entire *d* block (colored yellow in Figure 2.5.6), and we will adopt this usage in this textbook.
3. **Inner transition elements** are metallic elements in which the last electron added occupies an *f* orbital. They are shown in green in Figure 2.5.6. The valence shells of the inner transition elements consist of the (*n* – 2)*f,* the (*n* – 1)*d*, and the *ns* subshells. There are two inner transition series:
   a. The lanthanide series: lanthanum (La) through lutetium (Lu)
   b. The actinide series: actinium (Ac) through lawrencium (Lr)

Lanthanum and actinium, because of their similarities to the other members of the series, are included and used to name the series, even though they are transition metals with no *f* electrons.

Electron Configurations of Ions

Ions are formed when atoms gain or lose electrons. A cation (positively charged ion) forms when one or more electrons are removed from a parent atom. For main group elements, the electrons that were added last are the first electrons removed. For transition metals and inner transition metals, however, electrons in the *s* orbital are easier to remove than the *d* or *f* electrons, and so the highest *ns* electrons are lost, and then the (*n* – 1)*d* or (*n* – 2)*f* electrons are removed. An anion (negatively charged ion) forms when one or more electrons are added to a parent atom. The added electrons fill in the order predicted by the Aufbau principle.

Example 2.5.2: Predicting Electron Configurations of Ions

What is the electron configuration of:

a. Na^+
b. P^{3-}
c. Al^{2+}
d. Fe^{2+}
e. Sm^{3+}

Solution

First, write out the electron configuration for each parent atom. We have chosen to show the full, unabbreviated configurations to provide more practice for students who want it, but listing the core-abbreviated electron configurations is also acceptable.

Next, determine whether an electron is gained or lost. Remember electrons are negatively charged, so ions with a positive charge have *lost* an electron. For main group elements, the last orbital gains or loses the electron. For transition metals, the last *s* orbital loses an electron before the *d* orbitals.

a. Na: $1s^2 2s^2 2p^6 3s^1$. Sodium cation loses one electron, so Na^+: $1s^2 2s^2 2p^6 3s^1$ = Na^+: $1s^2 2s^2 2p^6$.
b. P: $1s^2 2s^2 2p^6 3s^2 3p^3$. Phosphorus trianion gains three electrons, so P^{3-}: $1s^2 2s^2 2p^6 3s^2 3p^6$.

c. Al: $1s^2 2s^2 2p^6 3s^2 3p^1$. Aluminum dication loses two electrons Al^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^1 = Al^{2+}$: $1s^2 2s^2 2p^6 3s^1$.
d. Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$. Iron(II) loses two electrons and, since it is a transition metal, they are removed from the 4s orbital Fe^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$.
e. Sm: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6$. Samarium trication loses three electrons. The first two will be lost from the 6s orbital, and the final one is removed from the 4*f* orbital. Sm^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6 = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^5$.

Exercise 2.5.21

Which ion with a +2 charge has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 4d^5$? Which ion with a +3 charge has this configuration?

Answer available at the end of this section.

Answers

Exercise 2.5.1

a. Mn
b. Xe

Exercise 2.5.21

Tc^{2+}, Ru^{3+}

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2.6: Periodic Variations in Element Properties

Learning Objectives

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

- Describe and explain the observed trends in atomic size, ionization energy, and electron affinity of the elements

The elements in groups (vertical columns) of the periodic table exhibit similar chemical behavior. This similarity occurs because the members of a group have the same number and distribution of electrons in their valence shells. However, there are also other patterns in chemical properties on the periodic table. For example, as we move down a group, the metallic character of the atoms increases. Oxygen, at the top of group 16 (6A), is a colorless gas; in the middle of the group, selenium is a semiconducting solid; and, toward the bottom, polonium is a silver-grey solid that conducts electricity.

As we go across a period from left to right, we add a proton to the nucleus and an electron to the valence shell with each successive element. As we go down the elements in a group, the number of electrons in the valence shell remains constant, but the principal quantum number increases by one each time. An understanding of the electronic structure of the elements allows us to examine some of the properties that govern their chemical behavior. These properties vary periodically as the electronic structure of the elements changes. They are (1) size (radius) of atoms and ions, (2) ionization energies, and (3) electron affinities.

Link to Learning

Explore visualizations of the periodic trends discussed in this section (and many more trends). With just a few clicks, you can create three-dimensional versions of the periodic table showing atomic size or graphs of ionization energies from all measured elements.

Variation in Covalent Radius

The quantum mechanical picture makes it difficult to establish a definite size of an atom. However, there are several practical ways to define the radius of atoms and, thus, to determine their relative sizes that give roughly similar values. We will use the covalent radius (Figure 2.6.1), which is defined as one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond (this measurement is possible because atoms within molecules still retain much of their atomic identity). We know that as we scan down a group, the principal quantum number, *n*, increases by one for each element. Thus, the electrons are being added to a region of space that is increasingly distant from the nucleus. Consequently, the size of the atom (and its covalent radius) must increase as we increase the distance of the outermost electrons from the nucleus. This trend is illustrated for the covalent radii of the halogens in Table 2.6.1 and Figure 2.6.1. The trends for the entire periodic table can be seen in Figure 2.6.2.

Table 2.6.1: Covalent Radii of the Halogen Group Elements

Atom	Covalent radius (pm)	Nuclear charge
F	64	+9
Cl	99	+17
Br	114	+35
I	133	+53
At	148	+85

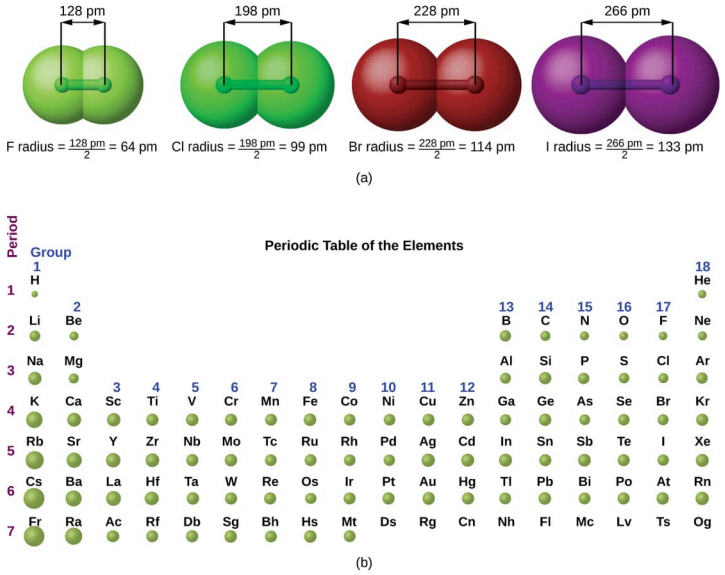


Figure 2.6.1: (a) The radius of an atom is defined as one-half the distance between the nuclei in a molecule consisting of two identical atoms joined by a covalent bond. The atomic radius for the halogens increases down the group as *n* increases. (b) Covalent radii of the elements are shown to scale. The general trend is that radii increase down a group and decrease across a period.

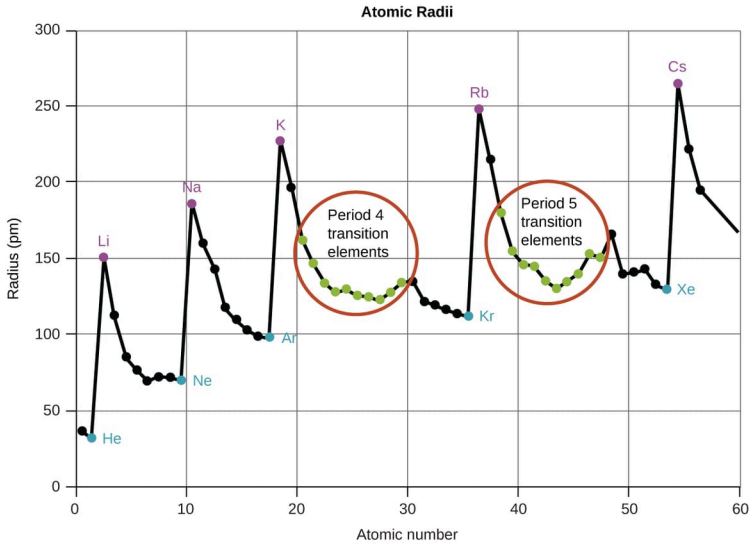


Figure 2.6.2: Within each period, the trend in atomic radius decreases as *Z* increases; for example, from K to Kr. Within each group (e.g., the alkali metals shown in purple), the trend is that atomic radius increases as *Z* increases.

As shown in Figure 2.6.2, as we move across a period from left to right, we generally find that each element has a smaller covalent radius than the element preceding it. This might seem counterintuitive because it implies that atoms with more electrons have a smaller atomic radius. This can be explained with the concept of **effective nuclear charge**, Z_{eff}. This is the pull exerted on a specific electron by the nucleus, taking into account any electron–electron repulsions. For hydrogen, there is only one electron and so the nuclear charge (Z) and the effective nuclear charge (Z_{eff}) are equal. For all other atoms, the inner electrons partially *shield* the outer electrons from the pull of the nucleus, and thus:

$$Z_{\text{eff}} = Z - \text{ shielding}$$

Shielding is determined by the probability of another electron being between the electron of interest and the nucleus, as well as by the electron–electron repulsions the electron of interest encounters. Core electrons are adept at shielding, while electrons in the same valence shell do not block the nuclear attraction experienced by each other as efficiently. Thus, each time we move from one element to the next across a period, Z increases by one, but the shielding increases only slightly. Thus, Z_{eff} increases as we move from left to right across a period. The stronger pull (higher effective nuclear charge) experienced by electrons on the right side of the periodic table draws them closer to the nucleus, making the covalent radii smaller.

Thus, as we would expect, the outermost or valence electrons are easiest to remove because they have the highest energies, are shielded more, and are farthest from the nucleus. As a general rule, when the representative elements form cations, they do so by the loss of the *ns* or *np* electrons that were added last in the Aufbau process. The transition elements, on the other hand, lose the *ns* electrons before they begin to lose the $(n - 1)d$ electrons, even though the *ns* electrons are added first, according to the Aufbau principle.

Example 2.6.1: Sorting Atomic Radii

Predict the order of increasing covalent radius for Ge, Fl, Br, Kr.

Solution

Radius increases as we move down a group, so Ge < Fl (Note: Fl is the symbol for flerovium, element 114, NOT fluorine). Radius decreases as we move across a period, so Kr < Br < Ge. Putting the trends together, we obtain Kr < Br < Ge < Fl.

Exercise 2.6.1

Give an example of an atom whose size is smaller than fluorine.

Answer available at the end of this section.

Variation in Ionic Radii

Ionic radius is the measure used to describe the size of an ion. A cation always has fewer electrons and the same number of protons as the parent atom; it is smaller than the atom from which it is derived (Figure 2.6.3). For example, the covalent radius of an aluminum atom ($1s^2 2s^2 2p^6 3s^2 3p^1$) is 118 pm, whereas the ionic radius of an Al^{3+} ($1s^2 2s^2 2p^6$) is 68 pm. As electrons are removed from the outer valence shell, the remaining core electrons occupying smaller shells experience a greater effective nuclear charge Z_{eff} (as discussed) and are drawn even closer to the nucleus.



Figure 2.6.3: The radius for a cation is smaller than the parent atom (Al), due to the lost electrons; the radius for an anion is larger than the parent (S), due to the gained electrons.

Cations with larger charges are smaller than cations with smaller charges (e.g., V^{2+} has an ionic radius of 79 pm, while that of V^{3+} is 64 pm). Proceeding down the groups of the periodic table, we find that cations of successive elements with the same charge generally have larger radii, corresponding to an increase in the principal quantum number, *n*.

An anion (negative ion) is formed by the addition of one or more electrons to the valence shell of an atom. This results in a greater repulsion among the electrons and a decrease in Z_{eff} per electron. Both effects (the increased number of electrons and the decreased Z_{eff}) cause the radius of an anion to be larger than that of the parent atom (Figure 2.6.3). For example, a sulfur atom ($[Ne]3s^2 3p^4$) has a covalent radius of 104 pm, whereas the ionic radius of the sulfide anion ($[Ne]3s^2 3p^6$) is 170 pm. For consecutive elements proceeding down any group, anions have larger principal quantum numbers and, thus, larger radii.

Atoms and ions that have the same electron configuration are said to be **isoelectronic**. Examples of isoelectronic species are N^{3-}, O^{2-}, F^-, Ne, Na^+, Mg^{2+}, and Al^{3+} ($1s^2 2s^2 2p^6$). Another isoelectronic series is P^{3-}, S^{2-}, Cl^-, Ar, K^+, Ca^{2+}, and Sc^{3+} ($[Ne]3s^2 3p^6$). For atoms or ions that are isoelectronic, the number of protons determines the size. The greater the nuclear charge, the smaller the radius in a series of isoelectronic ions and atoms.

Variation in Ionization Energies

The amount of energy required to remove the most loosely bound electron from a gaseous atom in its ground state is called its first **ionization energy** (IE_1). The first ionization energy for an element, X, is the energy required to form a cation with +1 charge:

$$\mathrm{X\,(g)} \longrightarrow \mathrm{X^{+}\,(g)} + \mathrm{e^{-}} \qquad IE_1$$

The energy required to remove the second most loosely bound electron is called the second ionization energy (IE_2).

$$\mathrm{X^{+}\,(g)} \longrightarrow \mathrm{X^{2+}\,(g)} + \mathrm{e^{-}} \qquad IE_2$$

The energy required to remove the third electron is the third ionization energy, and so on. Energy is always required to remove electrons from atoms or ions, so ionization processes are endothermic and IE values are always positive. For larger atoms, the most loosely bound electron is located farther from the nucleus and so is easier to remove. Thus, as size (atomic radius) increases, the ionization energy should decrease. Relating this logic to what we have just learned about radii, we would expect first ionization energies to decrease down a group and to increase across a period.

Figure 2.6.4 graphs the relationship between the first ionization energy and the atomic number of several elements. The values of first ionization energy for the elements are given in Figure 2.6.5. Within a period, the IE_1 generally increases with increasing *Z*. Down a group, the IE_1 value generally decreases with increasing *Z*. There are some systematic deviations from this trend, however. Note that the ionization energy of boron (atomic number 5) is less than that of beryllium (atomic number 4) even though the nuclear charge of boron is greater by one proton. This can be explained because the energy of the subshells increases as *l* increases, due to penetration and shielding (as discussed previously in this chapter). Within any one shell, the *s* electrons are lower in energy than the *p* electrons. This means that an *s* electron is harder to remove from an atom than a *p* electron in the same shell. The electron removed during the ionization of beryllium ([He]$2s^2$) is an *s* electron, whereas the electron removed during the ionization of boron ([He]$2s^2 2p^1$) is a *p* electron; this results in a lower first ionization energy for boron, even though its nuclear charge is greater by one proton. Thus, we see a small deviation from the predicted trend occurring each time a new subshell begins.

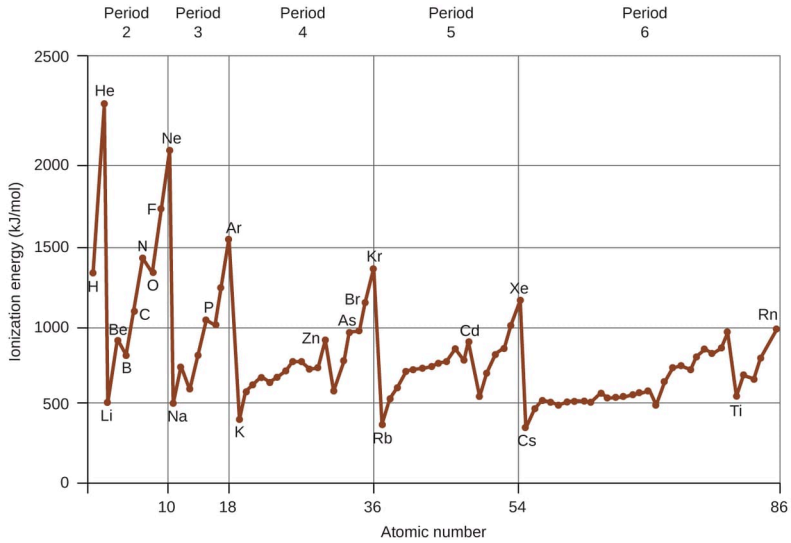


Figure 2.6.4: The first ionization energy of the elements in the first five periods are plotted against their atomic number.

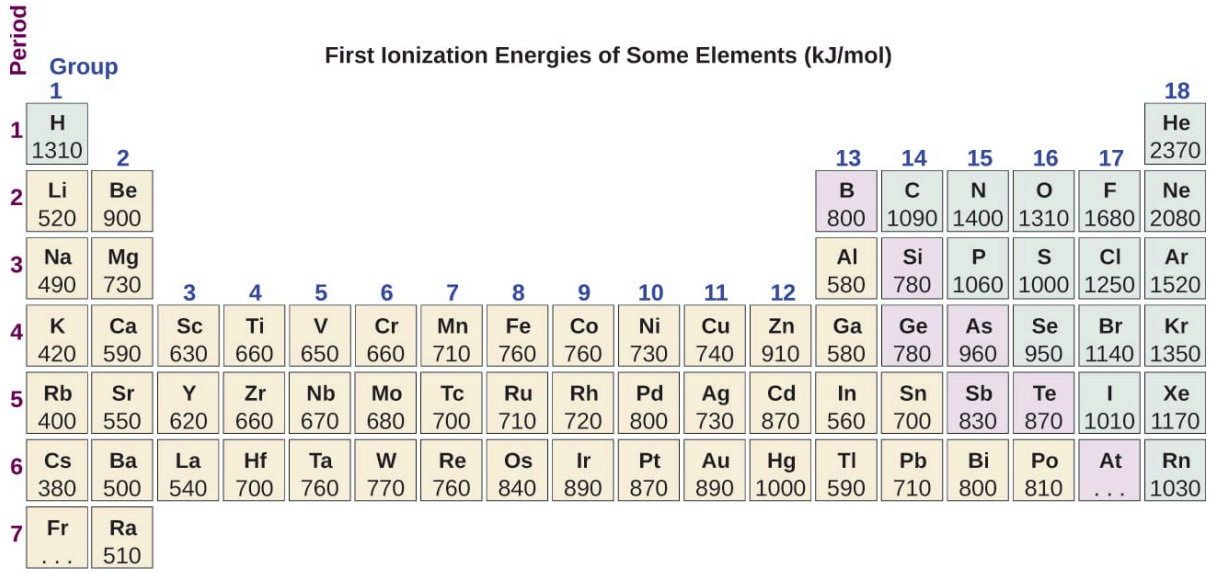
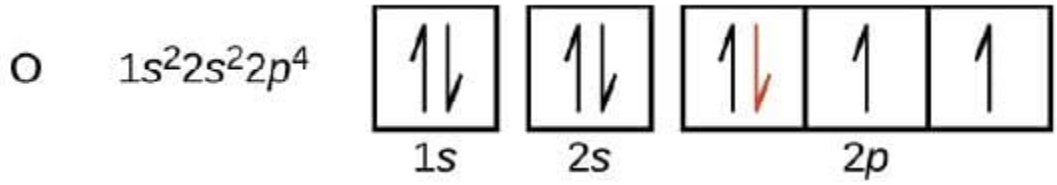


Figure 2.6.5: This version of the periodic table shows the first ionization energy (IE_1), in kJ/mol, of selected elements.

Another deviation occurs as orbitals become more than one-half filled. The first ionization energy for oxygen is slightly less than that for nitrogen, despite the trend in increasing IE_1 values across a period. Looking at the orbital diagram of oxygen, we can see that removing one electron will eliminate the electron–electron repulsion caused by pairing the electrons in the *2p* orbital and will result in a half-filled orbital (which is energetically favorable). Analogous changes occur in succeeding periods (note the dip for sulfur after phosphorus in Figure 2.6.5).



Removing an electron from a cation is more difficult than removing an electron from a neutral atom because of the greater electrostatic attraction to the cation. Likewise, removing an electron from a cation with a higher positive charge is more difficult than removing an electron from an ion with a lower charge. Thus, successive ionization energies for one element always increase. As seen in Table 2.6.2, there is a large increase in the ionization energies for each element. This jump corresponds to removal of the core electrons, which are harder to remove than the valence electrons. For example, Sc and Ga both have three valence electrons, so the rapid increase in ionization energy occurs after the third ionization.

Table 2.6.2: Successive Ionization Energies for Selected Elements (kJ/mol)

Element	IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7
K	418.8	3051.8	4419.6	5876.9	7975.5	9590.6	11343
Ca	589.8	1145.4	4912.4	6490.6	8153.0	10495.7	12272.9
Sc	633.1	1235.0	2388.7	7090.6	8842.9	10679.0	13315.0
Ga	578.8	1979.4	2964.6	6180	8298.7	10873.9	13594.8
Ge	762.2	1537.5	3302.1	4410.6	9021.4	Not available	Not available
As	944.5	1793.6	2735.5	4836.8	6042.9	12311.5	Not available

Example 2.6.2: Ranking Ionization Energies

Predict the order of increasing energy for the following processes: IE_1 for Al, IE_1 for Tl, IE_2 for Na, IE_3 for Al.

Solution

Removing the $6p^1$ electron from Tl is easier than removing the $3p^1$ electron from Al because the higher *n* orbital is farther from the nucleus, so IE_1(Tl) < IE_1(Al). Ionizing the third electron from Al ($Al^{2+} \longrightarrow Al^{3+} + e^-$) requires more energy because the cation Al^{2+} exerts a stronger pull on the electron than the neutral Al atom, so IE_1(Al) < IE_3(Al). The second ionization energy for sodium removes a core electron, which is a much higher energy process than removing valence electrons. Putting this all together, we obtain: IE_1(Tl) < IE_1(Al) < IE_3(Al) < IE_2(Na).

Exercise 2.6.2

Which has the lowest value for IE_1: O, Po, Pb, or Ba?

Answer available at the end of this section.

Variation in Electron Affinities

The **electron affinity** (EA) is the energy change for the process of adding an electron to a gaseous atom to form an anion (negative ion).

$$X(g) + e^- \longrightarrow X^-(g) \quad EA_1$$

This process can be either endothermic or exothermic, depending on the element. The EA of some of the elements is given in Figure 2.6.6. You can see that many of these elements have negative values of EA, which means that energy is released when the gaseous atom accepts an electron. However, for some elements, energy is required for the atom to become negatively charged and the value of their EA is positive. Just as with ionization energy, subsequent EA values are associated with forming ions with more charge. The second EA is the energy associated with adding an electron to an anion to form a –2 ion, and so on.

As we might predict, it becomes easier to add an electron across a series of atoms as the effective nuclear charge of the atoms increases. We find, as we go from left to right across a period, EAs tend to become more negative. The exceptions found among the elements of group 2 (2A), group 15 (5A), and group 18 (8A) can be understood based on the electronic structure of these groups. The noble gases, group 18 (8A), have a completely filled shell and the incoming electron must be added to a higher *n* level, which is more difficult to do. Group 2 (2A) has a filled *ns* subshell, and so the next electron added goes into the higher energy *np*, so, again, the observed EA value is not as the trend would predict. Finally, group 15 (5A) has a half-filled *np* subshell and the next electron must be paired with an existing *np* electron. In all of these cases, the initial relative stability of the electron configuration disrupts the trend in EA.

We also might expect the atom at the top of each group to have the most negative EA; their first ionization potentials suggest that these atoms have the largest effective nuclear charges. However, as we move down a group, we see that the *second* element in the group most often has the most negative EA. This can be attributed to the small size of the *n* = 2 shell and the resulting large electron–electron repulsions. For example, chlorine, with an EA value of –348 kJ/mol, has the highest value of any element in the periodic table. The EA of fluorine is –322 kJ/mol. When we add an electron to a fluorine atom to form a fluoride anion (F^-), we add an electron to the *n* = 2 shell. The electron is attracted to the nucleus, but there is also significant repulsion from the other electrons already present in this small valence shell. The chlorine atom has the same electron configuration in the valence shell, but because the entering electron is going into the *n* = 3 shell, it occupies a considerably larger region of space and the electron–electron repulsions are reduced. The entering electron does not experience as much repulsion and the chlorine atom accepts an additional electron more readily, resulting in a more negative EA.

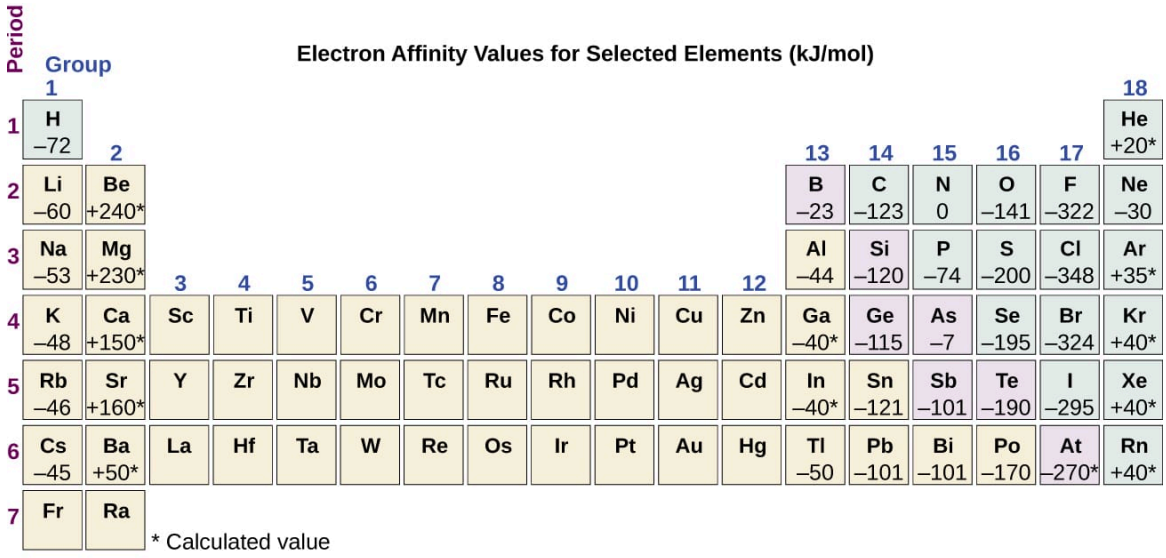


Figure 2.6.6: This version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements.

The properties discussed in this section (size of atoms and ions, effective nuclear charge, ionization energies, and electron affinities) are central to understanding chemical reactivity. For example, because fluorine has an energetically favorable EA and a large energy barrier to ionization (IE), it is much easier to form fluorine anions than cations. Metallic properties including conductivity and malleability (the ability to be formed into sheets) depend on having electrons that can be removed easily. Thus, metallic character increases as we move down a group and decreases across a period in the same trend observed for atomic size because it is easier to remove an electron that is farther away from the nucleus.

Answers

Exercise 2.6.1

Ne or He

Exercise 2.6.2

Ba

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2.7: The Periodic Table

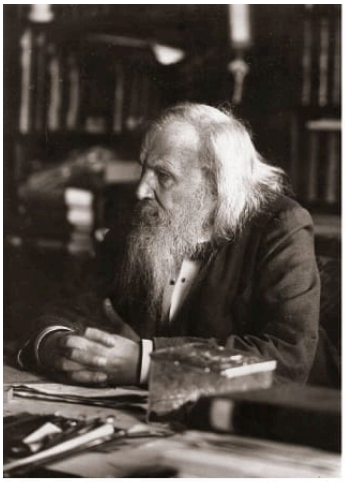
Learning Objectives

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

- 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 2.7.1).



(a)

Reihen	Gruppo I. — R^1O	Gruppo II. — RO	Gruppo III. — R^2O^3	Gruppo IV. RH^4 RO^2	Gruppo V. RH^3 R^2O^5	Gruppo VI. RH^2 RO^3	Gruppo VII. RH R^2O^7	Gruppo VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

(b)

Figure 2.7.1: (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)

By the twentieth century, it became apparent that the periodic relationship involved atomic numbers rather than atomic masses. The modern statement of this relationship, the **periodic law**, is as follows: *the properties of the elements are periodic functions of their atomic numbers*. A modern **periodic table** arranges the elements in increasing order of their atomic numbers and groups atoms with similar properties in the same vertical column (Figure 2.7.2). 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.

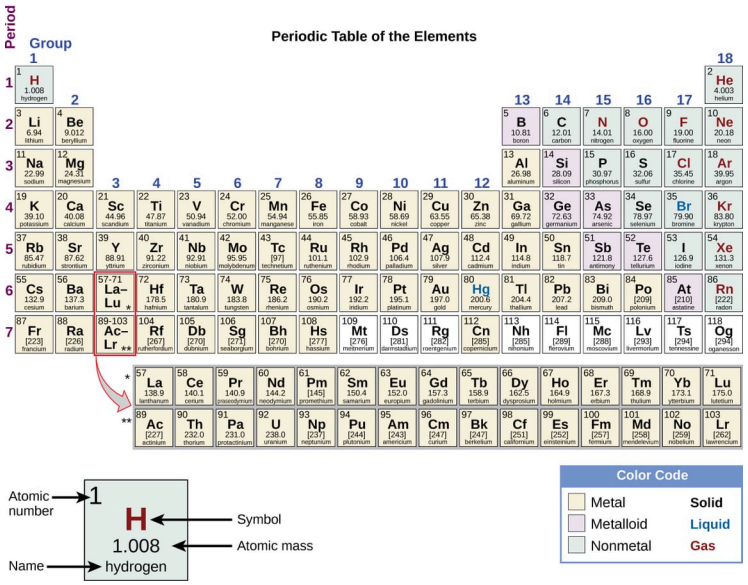


Figure 2.7.2: Elements in the periodic table are organized according to their properties.

Even after the periodic nature of elements and the table itself were widely accepted, gaps remained. Mendeleev had predicted, and others including Henry Moseley had later confirmed, that there should be elements below Manganese in Group 7. German chemists Ida Tacke and Walter Noddack set out to find the elements, a quest being pursued by scientists around the world. Their method was unique in that they did not only consider the properties of manganese, but also the elements horizontally adjacent to the missing elements 43 and 75 on the table. Thus, by investigating ores containing minerals of ruthenium (Ru), tungsten (W), osmium (Os), and so on, they were able to identify naturally occurring elements that helped complete the table. Rhenium, one of their discoveries, was one of the last natural elements to be discovered and is the last stable element to be discovered. (Francium, the last natural element to be discovered, was identified by Marguerite Perey in 1939.)

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[3]; and inner transition metals in the two rows at the bottom of the table (the top-row elements are called lanthanides and the bottom-row elements are actinides; Figure 2.7.3). 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.

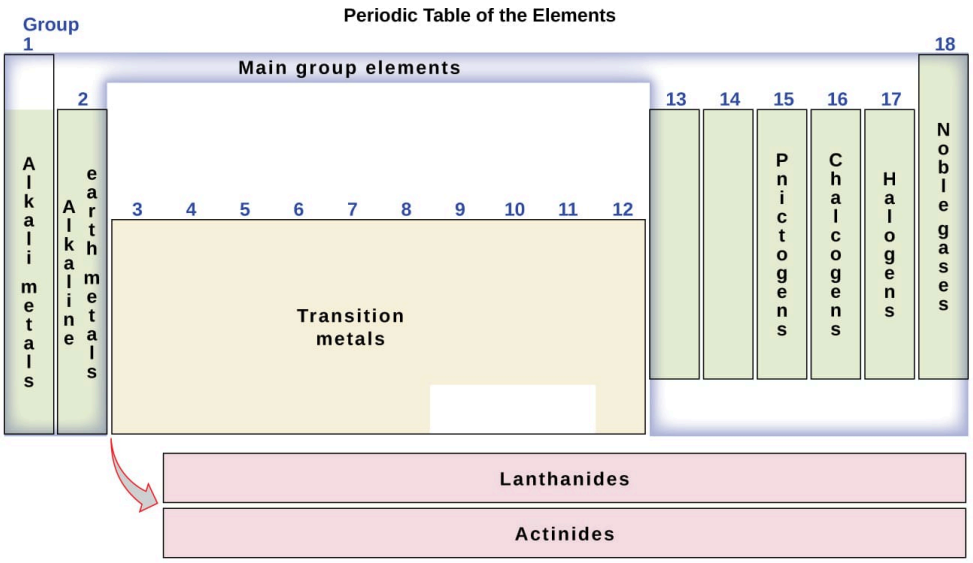


Figure 2.7.3: The periodic table organizes elements with similar properties into groups.

Link to Learning

Click on this link for an interactive periodic table, which you can use to explore the properties of the elements (includes podcasts and videos of each element). You may also want to try this one that shows photos of all the elements.

Example 2.7.1: 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 2.7.1

Give the group name for each of the following elements:

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

Answer available at the end of this section.

As you will learn in your further study of chemistry, elements in groups often behave in a somewhat similar manner. This is partly due to the number of electrons in their outer shell and their similar readiness to bond. These shared properties can have far-ranging implications in nature, science, and medicine. For example, when Gertrude Elion and George Hitchens were investigating ways to interrupt cell and virus replication to fight diseases, they utilized the similarity between sulfur and oxygen (both in Group 16) and their capacity to bond in similar ways. Elion focused on purines, which are key components of DNA and which contain oxygen. She found that by introducing sulfur-based compounds (called purine analogues) that mimic the structure of purines, molecules within DNA would bond to the analogues rather than the "regular" DNA purine. With the normal DNA bonding and structure altered, Elion successfully interrupted cell replication. At its core, the strategy worked because of the similarity between sulfur and oxygen. Her discovery led directly to important treatments for leukemia. Overall, Elion's work with George Hitchens not only led to more treatments, but also changed the entire methodology of drug development. By using specific elements and compounds to target specific aspects of tumor cells, viruses, and bacteria, they laid the groundwork for many of today's most common and important medicines, used to help millions of people each year. They were awarded the Nobel Prize in 1988.

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 (an approximate atomic mass) of the most stable isotope of that element.

Footnotes

- 3Per the IUPAC definition, group 12 elements are not transition metals, though they are often referred to as such. Additional details on this group's elements are provided in a chapter on transition metals and coordination chemistry.

Answers

Exercise 2.7.1

(a) noble gas; (b) chalcogen; (c) alkaline earth metal; (d) alkali metal

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2.8: Ionic and Molecular Compounds

Learning Objectives

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

- 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 2.8.1).

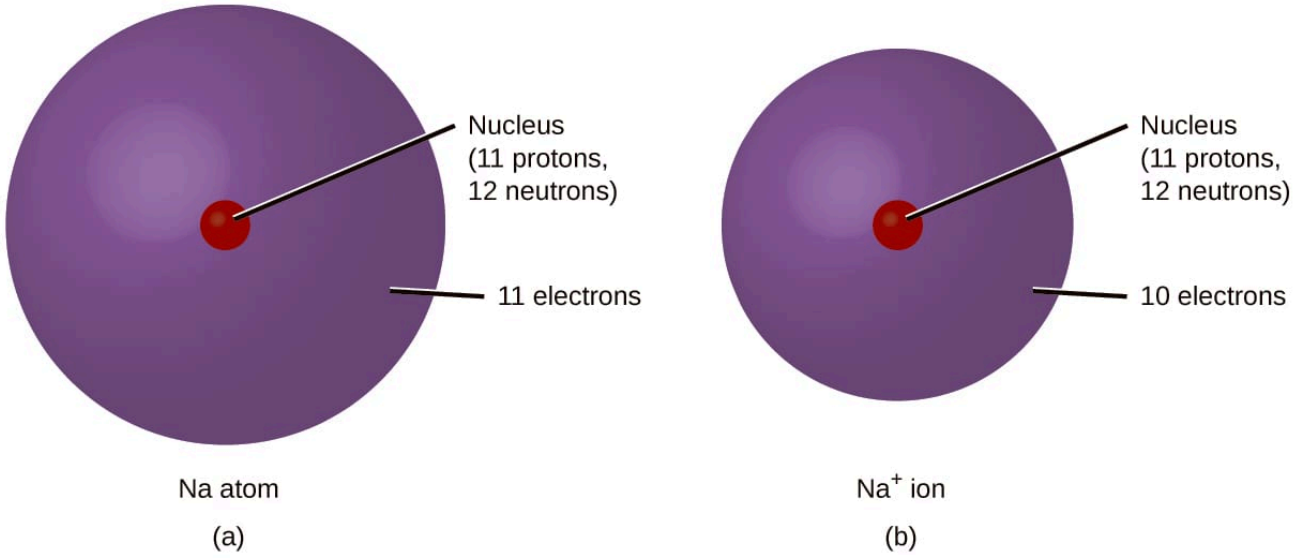


Table 2.8.1: (a) A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. (b) A sodium cation (Na^+) has lost an electron, so it has one more proton (11) than electrons (10), giving it an overall positive charge, signified by a superscripted plus sign.

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 2.8.2). 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.

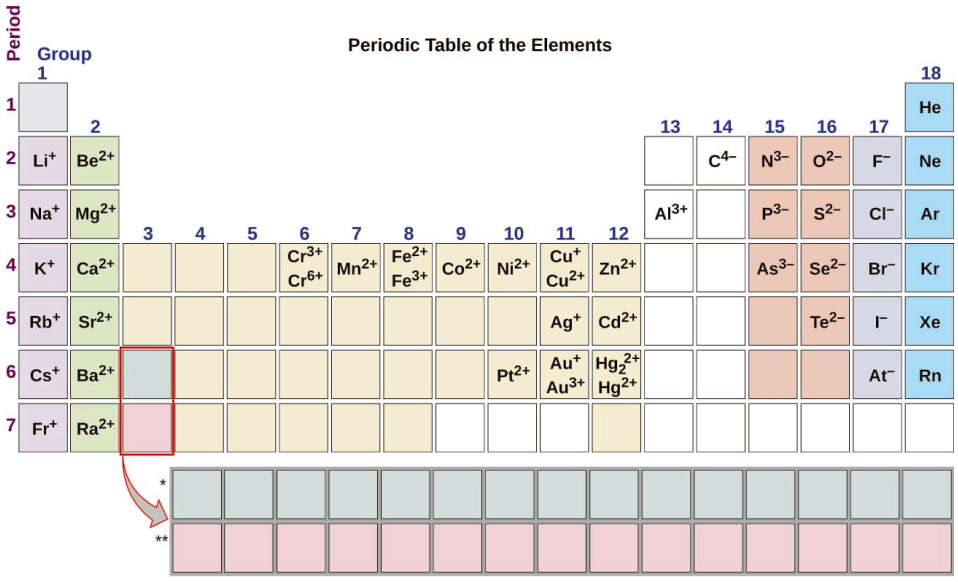


Table 2.8.2: Some elements exhibit a regular pattern of ionic charge when they form ions.

Example 2.8.1: 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 2.8.1

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

Answer available at the end of this section.

Example 2.8.2: 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 2.8.2

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 available at the end of this section.

The ions that we have discussed so far are called monatomic ions, that is, they are ions formed from only one atom. We also find many polyatomic ions. These ions, which act as discrete units, are electrically charged molecules (a group of bonded atoms with an overall charge). Some of the more important polyatomic ions are listed in Table 2.8.1. 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 2.8.1: Common Polyatomic Ions

Name	Formula	Related Acid	Formula
ammonium	NH_4^+		
hydronium	H_3O		
peroxide	O_2^{2-}		
hydroxide	OH^-		
acetate	CH_3COO^-	acetic acid	CH_3COOH
cyanide	CN^-	hydrocyanic acid	HCN
azide	N_3^-	hydrazoic acid	HN_3
carbonate	CO_3^{2-}	carbonic acid	H_2CO_3
bicarbonate	HCO_3^-		
nitrate	NO_3^-	nitric acid	HNO_3
nitrite	NO_2^-	nitrous acid	HNO_2
sulfate	SO_{42}^-	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	$HClO_4$

Name	Formula	Related Acid	Formula
chlorate	$\mathrm{ClO_3^-}$	chloric acid	$\mathrm{HClO_3}$
chlorite	$\mathrm{ClO_2^-}$	chlorous acid	$\mathrm{HClO_2}$
hypochlorite	$\mathrm{ClO^-}$	hypochlorous acid	HClO
chromate	$\mathrm{CrO_4^{2-}}$	chromic acid	$\mathrm{H_2CrO_4}$
dichromate	$\mathrm{Cr_2O_7^{2-}}$	dichromic acid	$\mathrm{H_2Cr_2O_7}$
permanganate	$\mathrm{MnO_4^-}$	permanganic acid	$\mathrm{HMnO_4}$

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 $\mathrm{ClO_4^-}$, chlorate is $\mathrm{ClO_3^-}$, chlorite is $\mathrm{ClO_2^-}$ and hypochlorite is $\mathrm{ClO^-}$. Unfortunately, the number of oxygen atoms corresponding to a given suffix or prefix is not consistent; for example, nitrate is $\mathrm{NO_3^-}$ while sulfate is $\mathrm{SO_4^{2-}}$. 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.

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 $2.8.3$).

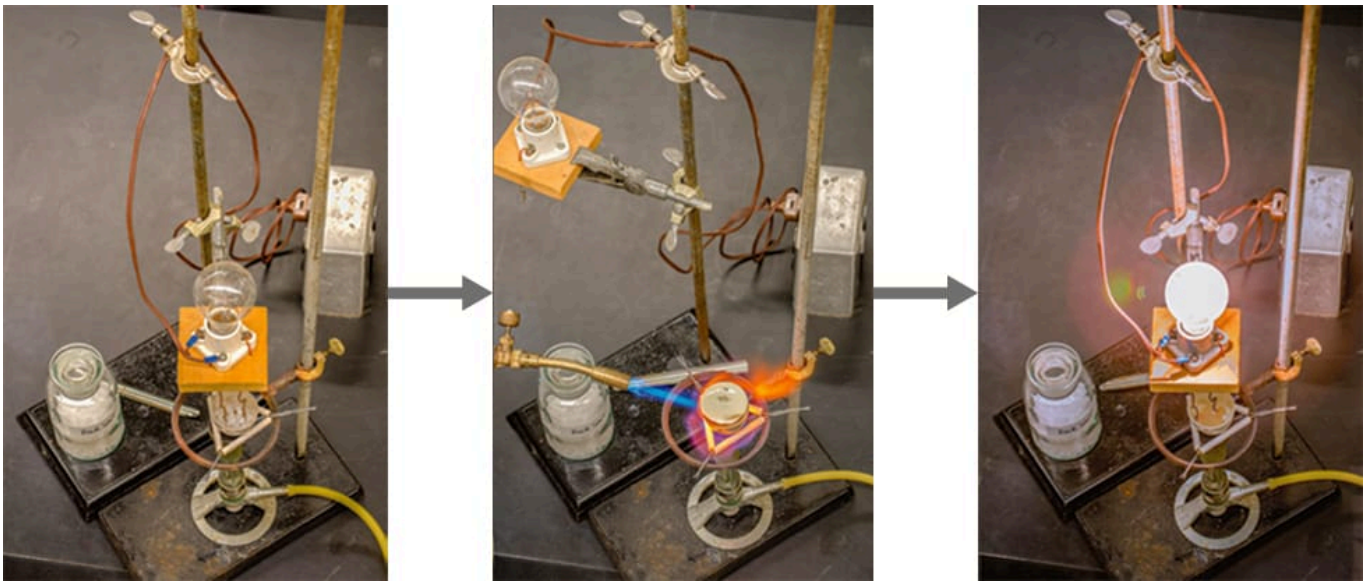


Table 2.8.3: Sodium chloride melts at 801 °C and conducts electricity when molten. (credit: modification of work by Mark Blaser and Matt Evans)

Link to Learning

Watch this video to see a mixture of salts melt and conduct electricity.

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

Example 2.8.3: Predicting the Formula of an Ionic Compound

The gemstone sapphire (Figure 2.8.4) 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?



Table 2.8.4: 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 via Wikipedia)

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 2.8.3

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

Answer available at the end of this section.

Many ionic compounds contain polyatomic ions (Table 2.8.1) 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 ($PO_4{}^{3-}$) groups. The $PO_4{}^{3-}$ groups are discrete units, each consisting of one phosphorus atom and four oxygen atoms, and having an overall charge of 3–. The compound is electrically neutral, and its formula shows a total count of three Ca, two P, and eight O atoms.

Example 2.8.4: 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 2.8.4

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 available at the end of this section.

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, $C_2O_4^{2-}$.

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 2.8.5: 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 2.8.5

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 available at the end of this section.

Answers

Exercise 2.8.1

Se^{2-}, the selenide ion

Exercise 2.8.2

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.

Exercise 2.8.3

Na_2S

Exercise 2.8.4

Li_2O_2

Exercise 2.8.5

a. molecular
b. ionic
c. molecular
d. ionic

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2.9: Key Terms

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

amplitude
extent of the displacement caused by a wave

atomic orbital
mathematical function that describes the behavior of an electron in an atom (also called the wavefunction)

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

blackbody
idealized perfect absorber of all incident electromagnetic radiation; such bodies emit electromagnetic radiation in characteristic continuous spectra called blackbody radiation

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

chalcogen
element in group 16

continuous spectrum
electromagnetic radiation given off in an unbroken series of wavelengths (e.g., white light from the sun)

core electron
electron in an atom that occupies the orbitals of the inner shells

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

covalent radius
one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond

***d* orbital**
region of space with high electron density that is either four lobed or contains a dumbbell and torus shape; describes orbitals with $l = 2$.

degenerate orbitals
orbitals that have the same energy

effective nuclear charge
charge that leads to the Coulomb force exerted by the nucleus on an electron, calculated as the nuclear charge minus shielding

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

electron affinity
energy change associated with addition of an electron to a gaseous atom or ion

electron configuration
listing that identifies the electron occupancy of an atom's shells and subshells

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

endothermic
processes that increase the energy of an atom and involve the absorption of light

excited state
state having an energy greater than the ground-state energy

exothermic
processes that decrease the energy of an atom and involve the emission of light

***f* orbital**
multilobed region of space with high electron density, describes orbitals with $l = 3$

frequency (ν)
number of wave cycles (peaks or troughs) that pass a specified point in space per unit time

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

halogen
element in group 17

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

hertz (Hz)
the unit of frequency, which is the number of cycles per second, s^{-1}

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

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

intensity
property of wave-propagated energy related to the amplitude of the wave, such as brightness of light or loudness of sound

interference pattern
pattern typically consisting of alternating bright and dark fringes; it results from constructive and destructive interference of waves

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

ionization energy
energy required to remove an electron from a gaseous atom or ion

isoelectronic
group of ions or atoms that have identical electron configurations

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

line spectrum
electromagnetic radiation emitted at discrete wavelengths by a specific atom (or atoms) in an excited state

magnetic quantum number (m_l)
quantum number signifying the orientation of an atomic orbital around the nucleus

main-group element
(also, representative element) element in groups 1, 2, and 13–18

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

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

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

node
any point of a standing wave with zero amplitude

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

orbital diagram
pictorial representation of the electron configuration showing each orbital as a box and each electron as an arrow

oxyanion
polyatomic anion composed of a central atom bonded to oxygen atoms

***p* orbital**
dumbbell-shaped region of space with high electron density, describes orbitals with $l = 1$

Pauli exclusion principle
specifies that no two electrons in an atom can have the same value for all four quantum numbers

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

photon
smallest possible packet of electromagnetic radiation, a particle of light

pnictogen
element in group 15

polyatomic ion
ion composed of more than one atom

principal quantum number (*n*)
quantum number specifying the shell an electron occupies in an atom

quantization
limitation of some property to 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
number having only specific allowed values and used to characterize the arrangement of electrons in an atom

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

s orbital
spherical region of space with high electron density, describes orbitals with $l = 0$

secondary (angular momentum) quantum number (*l*)
quantum number distinguishing the different shapes of orbitals; it is also a measure of the orbital angular momentum

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

shell
atomic orbitals with the same principal quantum number, *n*

spin quantum number (m_s)
number specifying the electron spin direction, either $+\frac{1}{2}$ or $-\frac{1}{2}$

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

subshell
atomic orbitals with the same values of *n* and *l*

transition metal
element in groups 3–12 (more strictly defined, 3–11; see chapter on transition metals and coordination chemistry)

valence electrons
electrons in the high energy outer shell(s) of an atom

valence shell
high energy outer shell(s) of an atom

wave
oscillation of a property over time or space; can transport energy from one point to another

wave-particle duality
observation that elementary particles can exhibit both wave-like and particle-like properties

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

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2.10: Key Equations

$c = \lambda v$

$E = h\nu = \dfrac{hc}{\lambda}, \text{ where } h = 6.626 \times 10^{-34} \text{ J s}$

$\dfrac{1}{\lambda} = R_{\infty}\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)$

$E_n = -\dfrac{kZ^2}{n^2}, n = 1, 2, 3, \ldots$

$\Delta E = kZ^2\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)$

$r = \dfrac{n^2}{Z}a_0$

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2.11: Summary

Light and other forms of electromagnetic radiation move through a vacuum with a constant speed, c, of 2.998×10^8 m s^{-1}. This radiation shows wavelike behavior, which can be characterized by a frequency, ν, and a wavelength, λ, such that $c = \lambda\nu$. Light is an example of a travelling wave. Other important wave phenomena include standing waves, periodic oscillations, and vibrations. Standing waves exhibit quantization, since their wavelengths are limited to discrete integer multiples of some characteristic lengths. Electromagnetic radiation that passes through two closely spaced narrow slits having dimensions roughly similar to the wavelength will show an interference pattern that is a result of constructive and destructive interference of the waves. Electromagnetic radiation also demonstrates properties of particles called photons. The energy of a photon is related to the frequency (or alternatively, the wavelength) of the radiation as $E = h\nu$ (or $E =$), where h is Planck's constant. That light demonstrates both wavelike and particle-like behavior is known as wave-particle duality. All forms of electromagnetic radiation share these properties, although various forms including X-rays, visible light, microwaves, and radio waves interact differently with matter and have very different practical applications. Electromagnetic radiation can be generated by exciting matter to higher energies, such as by heating it. The emitted light can be either continuous (incandescent sources like the sun) or discrete (from specific types of excited atoms). Continuous spectra often have distributions that can be approximated as blackbody radiation at some appropriate temperature. The line spectrum of hydrogen can be obtained by passing the light from an electrified tube of hydrogen gas through a prism. This line spectrum was simple enough that an empirical formula called the Rydberg formula could be derived from the spectrum. Three historically important paradoxes from the late 19th and early 20th centuries that could not be explained within the existing framework of classical mechanics and classical electromagnetism were the blackbody problem, the photoelectric effect, and the discrete spectra of atoms. The resolution of these paradoxes ultimately led to quantum theories that superseded the classical theories.

Bohr incorporated Planck's and Einstein's quantization ideas into a model of the hydrogen atom that resolved the paradox of atom stability and discrete spectra. The Bohr model of the hydrogen atom explains the connection between the quantization of photons and the quantized emission from atoms. Bohr described the hydrogen atom in terms of an electron moving in a circular orbit about a nucleus. He postulated that the electron was restricted to certain orbits characterized by discrete energies. Transitions between these allowed orbits result in the absorption or emission of photons. When an electron moves from a higher-energy orbit to a more stable one, energy is emitted in the form of a photon. To move an electron from a stable orbit to a more excited one, a photon of energy must be absorbed. Using the Bohr model, we can calculate the energy of an electron and the radius of its orbit in any one-electron system.

Macroscopic objects act as particles. Microscopic objects (such as electrons) have properties of both a particle and a wave. Their exact trajectories cannot be determined. The quantum mechanical model of atoms describes the three-dimensional position of the electron in a *probabilistic* manner according to a mathematical function called a wavefunction, often denoted as ψ. Atomic wavefunctions are also called orbitals. The squared magnitude of the wavefunction describes the distribution of the probability of finding the electron in a particular region in space. Therefore, atomic orbitals describe the areas in an atom where electrons are most likely to be found.

An atomic orbital is characterized by three quantum numbers. The principal quantum number, n, can be any positive integer. The general region for value of energy of the orbital and the average distance of an electron from the nucleus are related to n. Orbitals having the same value of n are said to be in the same shell. The secondary (angular momentum) quantum number, l, can have any integer value from 0 to $n - 1$. This quantum number describes the shape or type of the orbital. Orbitals with the same principal quantum number and the same l value belong to the same subshell. The magnetic quantum number, m_l, with $2l + 1$ values ranging from $-l$ to $+l$, describes the orientation of the orbital in space. In addition, each electron has a spin quantum number, m_s, that can be equal to $\pm \frac{1}{2}$. No two electrons in the same atom can have the same set of values for all the four quantum numbers.

The relative energy of the subshells determine the order in which atomic orbitals are filled (1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, and so on). Electron configurations and orbital diagrams can be determined by applying the Pauli exclusion principle (no two electrons can have the same set of four quantum numbers) and Hund's rule (whenever possible, electrons retain unpaired spins in degenerate orbitals).

Electrons in the outermost orbitals, called valence electrons, are responsible for most of the chemical behavior of elements. In the periodic table, elements with analogous valence electron configurations usually occur within the same group. There are some exceptions to the predicted filling order, particularly when half-filled or completely filled orbitals can be formed. The periodic table can be divided into three categories based on the orbital in which the last electron to be added is placed: main group elements (s and p orbitals), transition elements (d orbitals), and inner transition elements (f orbitals).

Electron configurations allow us to understand many periodic trends. Covalent radius increases as we move down a group because the *n* level (orbital size) increases. Covalent radius mostly decreases as we move left to right across a period because the effective nuclear charge experienced by the electrons increases, and the electrons are pulled in tighter to the nucleus. Anionic radii are larger than the parent atom, while cationic radii are smaller, because the number of valence electrons has changed while the nuclear charge has remained constant. Ionization energy (the energy associated with forming a cation) decreases down a group and mostly increases across a period because it is easier to remove an electron from a larger, higher energy orbital. Electron affinity (the energy associated with forming an anion) is more favorable (exothermic) when electrons are placed into lower energy orbitals, closer to the nucleus. Therefore, electron affinity becomes increasingly negative as we move left to right across the periodic table and decreases as we move down a group. For both IE and electron affinity data, there are exceptions to the trends when dealing with completely filled or half-filled subshells.

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.

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 nonmetals.

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2.12: Exercises

1.

The light produced by a red neon sign is due to the emission of light by excited neon atoms. Qualitatively describe the spectrum produced by passing light from a neon lamp through a prism.

2.

An FM radio station found at 103.1 on the FM dial broadcasts at a frequency of $1.031 \times 10^{8}\ s^{-1}$ (103.1 MHz). What is the wavelength of these radio waves in meters?

3.

FM-95, an FM radio station, broadcasts at a frequency of $9.51 \times 10^{7}\ s^{-1}$ (95.1 MHz). What is the wavelength of these radio waves in meters?

4.

A bright violet line occurs at 435.8 nm in the emission spectrum of mercury vapor. What amount of energy, in joules, must be released by an electron in a mercury atom to produce a photon of this light?

5.

Light with a wavelength of 614.5 nm looks orange. What is the energy, in joules, per photon of this orange light? What is the energy in eV (1 eV = 1.602×10^{-19} J)?

6.

Heated lithium atoms emit photons of light with an energy of 2.961×10^{-19} J. Calculate the frequency and wavelength of one of these photons. What is the total energy in 1 mole of these photons? What is the color of the emitted light?

7.

A photon of light produced by a surgical laser has an energy of 3.027×10^{-19} J. Calculate the frequency and wavelength of the photon. What is the total energy in 1 mole of photons? What is the color of the emitted light?

8.

When rubidium ions are heated to a high temperature, two lines are observed in its line spectrum at wavelengths (a) 7.9×10^{-7} m and (b) 4.2×10^{-7} m. What are the frequencies of the two lines? What color do we see when we heat a rubidium compound?

9.

The emission spectrum of cesium contains two lines whose frequencies are (a) 3.45×10^{14} Hz and (b) 6.53×10^{14} Hz. What are the wavelengths and energies per photon of the two lines? What color are the lines?

10.

Photons of infrared radiation are responsible for much of the warmth we feel when holding our hands before a fire. These photons will also warm other objects. How many infrared photons with a wavelength of 1.5×10^{-6} m must be absorbed by the water to warm a cup of water (175 g) from 25.0 °C to 40 °C?

11.

One of the radiographic devices used in a dentist's office emits an X-ray of wavelength 2.090×10^{-11} m. What is the energy, in joules, and frequency of this X-ray?

12.

The eyes of certain reptiles pass a single visual signal to the brain when the visual receptors are struck by photons of a wavelength of 850 nm. If a total energy of 3.15×10^{-14} J is required to trip the signal, what is the minimum number of photons that must strike the receptor?

13.

RGB color television and computer displays use cathode ray tubes that produce colors by mixing red, green, and blue light. If we look at the screen with a magnifying glass, we can see individual dots turn on and off as the colors change. Using a spectrum of visible light, determine the approximate wavelength of each of these colors. What is the frequency and energy of a photon of each of these colors?

14.

Answer the following questions about a Blu-ray laser:

(a) The laser on a Blu-ray player has a wavelength of 405 nm. In what region of the electromagnetic spectrum is this radiation? What is its frequency?

(b) A Blu-ray laser has a power of 5 milliwatts (1 watt = 1 J s^{-1}). How many photons of light are produced by the laser in 1 hour?

(c) The ideal resolution of a player using a laser (such as a Blu-ray player), which determines how close together data can be stored on a compact disk, is determined using the following formula: Resolution = $0.60(\lambda/\text{NA})$, where λ is the wavelength of the laser and NA is the numerical aperture. Numerical aperture is a measure of the size of the spot of light on the disk; the larger the NA, the smaller the spot. In a typical Blu-ray system, NA = 0.95. If the 405-nm laser is used in a Blu-ray player, what is the closest that information can be stored on a Blu-ray disk?

(d) The data density of a Blu-ray disk using a 405-nm laser is 1.5×10^{7} bits mm^{-2}. Disks have an outside diameter of 120 mm and a hole of 15-mm diameter. How many data bits can be contained on the disk? If a Blu-ray disk can hold 9,400,000 pages of text, how many data bits are needed for a typed page? (Hint: Determine the area of the disk that is available to hold data. The area inside a circle is given by $A = \pi r^2$, where the radius r is one-half of the diameter.)

15.

What is the threshold frequency for sodium metal if a photon with frequency 6.66×10^{14} s^{-1} ejects an electron with 7.74×10^{-20} J kinetic energy? Will the photoelectric effect be observed if sodium is exposed to orange light?

16.

Why is the electron in a Bohr hydrogen atom bound less tightly when it has a quantum number of 3 than when it has a quantum number of 1?

17.

What does it mean to say that the energy of the electrons in an atom is quantized?

18.

Using the Bohr model, determine the energy, in joules, necessary to ionize a ground-state hydrogen atom. Show your calculations.

19.

The electron volt (eV) is a convenient unit of energy for expressing atomic-scale energies. It is the amount of energy that an electron gains when subjected to a potential of 1 volt; 1 eV = 1.602×10^{-19} J. Using the Bohr model, determine the energy, in electron volts, of the photon produced when an electron in a hydrogen atom moves from the orbit with $n = 5$ to the orbit with $n = 2$. Show your calculations.

20.

Using the Bohr model, determine the lowest possible energy, in joules, for the electron in the Li^{2+} ion.

21.

Using the Bohr model, determine the lowest possible energy for the electron in the He^{+} ion.

22.

Using the Bohr model, determine the energy of an electron with $n = 6$ in a hydrogen atom.

23.

Using the Bohr model, determine the energy of an electron with $n = 8$ in a hydrogen atom.

24.

How far from the nucleus in angstroms (1 angstrom = 1×10^{-10} m) is the electron in a hydrogen atom if it has an energy of -8.72×10^{-20} J?

25.

What is the radius, in angstroms, of the orbital of an electron with $n = 8$ in a hydrogen atom?

26.

Using the Bohr model, determine the energy in joules of the photon produced when an electron in a He^{+} ion moves from the orbit with $n = 5$ to the orbit with $n = 2$.

27.

Using the Bohr model, determine the energy in joules of the photon produced when an electron in a Li^{2+} ion moves from the orbit with $n = 2$ to the orbit with $n = 1$.

28.

Consider a large number of hydrogen atoms with electrons randomly distributed in the $n = 1$, 2, 3, and 4 orbits.

(a) How many different wavelengths of light are emitted by these atoms as the electrons fall into lower-energy orbits?

(b) Calculate the lowest and highest energies of light produced by the transitions described in part (a).

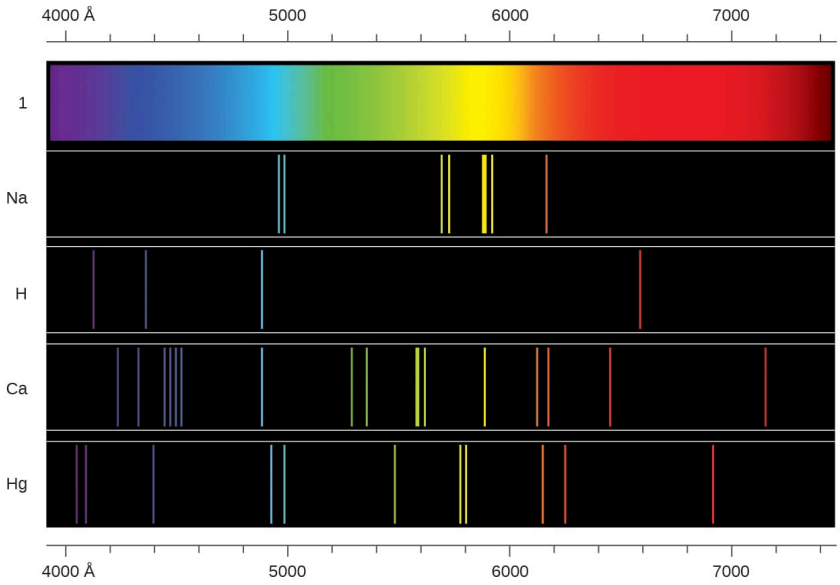
(c) Calculate the frequencies and wavelengths of the light produced by the transitions described in part (b).

29.

How are the Bohr model and the Rutherford model of the atom similar? How are they different?

30.

The spectra of hydrogen and of calcium are shown here.



What causes the lines in these spectra? Why are the colors of the lines different? Suggest a reason for the observation that the spectrum of calcium is more complicated than the spectrum of hydrogen.

31.

How are the Bohr model and the quantum mechanical model of the hydrogen atom similar? How are they different?

32.

What are the allowed values for each of the four quantum numbers: n, l, m_l, and m_s?

33.

Describe the properties of an electron associated with each of the following four quantum numbers: n, l, m_l, and m_s.

34.

Answer the following questions:

(a) Without using quantum numbers, describe the differences between the shells, subshells, and orbitals of an atom.

(b) How do the quantum numbers of the shells, subshells, and orbitals of an atom differ?

35.

Identify the subshell in which electrons with the following quantum numbers are found:

(a) $n = 2$, $l = 1$

(b) $n = 4$, $l = 2$

(c) $n = 6$, $l = 0$

36.

Which of the subshells described in the previous question contain degenerate orbitals? How many degenerate orbitals are in each?

37.

Identify the subshell in which electrons with the following quantum numbers are found:

(a) $n = 3$, $l = 2$

(b) $n = 1$, $l = 0$

(c) $n = 4$, $l = 3$

38.

Which of the subshells described in the previous question contain degenerate orbitals? How many degenerate orbitals are in each?

39.

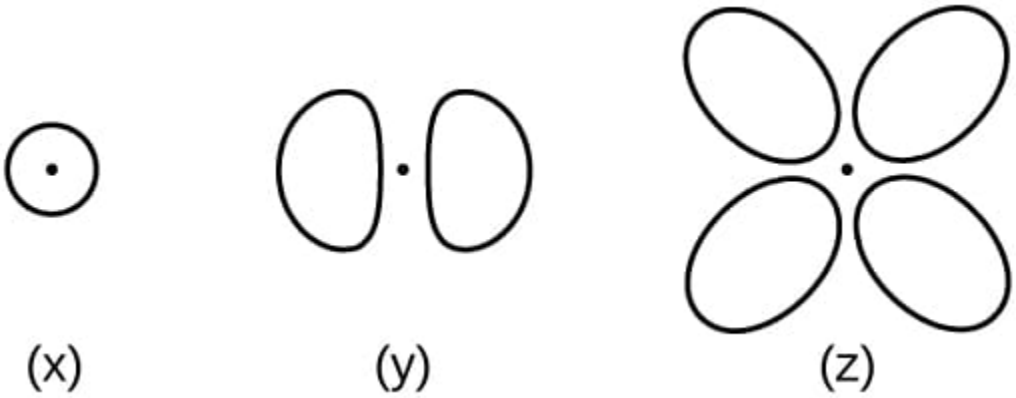
Sketch the boundary surface of a $d_{x^2-y^2}$ and a p_y orbital. Be sure to show and label the axes.

40.

Sketch the p_x and d_{xz} orbitals. Be sure to show and label the coordinates.

41.

Consider the orbitals shown here in outline.



(a) What is the maximum number of electrons contained in an orbital of type (x)? Of type (y)? Of type (z)?

(b) How many orbitals of type (x) are found in a shell with n = 2? How many of type (y)? How many of type (z)?

(c) Write a set of quantum numbers for an electron in an orbital of type (x) in a shell with n = 4. Of an orbital of type (y) in a shell with n = 2. Of an orbital of type (z) in a shell with n = 3.

(d) What is the smallest possible n value for an orbital of type (x)? Of type (y)? Of type (z)?

(e) What are the possible l and m_l values for an orbital of type (x)? Of type (y)? Of type (z)?

42.

State the Heisenberg uncertainty principle. Describe briefly what the principle implies.

43.

How many electrons could be held in the second shell of an atom if the spin quantum number m_s could have three values instead of just two? (Hint: Consider the Pauli exclusion principle.)

44.

Which of the following equations describe particle-like behavior? Which describe wavelike behavior? Do any involve both types of behavior? Describe the reasons for your choices.

(a) $c = \lambda\nu$

(b) $E = \frac{m\nu^2}{2}$

(c) $r = \frac{n^2 a_0}{Z}$

(d) $E = h\nu$

(e) $\lambda = \frac{h}{m\nu}$

45.

Write a set of quantum numbers for each of the electrons with an n of 4 in a Se atom.

46.

Read the labels of several commercial products and identify monatomic ions of at least four transition elements contained in the products. Write the complete electron configurations of these cations.

47.

Read the labels of several commercial products and identify monatomic ions of at least six main group elements contained in the products. Write the complete electron configurations of these cations and anions.

48.

Using complete subshell notation (not abbreviations, $1s^2 2s^2 2p^6$, and so forth), predict the electron configuration of each of the following atoms:

(a) C

(b) P

(c) V

(d) Sb

(e) Sm

49.

Using complete subshell notation ($1s^2 2s^2 2p^6$, and so forth), predict the electron configuration of each of the following atoms:

(a) N

(b) Si

(c) Fe

(d) Te

(e) Tb

50.

Is $1s^2 2s^2 2p^6$ the symbol for a macroscopic property or a microscopic property of an element? Explain your answer.

51.

What additional information do we need to answer the question “Which ion has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6$”?

52.

Draw the orbital diagram for the valence shell of each of the following atoms:

(a) C

(b) P

(c) V

(d) Sb

(e) Ru

53.

Use an orbital diagram to describe the electron configuration of the valence shell of each of the following atoms:

(a) N

(b) Si

(c) Fe

(d) Te

(e) Mo

54.

Using complete subshell notation ($1s^2 2s^2 2p^6$, and so forth), predict the electron configurations of the following ions.

(a) N^{3-}

(b) Ca^{2+}

(c) S^-

(d) Cs^{2+}

(e) Cr^{2+}

(f) Gd^{3+}

55.

Which atom has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^2$?

56.

Which atom has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$?

57.

Which ion with a +1 charge has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$? Which ion with a –2 charge has this configuration?

58.

Which of the following atoms contains only three valence electrons: Li, B, N, F, Ne?

59.

Which of the following has two unpaired electrons?

(a) Mg

(b) Si

(c) S

(d) Both Mg and S

(e) Both Si and S.

60.

Which atom would be expected to have a half-filled 6*p* subshell?

61.

Which atom would be expected to have a half-filled 4*s* subshell?

62.

In one area of Australia, the cattle did not thrive despite the presence of suitable forage. An investigation showed the cause to be the absence of sufficient cobalt in the soil. Cobalt forms cations in two oxidation states, Co^{2+} and Co^{3+}. Write the electron structure of the two cations.

63.

Thallium was used as a poison in the Agatha Christie mystery story “The Pale Horse.” Thallium has two possible cationic forms, +1 and +3. The +1 compounds are the more stable. Write the electron structure of the +1 cation of thallium.

64.

Write the electron configurations for the following atoms or ions:

(a) B^{3+}

(b) O^{-}

(c) Cl^{3+}

(d) Ca^{2+}

(e) Ti

65.

Cobalt-60 and iodine-131 are radioactive isotopes commonly used in nuclear medicine. How many protons, neutrons, and

electrons are in atoms of these isotopes? Write the complete electron configuration for each isotope.

66.

Write a set of quantum numbers for each of the electrons with an n of 3 in a Sc atom.

67.

Based on their positions in the periodic table, predict which has the smallest atomic radius: Mg, Sr, Si, Cl, I.

68.

Based on their positions in the periodic table, predict which has the largest atomic radius: Li, Rb, N, F, I.

69.

Based on their positions in the periodic table, predict which has the largest first ionization energy: Mg, Ba, B, O, Te.

70.

Based on their positions in the periodic table, predict which has the smallest first ionization energy: Li, Cs, N, F, I.

71.

Based on their positions in the periodic table, rank the following atoms in order of increasing first ionization energy: F, Li, N, Rb

72.

Based on their positions in the periodic table, rank the following atoms in order of increasing first ionization energy: Mg, O, S, Si

73.

Atoms of which group in the periodic table have a valence shell electron configuration of ns^2np^3?

74.

Atoms of which group in the periodic table have a valence shell electron configuration of ns^2?

75.

Based on their positions in the periodic table, list the following atoms in order of increasing radius: Mg, Ca, Rb, Cs.

76.

Based on their positions in the periodic table, list the following atoms in order of increasing radius: Sr, Ca, Si, Cl.

77.

Based on their positions in the periodic table, list the following ions in order of increasing radius: K^+, Ca^{2+}, Al^{3+}, Si^{4+}.

78.

List the following ions in order of increasing radius: Li^+, Mg^{2+}, Br^-, Te^{2-}.

79.

Which atom and/or ion is (are) isoelectronic with Br^+: Se^{2+}, Se, As^-, Kr, Ga^{3+}, Cl^-?

80.

Which of the following atoms and ions is (are) isoelectronic with S^{2+}: Si^{4+}, Cl^{3+}, Ar, As^{3+}, Si, Al^{3+}?

81.

Compare both the numbers of protons and electrons present in each to rank the following ions in order of increasing radius: As^{3-}, Br^-, K^+, Mg^{2+}.

82.

Of the five elements Al, Cl, I, Na, Rb, which has the most exothermic reaction? (E represents an atom.) What name is given to the energy for the reaction? Hint: Note the process depicted does *not* correspond to electron affinity.)
$\mathrm{E}^+(g) + \mathrm{e}^- \longrightarrow \mathrm{E}(g)$

83.

Of the five elements Sn, Si, Sb, O, Te, which has the most endothermic reaction? (E represents an atom.) What name is given to the energy for the reaction?
$\mathrm{E}(g) \longrightarrow \mathrm{E}^+(g) + \mathrm{e}^-$

84.

The ionic radii of the ions S^{2-}, Cl^-, and K^+ are 184, 181, 138 pm respectively. Explain why these ions have different sizes even though they contain the same number of electrons.

85.

Which main group atom would be expected to have the lowest second ionization energy?

86.

Explain why Al is a member of group 13 rather than group 3?

87.

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

88.

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) cobalt

(b) europium

(c) iodine

(d) indium

(e) lithium

(f) oxygen

(g) cadmium

(h) terbium

(i) rhenium

89.

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

(a) noble gases

(b) alkaline earth metals

(c) alkali metals

(d) chalcogens

90.

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

(a) alkali metals

(b) chalcogens

(c) noble gases

(d) alkaline earth metals

91.

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

(a) the noble gas in the same period as germanium

(b) the alkaline earth metal in the same period as selenium

(c) the halogen in the same period as lithium

(d) the chalcogen in the same period as cadmium

92.

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

(a) the halogen in the same period as the alkali metal with 11 protons

(b) the alkaline earth metal in the same period with the neutral noble gas with 18 electrons

(c) the noble gas in the same row as an isotope with 30 neutrons and 25 protons

(d) the noble gas in the same period as gold

93.

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

(a) the alkali metal with 11 protons and a mass number of 23

(b) the noble gas element with 75 neutrons in its nucleus and 54 electrons in the neutral atom

(c) the isotope with 33 protons and 40 neutrons in its nucleus

(d) the alkaline earth metal with 88 electrons and 138 neutrons

94.

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

(a) the chalcogen with a mass number of 125

(b) the halogen whose longest-lived isotope is radioactive

(c) the noble gas, used in lighting, with 10 electrons and 10 neutrons

(d) the lightest alkali metal with three neutrons

95.

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

96.

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

97.

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

(a) NF_3

(b) BaO,

(c) $(NH_4)_2CO_3$

(d) $Sr(H_2PO_4)_2$

(e) IBr

(f) Na_2O

98.

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:

(a) $KClO_4$

(b) $Mg(C_2H_3O_2)_2$

(c) H_2S

(d) Ag_2S

(e) N_2Cl_4

(f) $Co(NO_3)_2$

99.

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

(a) Ca^{2+}, S^{2-}

(b) NH_4^+, SO_4^{2-}

(c) Al^{3+}, Br^-

(d) Na^+, HPO_4^{2-}

(e) Mg^{2+}, PO_4^{3-}

100.

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

(a) K^+, O^{2-}

(b) NH_4^+, PO_4^{3-}

(c) Al^{3+}, O^{2-}

(d) Na^+, CO_3^{2-}

(e) Ba^{2+}, PO_4^{3-}

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3: CHEMICAL BONDING AND MOLECULAR GEOMETRY

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3.2: Ionic Bonding

3.3: Covalent Bonding

3.4: Chemical Nomenclature

3.5: Lewis Symbols and Structures

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3.1: Introduction

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



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

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3.2: Ionic Bonding

Learning Objectives

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

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

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

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

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



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

The Formation of Ionic Compounds

Binary ionic compounds are composed of just two elements: a metal (which forms the cations) and a nonmetal (which forms the anions). For example, NaCl is a binary ionic compound. We can think about the formation of such compounds in terms of the periodic properties of the elements. Many metallic elements have relatively low ionization potentials and lose electrons easily.

These elements lie to the left in a period or near the bottom of a group on the periodic table. Nonmetal atoms have relatively high electron affinities and thus readily gain electrons lost by metal atoms, thereby filling their valence shells. Nonmetallic elements are found in the upper-right corner of the periodic table.

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

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

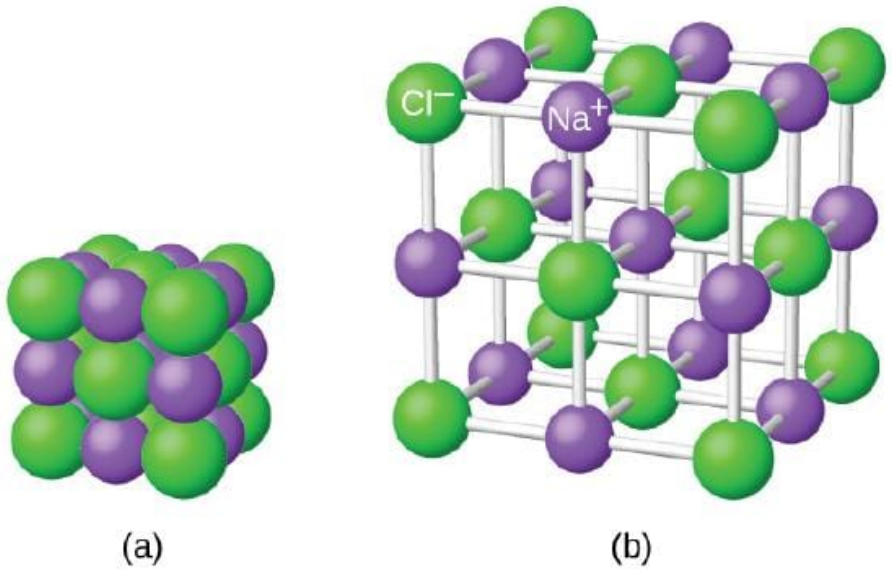


Figure 3.2.2: The atoms in sodium chloride (common table salt) are arranged to (a) maximize opposite charges interacting. The smaller spheres represent sodium ions, the larger ones represent chloride ions. In the expanded view (b), the geometry can be seen more clearly. Note that each ion is "bonded"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

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

$$\mathrm{NaCl\,(s)} \longrightarrow \mathrm{Na^+\,(g) + Cl^-\,(g)} \qquad \Delta H = 769\,\mathrm{kJ}$$

Electronic Structures of Cations

When forming a cation, an atom of a main group element tends to lose all of its valence electrons, thus assuming the electronic structure of the noble gas that precedes it in the periodic table. For groups 1 (the alkali metals) and 2 (the alkaline earth metals), the group numbers are equal to the numbers of valence shell electrons and, consequently, to the charges of the cations formed from atoms of these elements when all valence shell electrons are removed. For example, calcium is a group 2 element whose neutral atoms have 20 electrons and a ground state electron configuration of $1s^22s^22p^63s^23p^64s^2$. When a Ca atom loses both of its valence electrons, the result is a cation with 18 electrons, a 2+ charge, and an electron configuration of $1s^22s^22p^63s^23p^6$. The Ca^{2+} ion is therefore isoelectronic with the noble gas Ar.

For groups 13–17, the group numbers exceed the number of valence electrons by 10 (accounting for the possibility of full *d*

subshells in atoms of elements in the fourth and greater periods). Thus, the charge of a cation formed by the loss of all valence electrons is equal to the group number minus 10. For example, aluminum (in group 13) forms 3+ ions (Al^{3+}).

Exceptions to the expected behavior involve elements toward the bottom of the groups. In addition to the expected ions Tl^{3+}, Sn^{4+}, Pb^{4+}, and Bi^{5+}, a partial loss of these atoms' valence shell electrons can also lead to the formation of Tl^{+}, Sn^{2+}, Pb^{2+}, and Bi^{3+} ions. The formation of these 1+, 2+, and 3+ cations is ascribed to the inert pair effect, which reflects the relatively low energy of the valence s-electron pair for atoms of the heavy elements of groups 13, 14, and 15. Mercury (group 12) also exhibits an unexpected behavior: it forms a diatomic ion, (an ion formed from two mercury atoms, with an Hg-Hg bond), in addition to the expected monatomic ion Hg^{2+} (formed from only one mercury atom).

Transition and inner transition metal elements behave differently than main group elements. Most transition metal cations have 2+ or 3+ charges that result from the loss of their outermost *s* electron(s) first, sometimes followed by the loss of one or two *d* electrons from the next-to-outermost shell. For example, iron ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$) forms the ion Fe^{2+} ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$) by the loss of the 4*s* electrons and the ion Fe^{3+} ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$) by the loss of the 4*s* electrons and one of the 3*d* electrons. Although the *d* orbitals of the transition elements are—according to the Aufbau principle—the last to fill when building up electron configurations, the outermost *s* electrons are the first to be lost when these atoms ionize. When the inner transition metals form ions, they usually have a 3+ charge, resulting from the loss of their outermost *s* electrons and a *d* or *f* electron.

Example 3.2.1: Determining the Electronic Structures of Cations

There are at least 14 elements categorized as "essential trace elements" for the human body. They are called "essential" because they are required for healthy bodily functions, "trace" because they are required only in small amounts, and "elements" in spite of the fact that they are really ions. Two of these essential trace elements, chromium and zinc, are required as Cr^{3+} and Zn^{2+}. Write the electron configurations of these cations.

Solution

First, write the electron configuration for the neutral atoms:

Zn: $[Ar]3d^{10}4s^2$

Cr: $[Ar]3d^5 4s^1$

Next, remove electrons from the highest energy orbital. For the transition metals, electrons are removed from the *s* orbital first and then from the *d* orbital. For the *p*-block elements, electrons are removed from the *p* orbitals and then from the *s* orbital. Zinc is a member of group 12, so it should have a charge of 2+, and thus loses only the two electrons in its s orbital. Chromium is a transition element and should lose its s electrons and then its *d* electrons when forming a cation. Thus, we find the following electron configurations of the ions:

Zn^{2+}: $[Ar]3d^{10}$

Cr^{3+}: $[Ar]3d^3$

Exercise 3.2.1

Potassium and magnesium are required in our diet. Write the electron configurations of the ions expected from these elements.

Answer available at the end of this section.

Electronic Structures of Anions

Most monatomic anions form when a neutral nonmetal atom gains enough electrons to completely fill its outer s and *p* orbitals, thereby reaching the electron configuration of the next noble gas. Thus, it is simple to determine the charge on such a negative ion: The charge is equal to the number of electrons that must be gained to fill the s and *p* orbitals of the parent atom. Oxygen, for example, has the electron configuration $1s^2 2s^2 2p^4$, whereas the oxygen anion has the electron configuration of the noble gas neon (Ne), $1s^2 2s^2 2p^6$. The two additional electrons required to fill the valence orbitals give the oxide ion the charge of 2– (O^{2-}).

Example 3.2.1: Determining the Electronic Structure of Anions

Selenium and iodine are two essential trace elements that form anions. Write the electron configurations of the anions.

Solution

Se^{2-}: $[Ar]3d^{10}4s^2 4p^6$

I^-: $[Kr]4d^{10}5s^2 5p^6$

Exercise 3.2.2

Write the electron configurations of a phosphorus atom and its negative ion. Give the charge on the anion.

Answer available at the end of this section.

Answers

Exercise 3.2.1

K^+: [Ar], Mg^{2+}: [Ne]

Exercise 3.2.2

P: $[Ne]3s^2 3p^3$; P^{3-}: $[Ne]3s^2 3p^6$

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3.3: Covalent Bonding

Learning Objectives

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

- Describe the formation of covalent bonds
- Define electronegativity and assess the polarity of covalent bonds

Ionic bonding results from the electrostatic attraction of oppositely charged ions that are typically produced by the transfer of electrons between metallic and nonmetallic atoms. A different type of bonding results from the mutual attraction of atoms for a "shared" pair of electrons. Such bonds are called covalent bonds. Covalent bonds are formed between two atoms when both have similar tendencies to attract electrons to themselves (i.e., when both atoms have identical or fairly similar ionization energies and electron affinities). For example, two hydrogen atoms bond covalently to form an H_2 molecule; each hydrogen atom in the H_2 molecule has two electrons stabilizing it, giving each atom the same number of valence electrons as the noble gas He.

Compounds that contain covalent bonds exhibit different physical properties than ionic compounds. Because the attraction between molecules, which are electrically neutral, is weaker than that between electrically charged ions, covalent compounds generally have much lower melting and boiling points than ionic compounds. In fact, many covalent compounds are liquids or gases at room temperature, and, in their solid states, they are typically much softer than ionic solids. Furthermore, whereas ionic compounds are good conductors of electricity when dissolved in water, most covalent compounds are insoluble in water; since they are electrically neutral, they are poor conductors of electricity in any state.

Formation of Covalent Bonds

Nonmetal atoms frequently form covalent bonds with other nonmetal atoms. For example, the hydrogen molecule, H_2, contains a covalent bond between its two hydrogen atoms. Figure $3.3.1$ illustrates why this bond is formed. Starting on the far right, we have two separate hydrogen atoms with a particular potential energy, indicated by the red line. Along the *x*-axis is the distance between the two atoms. As the two atoms approach each other (moving left along the *x*-axis), their valence orbitals (1s) begin to overlap. The single electrons on each hydrogen atom then interact with both atomic nuclei, occupying the space around both atoms. The strong attraction of each shared electron to both nuclei stabilizes the system, and the potential energy decreases as the bond distance decreases. If the atoms continue to approach each other, the positive charges in the two nuclei begin to repel each other, and the potential energy increases. The bond length is determined by the distance at which the lowest potential energy is achieved.

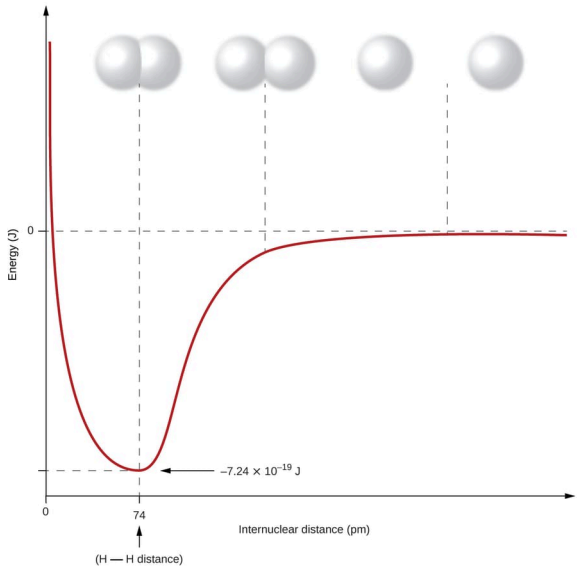


Figure 3.3.1: The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved.

It is essential to remember that energy must be added to break chemical bonds (an endothermic process), whereas forming chemical bonds releases energy (an exothermic process). In the case of H_2, the covalent bond is very strong; a large amount of energy, 436 kJ, must be added to break the bonds in one mole of hydrogen molecules and cause the atoms to separate:

$$\mathrm{H_2\,(g)} \longrightarrow 2\,\mathrm{H\,(g)} \quad \Delta H = 436\,\mathrm{kJ}$$

Conversely, the same amount of energy is released when one mole of H_2 molecules forms from two moles of H atoms:

$$2\,\mathrm{H\,(g)} \longrightarrow \mathrm{H_2\,(g)} \quad \Delta H = -436\,\mathrm{kJ}$$

Pure vs. Polar Covalent Bonds

If the atoms that form a covalent bond are identical, as in H_2, Cl_2, and other diatomic molecules, then the electrons in the bond must be shared equally. We refer to this as a pure covalent bond. Electrons shared in pure covalent bonds have an equal probability of being near each nucleus.

In the case of Cl_2, each atom starts off with seven valence electrons, and each Cl shares one electron with the other, forming one covalent bond:

$$\mathrm{Cl + Cl \longrightarrow Cl_2}$$

The total number of electrons around each individual atom consists of six nonbonding electrons and two shared (i.e., bonding) electrons for eight total electrons, matching the number of valence electrons in the noble gas argon. Since the bonding atoms are identical, Cl_2 also features a pure covalent bond.

When the atoms linked by a covalent bond are different, the bonding electrons are shared, but no longer equally. Instead, the bonding electrons are more attracted to one atom than the other, giving rise to a shift of electron density toward that atom. This unequal distribution of electrons is known as a polar covalent bond, characterized by a partial positive charge on one atom and a partial negative charge on the other. The atom that attracts the electrons more strongly acquires the partial negative charge and vice versa. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Thus, in an HCl molecule, the chlorine atom carries a partial negative charge and the hydrogen atom has a partial positive charge. Figure 3.3.2 shows the distribution of electrons in the H–Cl bond. Note that the shaded area around Cl is much larger than it is around H. Compare this to Figure 3.3.1, which shows the even distribution of electrons in the H_2 nonpolar bond.

We sometimes designate the positive and negative atoms in a polar covalent bond using a lowercase Greek letter “delta,” δ, with

a plus sign or minus sign to indicate whether the atom has a partial positive charge (δ+) or a partial negative charge (δ–). This symbolism is shown for the H–Cl molecule in Figure 3.3.2.

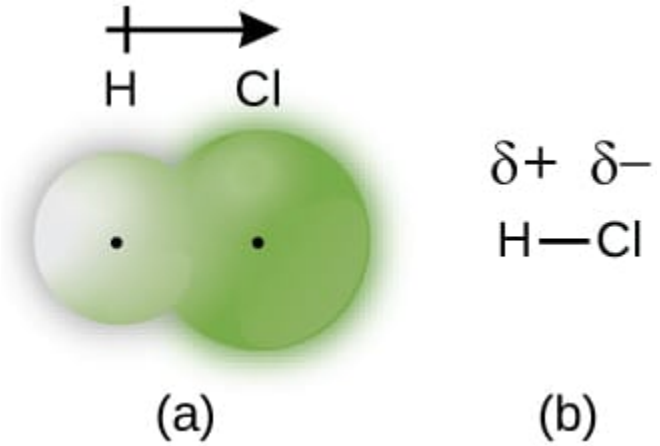


Figure 3.3.2: (a) The distribution of electron density in the HCl molecule is uneven. The electron density is greater around the chlorine nucleus. The small, black dots indicate the location of the hydrogen and chlorine nuclei in the molecule. (b) Symbols δ+ and δ– indicate the polarity of the H–Cl bond.

Electronegativity

Whether a bond is nonpolar or polar covalent is determined by a property of the bonding atoms called electronegativity. Electronegativity is a measure of the tendency of an atom to attract electrons (or electron density) towards itself. It determines how the shared electrons are distributed between the two atoms in a bond. The more strongly an atom attracts the electrons in its bonds, the larger its electronegativity. Electrons in a polar covalent bond are shifted toward the more electronegative atom; thus, the more electronegative atom is the one with the partial negative charge. The greater the difference in electronegativity, the more polarized the electron distribution and the larger the partial charges of the atoms.

Figure 3.3.3 shows the electronegativity values of the elements as proposed by one of the most famous chemists of the twentieth century: Linus Pauling (Figure 3.3.4). In general, electronegativity increases from left to right across a period in the periodic table and decreases down a group. Thus, the nonmetals, which lie in the upper right, tend to have the highest electronegativities, with fluorine the most electronegative element of all (EN = 4.0). Metals tend to be less electronegative elements, and the group 1 metals have the lowest electronegativities. Note that noble gases are excluded from this figure because these atoms usually do not share electrons with others atoms since they have a full valence shell. (While noble gas compounds such as XeO_2 do exist, they can only be formed under extreme conditions, and thus they do not fit neatly into the general model of electronegativity.)

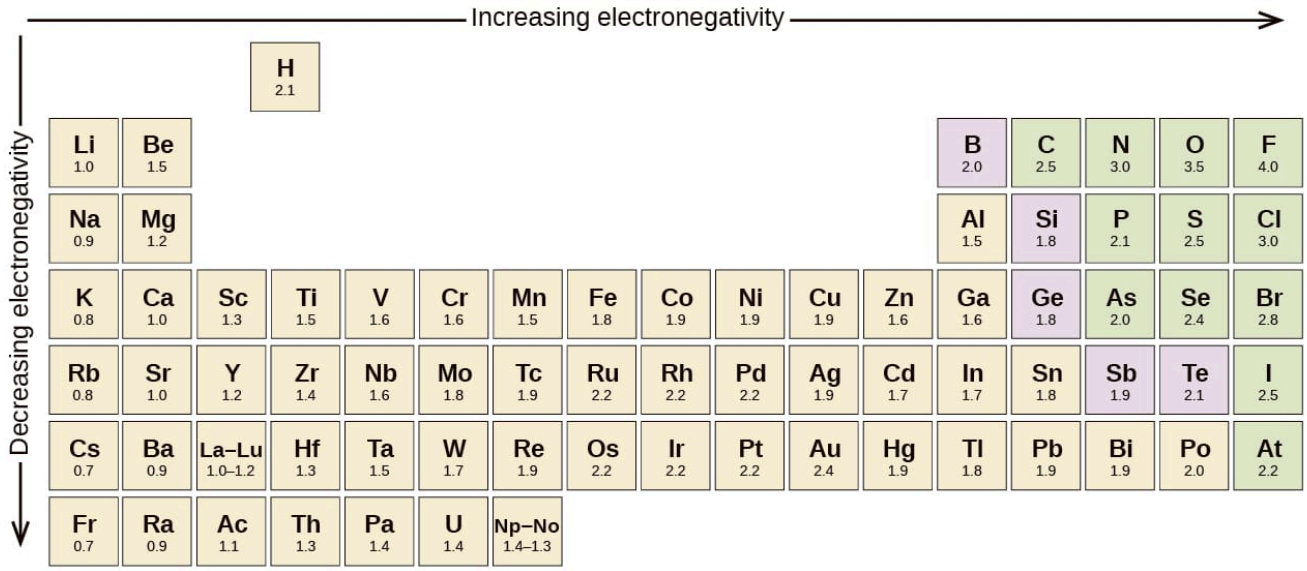


Figure 3.3.3: The electronegativity values derived by Pauling follow predictable periodic trends, with the higher electronegativities toward the upper right of the periodic table.

Electronegativity versus Electron Affinity

We must be careful not to confuse electronegativity and electron affinity. The electron affinity of an element is a measurable physical quantity, namely, the energy released or absorbed when an isolated gas-phase atom acquires an electron, measured in kJ/mol. Electronegativity, on the other hand, describes how tightly an atom attracts electrons in a bond. It is a dimensionless quantity that is calculated, not measured. Pauling derived the first electronegativity values by comparing the amounts of energy required to break different types of bonds. He chose an arbitrary relative scale ranging from 0 to 4.

Portrait of a Chemist: Linus Pauling

Linus Pauling, shown in Figure 3.3.4, is the only person to have received two unshared (individual) Nobel Prizes: one for chemistry in 1954 for his work on the nature of chemical bonds and one for peace in 1962 for his opposition to weapons of mass destruction. He developed many of the theories and concepts that are foundational to our current understanding of chemistry, including electronegativity and resonance structures.

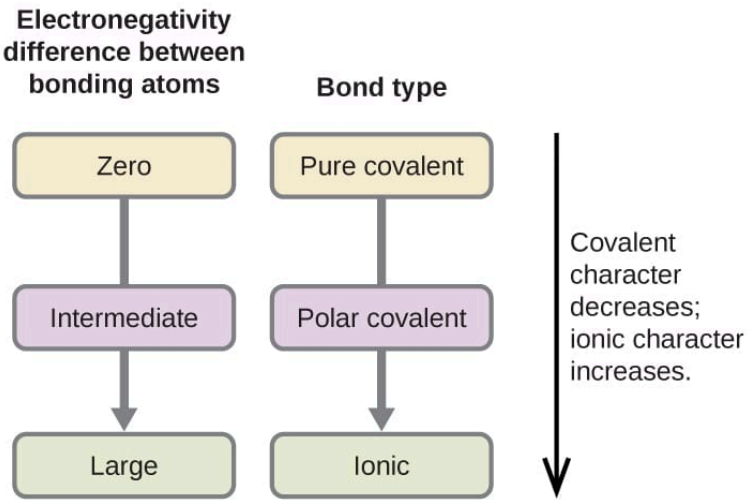


Figure 3.3.4: Linus Pauling (1901–1994) made many important contributions to the field of chemistry. He was also a prominent activist, publicizing issues related to health and nuclear weapons.

Pauling also contributed to many other fields besides chemistry. His research on sickle cell anemia revealed the cause of the disease—the presence of a genetically inherited abnormal protein in the blood—and paved the way for the field of molecular genetics. His work was also pivotal in curbing the testing of nuclear weapons; he proved that radioactive fallout from nuclear testing posed a public health risk.

Electronegativity and Bond Type

The absolute value of the difference in electronegativity (ΔEN) of two bonded atoms provides a rough measure of the polarity to be expected in the bond and, thus, the bond type. When the difference is very small or zero, the bond is covalent and nonpolar. When it is large, the bond is polar covalent or ionic. The absolute values of the electronegativity differences between the atoms in the bonds H–H, H–Cl, and Na–Cl are 0 (nonpolar), 0.9 (polar covalent), and 2.1 (ionic), respectively. The degree to which electrons are shared between atoms varies from completely equal (pure covalent bonding) to not at all (ionic bonding). Figure 3.3.5 shows the relationship between electronegativity difference and bond type.



Bond Type	Electronegativity Difference
pure covalent	< 0.4
polar covalent	between 0.4 and 1.8
ionic	> 1.8

Figure 3.3.5: As the electronegativity difference increases between two atoms, the bond becomes more ionic.

A rough approximation of the electronegativity differences associated with covalent, polar covalent, and ionic bonds is shown in Figure 3.3.5. This table is just a general guide, however, with many exceptions. For example, the H and F atoms in HF have an electronegativity difference of 1.9, and the N and H atoms in NH_3 a difference of 0.9, yet both of these compounds form bonds

that are considered polar covalent. Likewise, the Na and Cl atoms in NaCl have an electronegativity difference of 2.1, and the Mn and I atoms in MnI_2 have a difference of 1.0, yet both of these substances form ionic compounds.

The best guide to the covalent or ionic character of a bond is to consider the types of atoms involved and their relative positions in the periodic table. Bonds between two nonmetals are generally covalent; bonding between a metal and a nonmetal is often ionic.

Some compounds contain both covalent and ionic bonds. The atoms in polyatomic ions, such as OH^-, and are held together by polar covalent bonds. However, these polyatomic ions form ionic compounds by combining with ions of opposite charge. For example, potassium nitrate, KNO_3, contains the K^+ cation and the polyatomic anion. Thus, bonding in potassium nitrate is ionic, resulting from the electrostatic attraction between the ions K^+ and as well as covalent between the nitrogen and oxygen atoms in

Example 3.3.1: Electronegativity and Bond Polarity

Bond polarities play an important role in determining the structure of proteins. Using the electronegativity values in Figure 3.3.3, arrange the following covalent bonds—all commonly found in amino acids—in order of increasing polarity. Then designate the positive and negative atoms using the symbols δ+ and δ–:

C–H, C–N, C–O, N–H, O–H, S–H

Solution

The polarity of these bonds increases as the absolute value of the electronegativity difference increases. The atom with the δ– designation is the more electronegative of the two. Table 3.3.1 shows these bonds in order of increasing polarity.

Table 3.3.1: Bond Polarity and Electronegativity Difference

Bond	ΔEN	Polarity
C–H	0.4	
S–H	0.4	
C–N	0.5	
N–H	0.9	
C–O	1.0	
O–H	1.4	

Exercise 3.3.1

Silicones are polymeric compounds containing, among others, the following types of covalent bonds: Si–O, Si–C, C–H, and C–C. Using the electronegativity values in Figure 3.3.3, arrange the bonds in order of increasing polarity and designate the positive and negative atoms using the symbols δ+ and δ–.

Answer available at the end of this section.

Answers

Exercise 3.3.1

Bond	Electronegativity Difference	Polarity
C–C	0.0	nonpolar
C–H	0.4	

Bond	Electronegativity Difference	Polarity
Si–C	0.7	
Si–O	1.7	

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3.4: Chemical Nomenclature

Learning Objectives

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

- Derive names for common types of inorganic compounds using a systematic approach

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.

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.

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 3.4.1.

Table 3.4.1: 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

Compounds Containing Polyatomic Ions

Compounds containing polyatomic ions are named similarly to those containing only monatomic ions, i.e. by naming first the cation and then the anion. Examples are shown in Table 3.4.2.

Table 3.4.2: Names of Some Polyatomic Ionic Compounds

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

Chemistry in Everyday Life: Ionic Compounds in Your Cabinet

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 3.4.3. 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 3.4.3: Everyday Ionic Compounds

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

Compounds Containing a Metal Ion with a Variable Charge

Most of the transition metals and some main group metals can form two or more cations with different charges. Compounds of these metals with nonmetals are named with the same method as compounds in the first category, except the charge of the metal ion is specified by a Roman numeral in parentheses after the name of the metal. The charge of the metal ion is determined from the formula of the compound and the charge of the anion. For example, consider binary ionic compounds of iron and chlorine. Iron typically exhibits a charge of either 2+ or 3+ (see Figure 2.29), 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 3.4.4.

Table 3.4.4: Some Ionic Compounds with Variably Charged Metal Ions

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

Compound	Name
SnF_4	tin(IV) fluoride

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

Ionic Hydrates

Ionic compounds that contain water molecules as integral components of their crystals are called **hydrates**. The name for an ionic hydrate is derived by adding a term to the name for the anhydrous (meaning "not hydrated") compound that indicates the number of water molecules associated with each formula unit of the compound. The added word begins with a Greek prefix denoting the number of water molecules (see Table 3.4.5) and ends with "hydrate." For example, the anhydrous compound copper(II) sulfate also exists as a hydrate containing five water molecules and named copper(II) sulfate pentahydrate. Washing soda is the common name for a hydrate of sodium carbonate containing 10 water molecules; the systematic name is sodium carbonate decahydrate.

Formulas for ionic hydrates are written by appending a vertically centered dot, a coefficient representing the number of water molecules, and the formula for water. The two examples mentioned in the previous paragraph are represented by the formulas

$$\text{copper(II) sulfate pentahydrate} \quad CuSO_4 \cdot 5\,H_2O$$

$$\text{sodium carbonate decahydrate} \quad Na_2CO_3 \cdot 10\,H_2O$$

Table 3.4.5: Nomenclature Prefixes

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

Example 3.4.1: Naming Ionic Compounds

Name the following ionic compounds

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

Solution

The anions in these compounds have a fixed negative charge (S^{2-}, Se^{2-} , N^{3-}, and 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+}, Mg^{2+}, and Ti^{3+}. These charges are used in the names of the metal ions:

a. iron(III) sulfide

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

Exercise 3.4.1

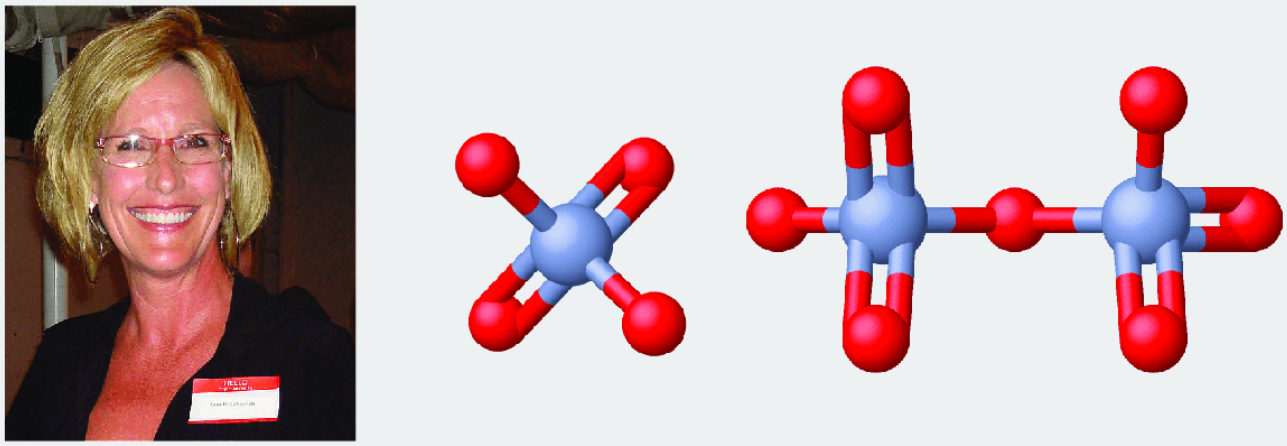
Write the formulas of the following ionic compounds:

a. chromium(III) phosphide
b. mercury(II) sulfide
c. manganese(II) phosphate
d. copper(I) oxide
e. iron(III) chloride dihydrate

Answer available at the end of this section.

Chemistry in Everyday Life: Erin Brockovich and Chromium Contamination

In the early 1990s, legal file clerk Erin Brockovich (Figure 3.4.1) 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 Brockovich* (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 3.4.1: (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, (left), and dichromate, (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. But Cr(VI) 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.

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.

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 3.4.5.

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 3.4.6.

Table 3.4.6: 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 3.4.2: 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 3.4.2

Write the formulas for the following compounds:

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

Answer available at the end of this section.

Link to Learning

The following website provides practice with naming chemical compounds and writing chemical formulas. You can choose binary, polyatomic, and variable charge ionic compounds, as well as molecular compounds.

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 3.4.7.

Table 3.4.7: 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

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 3.4.8. 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 3.4.8: 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

Answers

Exercise 3.4.1

(a) CrP; (b) HgS; (c) $Mn_3(PO_4)_2$; (d) Cu_2O; (e) $FeCl_3 \cdot 2H_2O$

Exercise 3.4.2

(a) PCl_5; (b) N_2O; (c) IF_7; (d) CCl_4

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3.5: Lewis Symbols and Structures

Learning Objectives

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

- Write Lewis symbols for neutral atoms and ions
- Draw Lewis structures depicting the bonding in simple molecules

Thus far in this chapter, we have discussed the various types of bonds that form between atoms and/or ions. In all cases, these bonds involve the sharing or transfer of valence shell electrons between atoms. In this section, we will explore the typical method for depicting valence shell electrons and chemical bonds, namely Lewis symbols and Lewis structures.

Lewis Symbols

We use Lewis symbols to describe valence electron configurations of atoms and monatomic ions. A Lewis symbol consists of an elemental symbol surrounded by one dot for each of its valence electrons:



Figure 3.5.1: shows the Lewis symbols for the elements of the third period of the periodic table.

Atoms	Electronic Configuration	Lewis Symbol
sodium	$[Ne]3s^1$	Na•
magnesium	$[Ne]3s^2$	•Mg•
aluminum	$[Ne]3s^23p^1$	•Al•
silicon	$[Ne]3s^23p^2$	•Si•
phosphorus	$[Ne]3s^23p^3$	•P•
sulfur	$[Ne]3s^23p^4$	:S•
chlorine	$[Ne]3s^23p^5$	:Cl•
argon	$[Ne]3s^23p^6$	:Ar:

Figure 3.5.1: Lewis symbols illustrating the number of valence electrons for each element in the third period of the periodic table.

Lewis symbols can also be used to illustrate the formation of cations from atoms, as shown here for sodium and calcium:



Likewise, they can be used to show the formation of anions from atoms, as shown here for chlorine and sulfur:



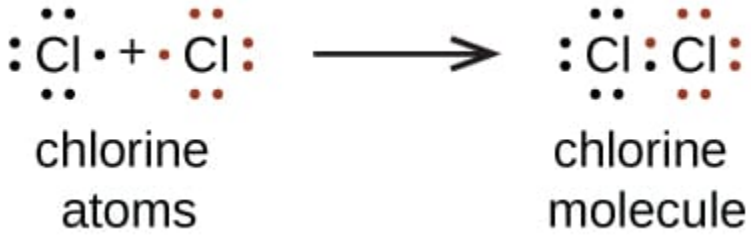
Figure 3.5.2 demonstrates the use of Lewis symbols to show the transfer of electrons during the formation of ionic compounds.

Metal		Nonmetal		Ionic Compound
Na ·	+	:Cl·	⟶	$Na^+[:Cl:]^-$
sodium atom		chlorine atom		sodium chloride (sodium ion and chloride ion)
·Mg·	+	:O·	⟶	$Mg^{2+}[:O:]^{2-}$
magnesium atom		oxygen atom		magnesium oxide (magnesium ion and oxide ion)
·Ca·	+	2 :F·	⟶	$Ca^{2+}[:F:]^-_2$
calcium atom		fluorine atoms		calcium fluoride (calcium ion and two fluoride ions)

Figure 3.5.2: Cations are formed when atoms lose electrons, represented by fewer Lewis dots, whereas anions are formed by atoms gaining electrons. The total number of electrons does not change.

Lewis Structures

We also use Lewis symbols to indicate the formation of covalent bonds, which are shown in Lewis structures, drawings that describe the bonding in molecules and polyatomic ions. For example, when two chlorine atoms form a chlorine molecule, they share one pair of electrons:



The Lewis structure indicates that each Cl atom has three pairs of electrons that are not used in bonding (called lone pairs) and one shared pair of electrons (written between the atoms). A dash (or line) is sometimes used to indicate a shared pair of electrons:

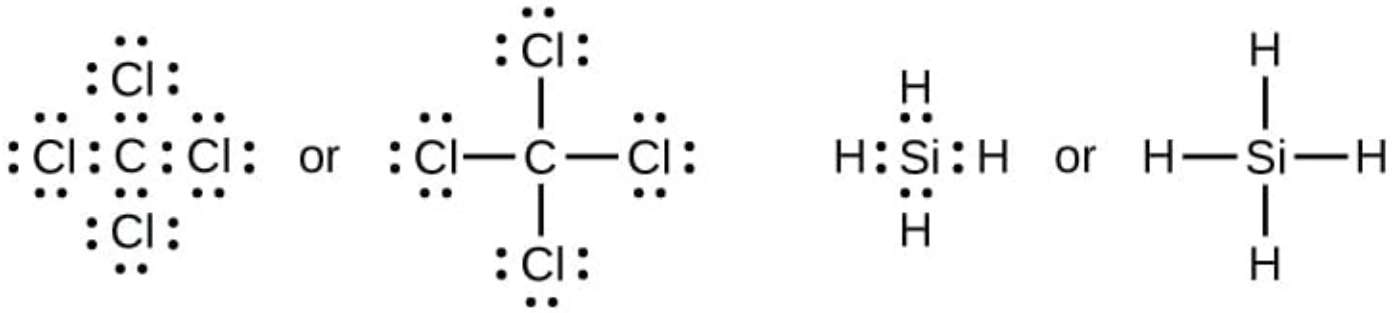


A single shared pair of electrons is called a single bond. Each Cl atom interacts with eight valence electrons: the six in the lone pairs and the two in the single bond.

The Octet Rule

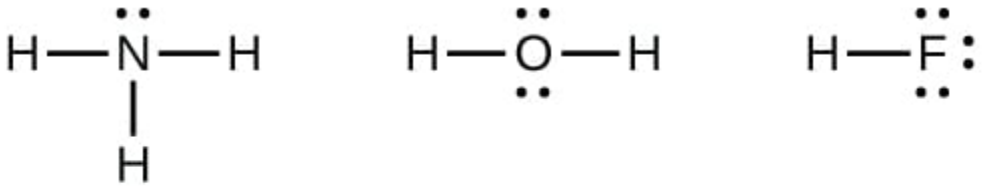
The other halogen molecules (F_2, Br_2, I_2, and At_2) form bonds like those in the chlorine molecule: one single bond between atoms and three lone pairs of electrons per atom. This allows each halogen atom to have a noble gas electron configuration. The tendency of main group atoms to form enough bonds to obtain eight valence electrons is known as the octet rule.

The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons); this is especially true of the nonmetals of the second period of the periodic table (C, N, O, and F). For example, each atom of a group 14 element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming four covalent bonds, as illustrated here for carbon in CCl_4 (carbon tetrachloride) and silicon in SiH_4 (silane). Because hydrogen only needs two electrons to fill its valence shell, it is an exception to the octet rule. The transition elements and inner transition elements also do not follow the octet rule:



carbon tetrachloride silane

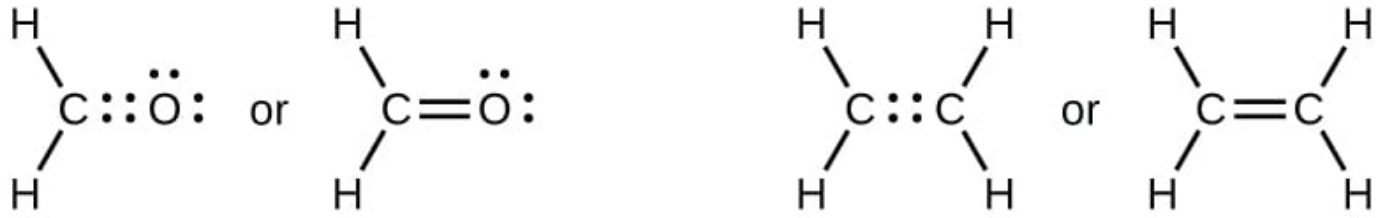
Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in NH_3 (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:



ammonia Water hydrogen fluoride

Double and Triple Bonds

As previously mentioned, when a pair of atoms shares one pair of electrons, we call this a single bond. However, a pair of atoms may need to share more than one pair of electrons in order to achieve the requisite octet. A double bond forms when two pairs of electrons are shared between a pair of atoms, as between the carbon and oxygen atoms in CH_2O (formaldehyde) and between the two carbon atoms in C_2H_4 (ethylene):



formaldehyde ethylene

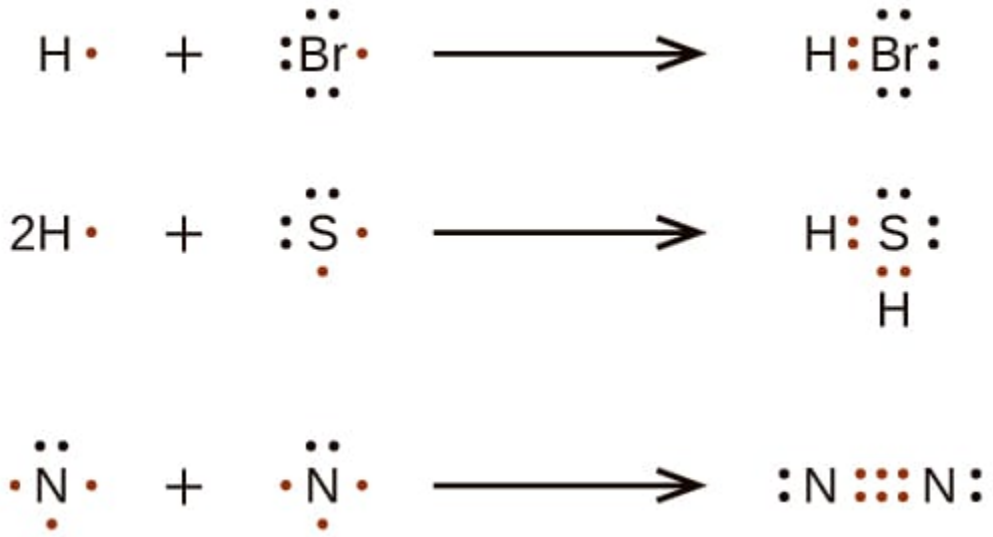
A triple bond forms when three electron pairs are shared by a pair of atoms, as in carbon monoxide (CO) and the cyanide ion (CN^-):



carbon monoxide cyanide ion

Writing Lewis Structures with the Octet Rule

For very simple molecules and molecular ions, we can write the Lewis structures by merely pairing up the unpaired electrons on the constituent atoms. See these examples:



For more complicated molecules and molecular ions, it is helpful to follow the step-by-step procedure outlined here.

Writing Lewis Structures

1. Determine the total number of valence (outer shell) electrons. For cations, subtract one electron for each positive charge. For anions, add one electron for each negative charge.
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom. (Generally, the least electronegative element should be placed in the center.) Connect each atom to the central atom with a single bond (one electron pair).

3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.
4. Place all remaining electrons on the central atom.
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

Let us determine the Lewis structures of SiH_4, CHO_2^-, NO^+, and OF_2 as examples in following this procedure:

1. Determine the total number of valence (outer shell) electrons in the molecule or ion.
   - For a molecule, we add the number of valence electrons on each atom in the molecule:

$$\begin{aligned} & SiH_4 \\ \text{Si: 4 valence electrons/atom} \times & \text{ 1 atom } = 4 \\ + \quad \text{H : 1 valence electron/atom} \times & \text{ 4 atoms} = 4 \\ & \text{total valence electrons} = 8 \end{aligned}$$

   - For a *negative ion*, such as CHO_2^-, we add the number of valence electrons on the atoms to the number of negative charges on the ion (one electron is gained for each single negative charge):

$$\begin{aligned} & CHO_2^- \\ \text{C: 4 valence electrons/atom} \times & \text{ 1 atom } = 4 \\ \text{H: 1 valence electron/atom} \times & \text{ 1 atoms} = 1 \\ \text{O: 6 valence electron/atom} \times & \text{ 2 atoms} = 12 \\ + & \text{ 1 electron} = 1 \\ & \text{total valence electrons} = 18 \end{aligned}$$

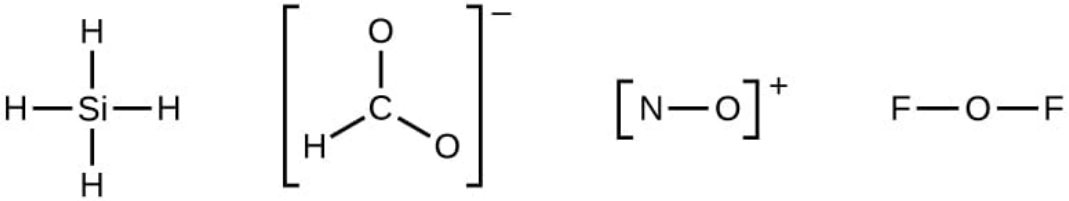
   - For a *positive ion*, such as NO^+, we add the number of valence electrons on the atoms in the ion and then subtract the number of positive charges on the ion (one electron is lost for each single positive charge) from the total number of valence electrons:

$$\begin{aligned} & NO^+ \\ \text{N: 5 valence electrons/atom} \times & \text{ 1 atom } = 5 \\ \text{O: 6 valence electron/atom} \times & \text{ 1 atoms} = 6 \\ + \quad \text{e: -1 electron (positive charge)} \times & \text{ 1 electron} = -1 \\ & \text{total valence electrons} = 10 \end{aligned}$$

   - Since OF_2 is a neutral molecule, we simply add the number of valence electrons:

$$\begin{aligned} & OF_2 \\ \text{O: 6 valence electrons/atom} \times & \text{ 1 atom } = 6 \\ + \quad \text{F: 7 valence electron/atom} \times & \text{ 2 atoms} = 14 \\ & \text{total valence electrons} = 20 \end{aligned}$$

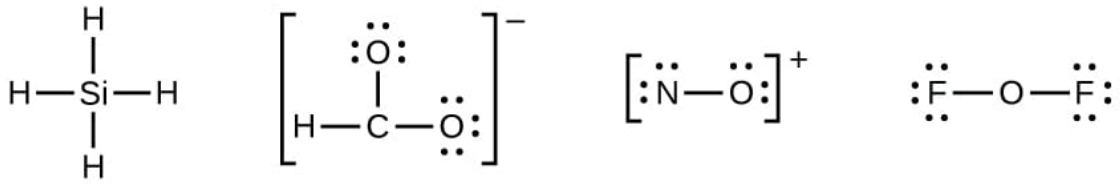
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. (Note that we denote ions with brackets around the structure, indicating the charge outside the brackets:)



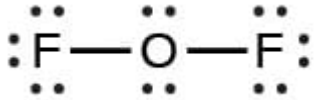
When several arrangements of atoms are possible, as for CHO_2^-, we must use experimental evidence to choose the correct

one. In general, the less electronegative elements are more likely to be central atoms. In CHO_2^-, the less electronegative carbon atom occupies the central position with the oxygen and hydrogen atoms surrounding it. Other examples include P in $POCl_3$, S in SO_2, and Cl in ClO_4^-. An exception is that hydrogen is almost never a central atom. As the most electronegative element, fluorine also cannot be a central atom.

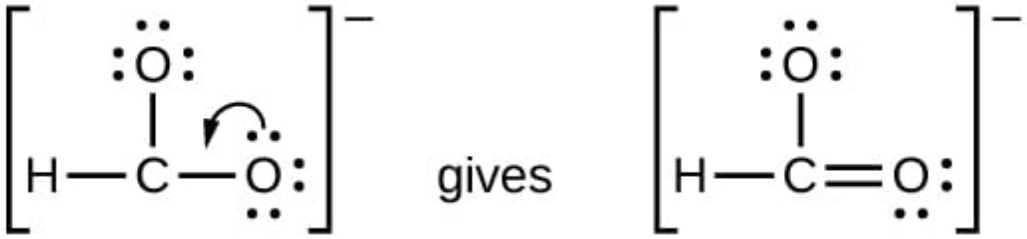
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.
   - There are no remaining electrons on SiH_4, so it is unchanged:



4. Place all remaining electrons on the central atom.
   - For SiH_4, CHO_2^-, and NO^+, there are no remaining electrons; we already placed all of the electrons determined in Step 1.
   - For OF_2, we had 16 electrons remaining in Step 3, and we placed 12, leaving 4 to be placed on the central atom:



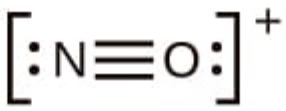
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.
   - SiH_4: Si already has an octet, so nothing needs to be done.
   - $CHO\ 2^-$: We have distributed the valence electrons as lone pairs on the oxygen atoms, but the carbon atom lacks an octet:



   - NO^+: For this ion, we added eight valence electrons, but neither atom has an octet. We cannot add any more electrons since we have already used the total that we found in Step 1, so we must move electrons to form a multiple bond:



   This still does not produce an octet, so we must move another pair, forming a triple bond:



- In OF_2, each atom has an octet as drawn, so nothing changes.

Example 3.5.1: Writing Lewis Structures

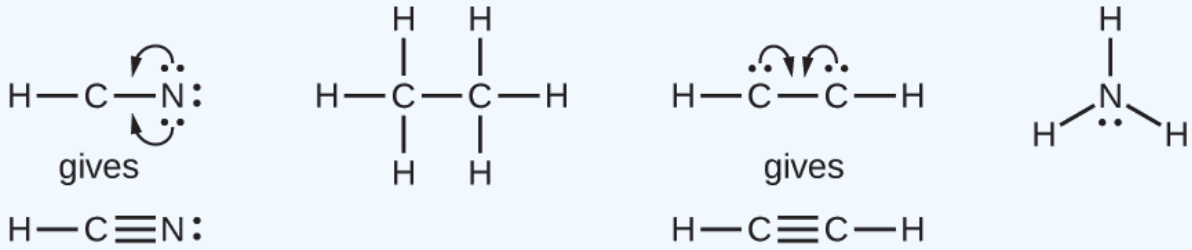
NASA's Cassini-Huygens mission detected a large cloud of toxic hydrogen cyanide (HCN) on Titan, one of Saturn's moons. Titan also contains ethane (H_3CCH_3), acetylene (HCCH), and ammonia (NH_3). What are the Lewis structures of these molecules?

Solution

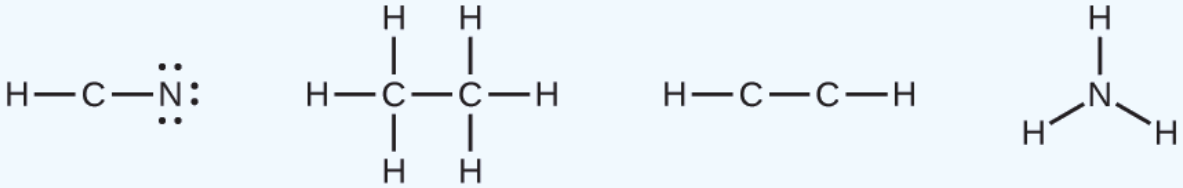
Step 1. *Calculate the number of valence electrons.*

HCN: (1 × 1) + (4 × 1) + (5 × 1) = 10
H_3CCH_3: (1 × 3) + (2 × 4) + (1 × 3) = 14
HCCH: (1 × 1) + (2 × 4) + (1 × 1) = 10
NH_3: (5 × 1) + (3 × 1) = 8

Step 2 *Draw a skeleton and connect the atoms with single bonds*. Remember that H is never a central atom:

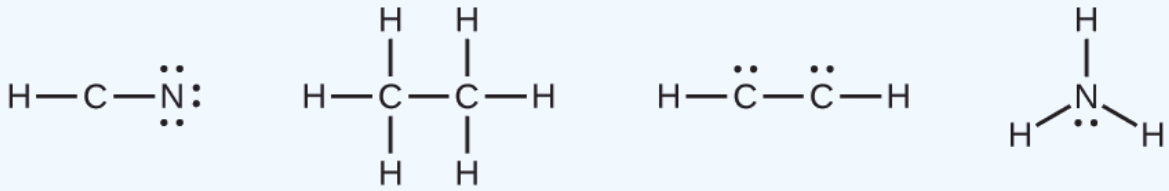


Step 3. *Where needed, distribute electrons to the terminal atoms:*



HCN: six electrons placed on N
H_3CCH_3: no electrons remain
HCCH: no terminal atoms capable of accepting electrons
NH_3: no terminal atoms capable of accepting electrons

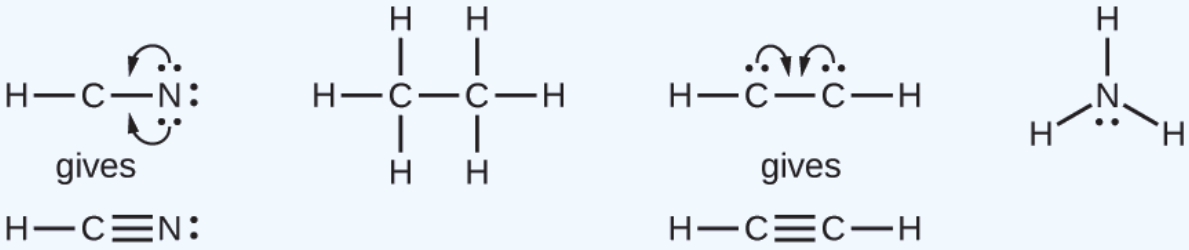
Step 4. *Where needed, place remaining electrons on the central atom:*



HCN: no electrons remain
H_3CCH_3: no electrons remain
HCCH: four electrons placed on carbon
NH_3: two electrons placed on nitrogen

Step 5. *Where needed, rearrange electrons to form multiple bonds in order to obtain an octet on each atom:*

HCN: form two more C–N bonds
H_3CCH_3: all atoms have the correct number of electrons
HCCH: form a triple bond between the two carbon atoms
NH_3: all atoms have the correct number of electrons



Exercise 3.5.1

Both carbon monoxide, CO, and carbon dioxide, CO_2, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic and CO_2 has been implicated in global climate change. What are the Lewis structures of these two molecules?

Answer available at the end of this section.

How Sciences Interconnect: Fullerene Chemistry

Carbon, in various forms and compounds, has been known since prehistoric times, . Soot has been used as a pigment (often called carbon black) for thousands of years. Charcoal, high in carbon content, has likewise been critical to human development. Carbon is the key additive to iron in the steelmaking process, and diamonds have a unique place in both culture and industry. With all this usage came significant study, particularly with the emergence of organic chemistry. And even with all the known forms and functions of the element, scientists began to uncover the potential for even more varied and extensive carbon structures.

As early as the 1960s, chemists began to observe complex carbon structures, but they had little evidence to support their concepts, or their work did not make it into the mainstream. Eiji Osawa predicted a spherical form based on observations of a similar structure, but his work was not widely known outside Japan. In a similar manner, the most comprehensive advance was likely computational chemist Elena Galpern's, who in 1973 predicted a highly stable, 60-carbon molecule; her work was also isolated to her native Russia. Still later, Harold Kroto, working with Canadian radio astronomers, sought to uncover the nature of long carbon chains that had been discovered in interstellar space.

Kroto sought to use a machine developed by Richard Smalley's team at Rice University to learn more about these structures. Together with Robert Curl, who had introduced them, and three graduate students—James Heath, Sean O'Brien, and Yuan Liu—they performed an intensive series of experiments that led to a major discovery.

In 1996, the Nobel Prize in Chemistry was awarded to Richard Smalley (Figure 3.5.3), Robert Curl, and Harold Kroto for their work in discovering a new form of carbon, the C_{60} buckminsterfullerene molecule. An entire class of compounds, including spheres and tubes of various shapes, were discovered based on C_{60}. This type of molecule, called a fullerene, shows promise in a variety of applications. Because of their size and shape, fullerenes can encapsulate other molecules, so they have shown potential in various applications from hydrogen storage to targeted drug delivery systems. They also possess unique electronic and optical properties that have been put to good use in solar powered devices and chemical sensors.

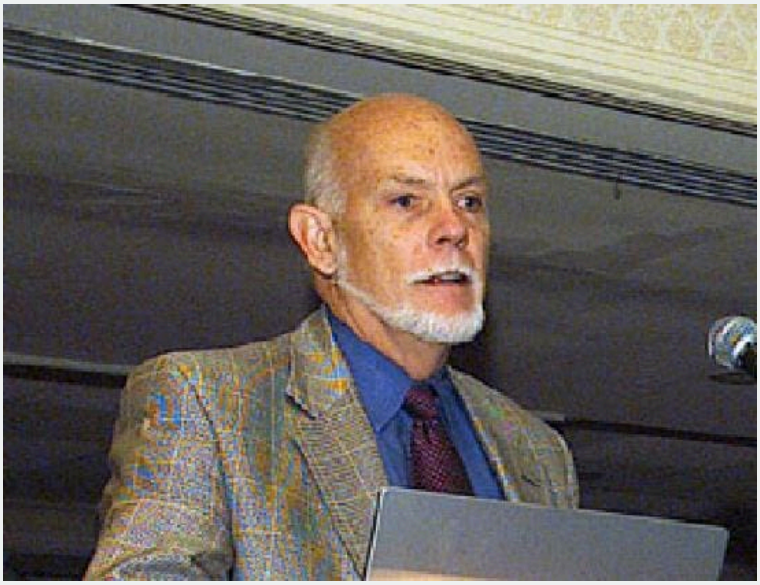


Figure 3.5.3: Richard Smalley (1943–2005), a professor of physics, chemistry, and astronomy at Rice University, was one of the leading advocates for fullerene chemistry. Upon his death in 2005, the US Senate honored him as the "Father of Nanotechnology." (credit: United States Department of Energy)

Exceptions to the Octet Rule

Many covalent molecules have central atoms that do not have eight electrons in their Lewis structures. These molecules fall into three categories:

- Odd-electron molecules have an odd number of valence electrons, and therefore have an unpaired electron.
- Electron-deficient molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
- Hypervalent molecules have a central atom that has more electrons than needed for a noble gas configuration.

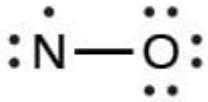
Odd-electron Molecules

We call molecules that contain an odd number of electrons free radicals. Nitric oxide, NO, is an example of an odd-electron molecule; it is produced in internal combustion engines when oxygen and nitrogen react at high temperatures.

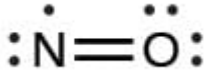
To draw the Lewis structure for an odd-electron molecule like NO, we follow the same five steps we would for other molecules, but with a few minor changes:

1. *Determine the total number of valence (outer shell) electrons*. The sum of the valence electrons is 5 (from N) + 6 (from O) = 11. The odd number immediately tells us that we have a free radical, so we know that not every atom can have eight electrons in its valence shell.
2. *Draw a skeleton structure of the molecule*. We can easily draw a skeleton with an N–O single bond:
   N–O
3. *Distribute the remaining electrons as lone pairs on the terminal atoms*. In this case, there is no central atom, so we distribute

the electrons around both atoms. We give eight electrons to the more electronegative atom in these situations; thus oxygen has the filled valence shell:

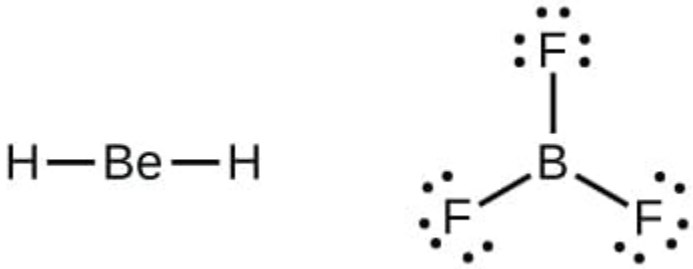


4. *Place all remaining electrons on the central atom*. Since there are no remaining electrons, this step does not apply.
5. *Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever possible*. We know that an odd-electron molecule cannot have an octet for every atom, but we want to get each atom as close to an octet as possible. In this case, nitrogen has only five electrons around it. To move closer to an octet for nitrogen, we take one of the lone pairs from oxygen and use it to form a NO double bond. (We cannot take another lone pair of electrons on oxygen and form a triple bond because nitrogen would then have nine electrons:)

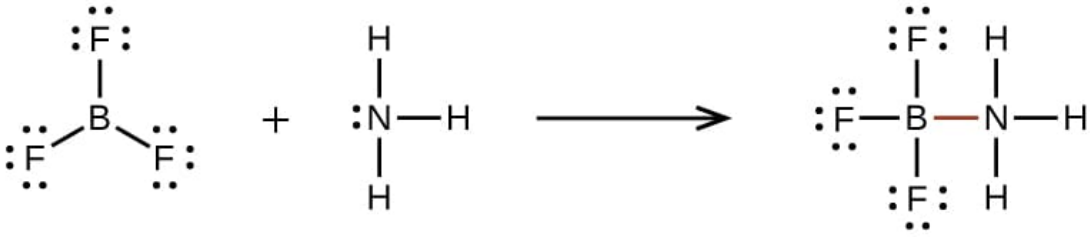


Electron-deficient Molecules

We will also encounter a few molecules that contain central atoms that do not have a filled valence shell. Generally, these are molecules with central atoms from groups 2 and 13, outer atoms that are hydrogen, or other atoms that do not form multiple bonds. For example, in the Lewis structures of beryllium dihydride, BeH_2, and boron trifluoride, BF_3, the beryllium and boron atoms each have only four and six electrons, respectively. It is possible to draw a structure with a double bond between a boron atom and a fluorine atom in BF_3, satisfying the octet rule, but experimental evidence indicates the bond lengths are closer to that expected for B–F single bonds. This suggests the best Lewis structure has three B–F single bonds and an electron deficient boron. The reactivity of the compound is also consistent with an electron deficient boron. However, the B–F bonds are slightly shorter than what is actually expected for B–F single bonds, indicating that some double bond character is found in the actual molecule.



An atom like the boron atom in BF_3, which does not have eight electrons, is very reactive. It readily combines with a molecule containing an atom with a lone pair of electrons. For example, NH_3 reacts with BF_3 because the lone pair on nitrogen can be shared with the boron atom:



Hypervalent Molecules

Elements in the second period of the periodic table ($n = 2$) can accommodate only eight electrons in their valence shell orbitals because they have only four valence orbitals (one 2*s* and three 2*p* orbitals). Elements in the third and higher periods ($n \geq 3$) have more than four valence orbitals and can share more than four pairs of electrons with other atoms because they have empty *d* orbitals in the same shell. Molecules formed from these elements are sometimes called hypervalent molecules. Figure 3.5.4: shows the Lewis structures for two hypervalent molecules, PCl_5 and SF_6.

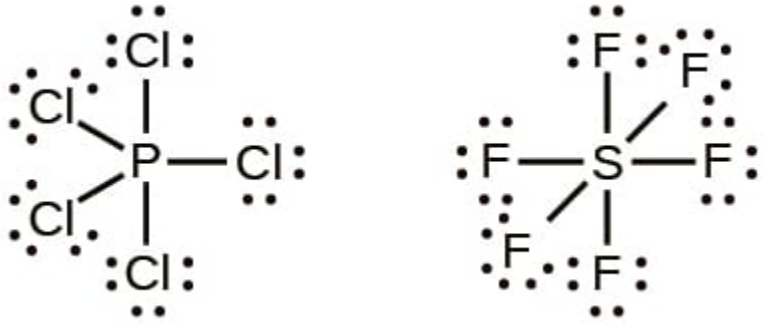
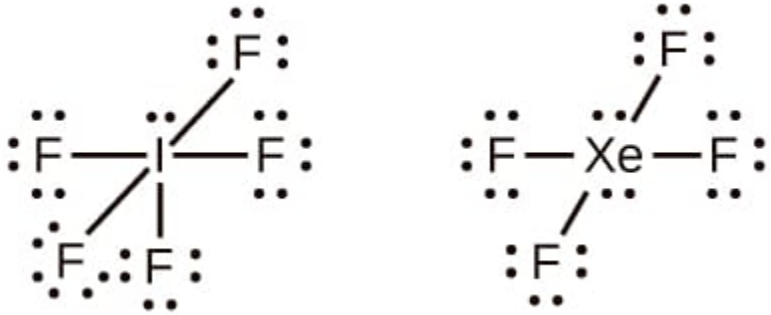


Figure 3.5.4: In PCl_5, the central atom phosphorus shares five pairs of electrons. In SF_6, sulfur shares six pairs of electrons.

In some hypervalent molecules, such as IF_5 and XeF_4, some of the electrons in the outer shell of the central atom are lone pairs:



When we write the Lewis structures for these molecules, we find that we have electrons left over after filling the valence shells of the outer atoms with eight electrons. These additional electrons must be assigned to the central atom.

Example 3.5.2: Writing Lewis Structures - Octet Rule Violations

Xenon is a noble gas, but it forms a number of stable compounds. We examined XeF_4 earlier. What are the Lewis structures of XeF_2 and XeF_6?

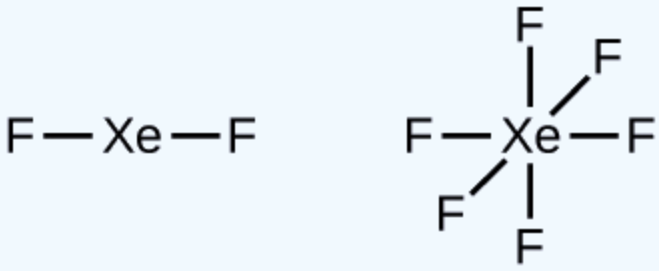
Solution

We can draw the Lewis structure of any covalent molecule by following the six steps discussed earlier. In this case, we can condense the last few steps, since not all of them apply.

Step 1. Calculate the number of valence electrons:

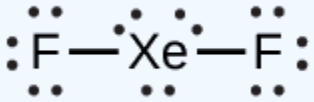
XeF_2: $8 + (2 \times 7) = 22$
XeF_6: $8 + (6 \times 7) = 50$

Step 2. Draw a skeleton joining the atoms by single bonds. Xenon will be the central atom because fluorine cannot be a central atom:

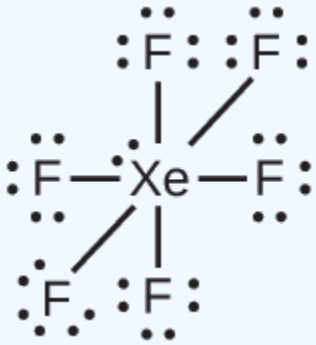


Step 3. Distribute the remaining electrons.

XeF_2: We place three lone pairs of electrons around each F atom, accounting for 12 electrons and giving each F atom 8 electrons. Thus, six electrons (three lone pairs) remain. These lone pairs must be placed on the Xe atom. This is acceptable because Xe atoms have empty valence shell *d* orbitals and can accommodate more than eight electrons. The Lewis structure of XeF_2 shows two bonding pairs and three lone pairs of electrons around the Xe atom:



XeF_6: We place three lone pairs of electrons around each F atom, accounting for 36 electrons. Two electrons remain, and this lone pair is placed on the Xe atom:



Exercise 3.5.2: Interhalogens

The halogens form a class of compounds called the interhalogens, in which halogen atoms covalently bond to each other. Write the Lewis structures for the interhalogens $BrCl_3$ and ICl_4^-.

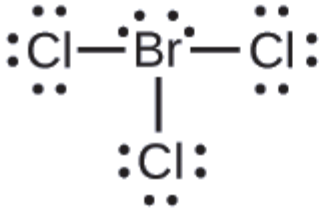
Answer available at the end of this section.

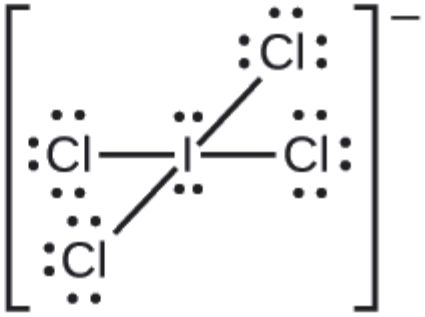
Answers

Exercise 3.5.1



Exercise 3.5.2**: Interhalogens**





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3.6: Introduction to Formal Charges and Resonance

Learning Objectives

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

- Compute formal charges for atoms in any Lewis structure
- Use formal charges to identify the most reasonable Lewis structure for a given molecule
- Explain the concept of resonance and draw Lewis structures representing resonance forms for a given molecule

In the previous section, we discussed how to write Lewis structures for molecules and polyatomic ions. As we have seen, however, in some cases, there is seemingly more than one valid structure for a molecule. We can use the concept of formal charges to help us predict the most appropriate Lewis structure when more than one is reasonable.

Calculating Formal Charge

The formal charge of an atom in a molecule is the *hypothetical* charge the atom would have if we could redistribute the electrons in the bonds evenly between the atoms. Another way of saying this is that formal charge results when we take the number of valence electrons of a neutral atom, subtract the nonbonding electrons, and then subtract the number of bonds connected to that atom in the Lewis structure.

Thus, we calculate formal charge as follows:

$$\text{formal charge } = \#\text{ valence shell electrons (free atom)} - \#\text{ lone pair electrons } - \frac{1}{2}\#\text{ bonding electrons}$$

We can double-check formal charge calculations by determining the sum of the formal charges for the whole structure. The sum of the formal charges of all atoms in a molecule must be zero; the sum of the formal charges in an ion should equal the charge of the ion.

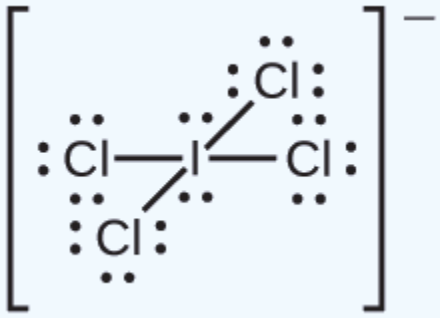
We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

Example 3.6.1: Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen ion

Solution

Step 1. *We divide the bonding electron pairs equally for all I–Cl bonds:*



Step 2. *We assign lone pairs of electrons to their atoms*. Each Cl atom now has seven electrons assigned to it, and the I atom has eight.

Step 3. *Subtract this number from the number of valence electrons for the neutral atom:*

I: 7 − 8 = −1
Cl: 7 − 7 = 0

The sum of the formal charges of all the atoms equals −1, which is identical to the charge of the ion (−1).

Exercise 3.6.1

Calculate the formal charge for each atom in the carbon monoxide molecule:



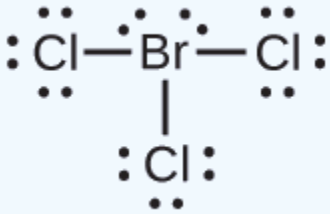
Answer available at the end of this section.

Example 3.6.2: Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen molecule $BrCl_3$.

Solution

Step 1. *Assign one of the electrons in each Br–Cl bond to the Br atom and one to the Cl atom in that bond:*



Step 2. *Assign the lone pairs to their atom*. Now each Cl atom has seven electrons and the Br atom has seven electrons.

Step 3. *Subtract this number from the number of valence electrons for the neutral atom*. This gives the formal charge:

Br: 7 − 7 = 0
Cl: 7 − 7 = 0

All atoms in $BrCl_3$ have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.

Exercise 3.6.2

Determine the formal charge for each atom in NCl_3.

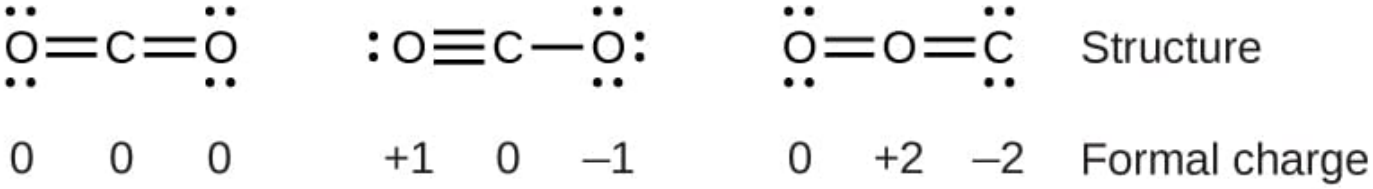
Answer available at the end of this section.

Using Formal Charge to Predict Molecular Structure

The arrangement of atoms in a molecule or ion is called its **molecular structure**. In many cases, following the steps for writing Lewis structures may lead to more than one possible molecular structure—different multiple bond and lone-pair electron placements or different arrangements of atoms, for instance. A few guidelines involving formal charge can be helpful in deciding which of the possible structures is most likely for a particular molecule or ion:

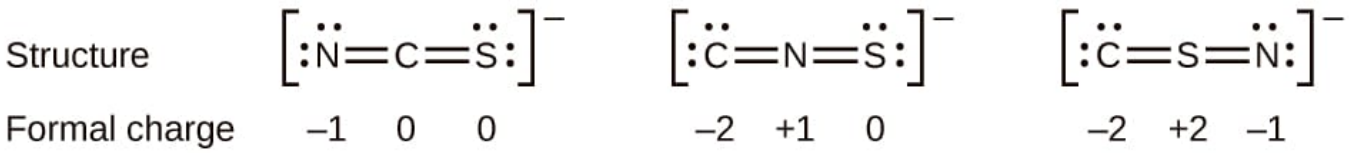
1. A molecular structure in which all formal charges are zero is preferable to one in which some formal charges are not zero.
2. If the Lewis structure must have nonzero formal charges, the arrangement with the smallest nonzero formal charges is preferable.
3. Lewis structures are preferable when adjacent formal charges are zero or of the opposite sign.
4. When we must choose among several Lewis structures with similar distributions of formal charges, the structure with the negative formal charges on the more electronegative atoms is preferable.

To see how these guidelines apply, let us consider some possible structures for carbon dioxide, CO_2. We know from our previous discussion that the less electronegative atom typically occupies the central position, but formal charges allow us to understand *why* this occurs. We can draw three possibilities for the structure: carbon in the center and double bonds, carbon in the center with a single and triple bond, and oxygen in the center with double bonds:



Comparing the three formal charges, we can definitively identify the structure on the left as preferable because it has only formal charges of zero (Guideline 1).

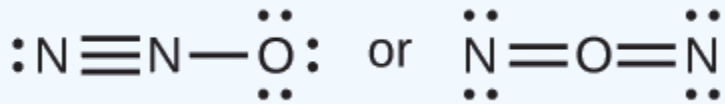
As another example, the thiocyanate ion, an ion formed from a carbon atom, a nitrogen atom, and a sulfur atom, could have three different molecular structures: NCS^-, CNS^-, or CSN^-. The formal charges present in each of these molecular structures can help us pick the most likely arrangement of atoms. Possible Lewis structures and the formal charges for each of the three possible structures for the thiocyanate ion are shown here:



Note that the sum of the formal charges in each case is equal to the charge of the ion (–1). However, the first arrangement of atoms is preferred because it has the lowest number of atoms with nonzero formal charges (Guideline 2). Also, it places the least electronegative atom in the center, and the negative charge on the more electronegative element (Guideline 4).

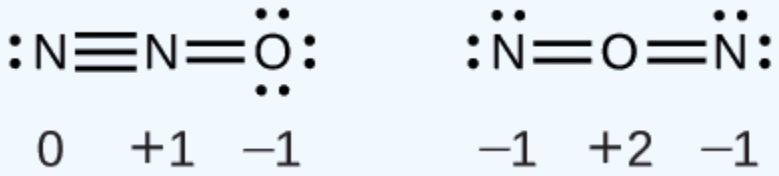
Example 3.6.3: Using Formal Charge to Determine Molecular Structure

Nitrous oxide, N_2O, commonly known as laughing gas, is used as an anesthetic in minor surgeries, such as the routine extraction of wisdom teeth. Which is the more likely structure for nitrous oxide?

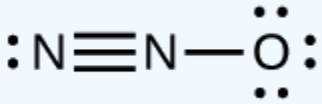


Solution

Determining formal charge yields the following:



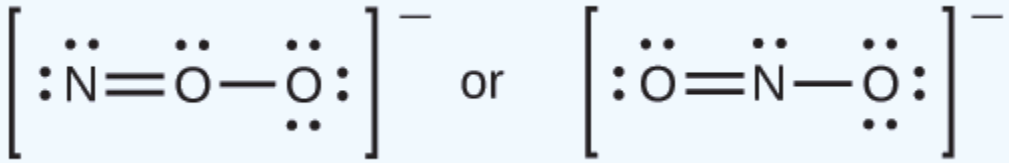
The structure with a terminal oxygen atom best satisfies the criteria for the most stable distribution of formal charge:



The number of atoms with formal charges are minimized (Guideline 2), there is no formal charge with a magnitude greater than one (Guideline 2), the negative formal charge is on the more electronegative element (Guideline 4), and the less electronegative atom is in the center position.

Exercise 3.6.3

Which is the most likely molecular structure for the nitrite ion?



Answer available at the end of this section.

Resonance

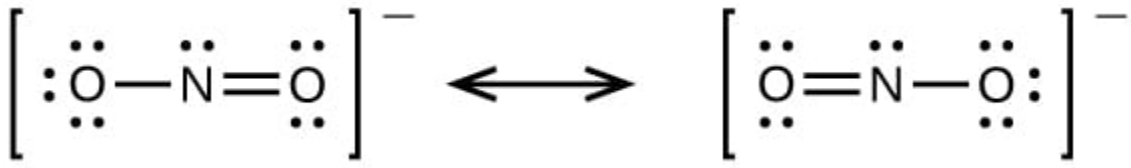
Notice that the more likely structure for the nitrite anion in Example 3.6.3 may actually be drawn in two different ways, distinguished by the locations of the N-O and N=O bonds:



If nitrite ions do indeed contain a single and a double bond, we would expect for the two bond lengths to be different. A double bond between two atoms is shorter (and stronger) than a single bond between the same two atoms. Experiments show, however, that both N–O bonds in have the same strength and length, and are identical in all other properties.

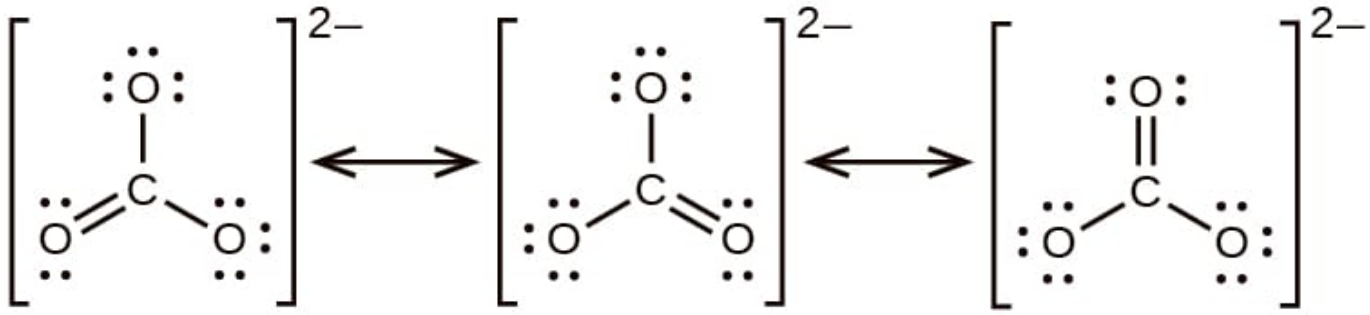
It is not possible to write a single Lewis structure for in which nitrogen has an octet and both bonds are equivalent. Instead, we use the concept of **resonance**: if two or more Lewis structures with the same arrangement of atoms can be written for a molecule or ion, the actual distribution of electrons is an *average* of that shown by the various Lewis structures. The actual distribution of electrons in each of the nitrogen-oxygen bonds in is the average of a double bond and a single bond. We call the individual Lewis structures **resonance forms**. The actual electronic structure of the molecule (the average of the resonance forms) is called

a **resonance hybrid** of the individual resonance forms. A double-headed arrow between Lewis structures indicates that they are resonance forms.



We should remember that a molecule described as a resonance hybrid *never* possesses an electronic structure described by either resonance form. It does not fluctuate between resonance forms; rather, the actual electronic structure is *always* the average of that shown by all resonance forms. George Wheland, one of the pioneers of resonance theory, used a historical analogy to describe the relationship between resonance forms and resonance hybrids. A medieval traveler, having never before seen a rhinoceros, described it as a hybrid of a dragon and a unicorn because it had many properties in common with both. Just as a rhinoceros is neither a dragon sometimes nor a unicorn at other times, a resonance hybrid is neither of its resonance forms at any given time. Like a rhinoceros, it is a real entity that experimental evidence has shown to exist. It has some characteristics in common with its resonance forms, but the resonance forms themselves are convenient, imaginary images (like the unicorn and the dragon).

The carbonate anion, provides a second example of resonance:



One oxygen atom must have a double bond to carbon to complete the octet on the central atom. All oxygen atoms, however, are equivalent, and the double bond could form from any one of the three atoms. This gives rise to three resonance forms of the carbonate ion. Because we can write three identical resonance structures, we know that the actual arrangement of electrons in the carbonate ion is the average of the three structures. Again, experiments show that all three C–O bonds are exactly the same.

Link to Learning

Use this online quiz to practice your skills in drawing resonance structures and estimating formal charges.

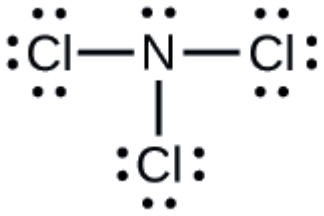
Answers

Exercise 3.6.1

C –1, O +1

Exercise 3.6.2

N: 0; all three Cl atoms: 0



Exercise 3.6.3

ONO^-

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3.7: Molecular Structure and Polarity

Learning Objectives

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

- Predict the structures of small molecules using valence shell electron pair repulsion (VSEPR) theory
- Explain the concepts of polar covalent bonds and molecular polarity
- Assess the polarity of a molecule based on its bonding and structure

Thus far, we have used two-dimensional Lewis structures to represent molecules. However, molecular structure is actually three-dimensional, and it is important to be able to describe molecular bonds in terms of their distances, angles, and relative arrangements in space (Figure 3.7.1). A bond angle is the angle between any two bonds that include a common atom, usually measured in degrees. A bond distance (or bond length) is the distance between the nuclei of two bonded atoms along the straight line joining the nuclei. Bond distances are measured in Ångstroms (1 Å = 10^{-10} m) or picometers (1 pm = 10^{-12} m, 100 pm = 1 Å).

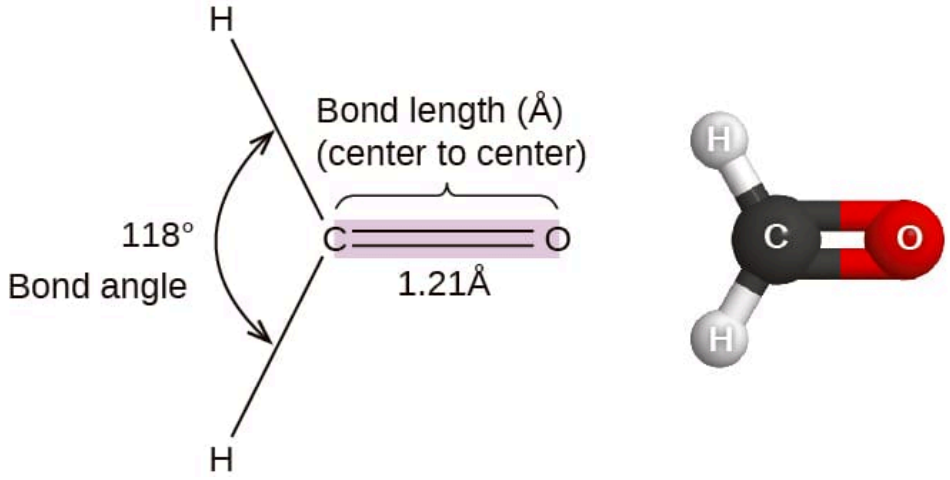


Figure 3.7.1: Bond distances (lengths) and angles are shown for the formaldehyde molecule, H_2CO.

VSEPR Theory

Valence shell electron-pair repulsion theory (VSEPR theory) enables us to predict the molecular structure, including approximate bond angles around a central atom, of a molecule from an examination of the number of bonds and lone electron pairs in its Lewis structure. The VSEPR model assumes that electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them. The electrons in the valence shell of a central atom form either bonding pairs of electrons, located primarily between bonded atoms, or lone pairs. The electrostatic repulsion of these electrons is reduced when the various regions of high electron density assume positions as far from each other as possible.

VSEPR theory predicts the arrangement of electron pairs around each central atom and, usually, the correct arrangement of atoms in a molecule. We should understand, however, that the theory only considers electron-pair repulsions. Other interactions, such as nuclear-nuclear repulsions and nuclear-electron attractions, are also involved in the final arrangement that atoms adopt in a particular molecular structure.

As a simple example of VSEPR theory, let us predict the structure of a gaseous BeF_2 molecule. The Lewis structure of BeF_2 (Figure 3.7.2) shows only two electron pairs around the central beryllium atom. With two bonds and no lone pairs of electrons on the central atom, the bonds are as far apart as possible, and the electrostatic repulsion between these regions of high electron density is reduced to a minimum when they are on opposite sides of the central atom. The bond angle is 180° (Figure 3.7.2).

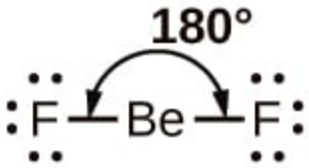


Figure 3.7.2: The BeF_2 molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom.

Figure 3.7.3 illustrates this and other electron-pair geometries that minimize the repulsions among regions of high electron density (bonds and/or lone pairs). Two regions of electron density around a central atom in a molecule form a linear geometry; three regions form a trigonal planar geometry; four regions form a tetrahedral geometry; five regions form a trigonal bipyramidal geometry; and six regions form an octahedral geometry.

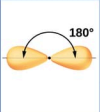
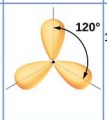
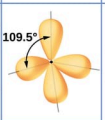
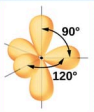
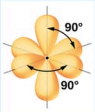
Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Spatial arrangement					
Line-dash-wedge notation					
Electron region geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

Figure 3.7.3: The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).

Electron-pair Geometry versus Molecular Structure

It is important to note that electron-pair geometry around a central atom is *not* the same thing as its molecular structure. The electron-pair geometries shown in Figure 3.7.3 describe all regions where electrons are located, bonds as well as lone pairs. Molecular structure describes the location of the *atoms*, not the electrons.

We differentiate between these two situations by naming the geometry that includes *all* electron pairs the electron-pair geometry. The structure that includes only the placement of the atoms in the molecule is called the molecular structure. The electron-pair geometries will be the same as the molecular structures when there are no lone electron pairs around the central atom, but they will be different when there are lone pairs present on the central atom.

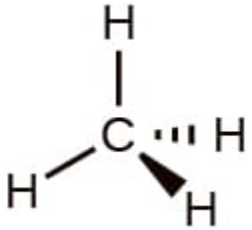


Figure 3.7.4: The molecular structure of the methane molecule, CH_4, is shown with a tetrahedral arrangement of the hydrogen atoms. VSEPR structures like this one are often drawn using the wedge and dash notation, in which solid lines represent bonds in the plane of the page, solid wedges represent bonds coming up out of the plane, and dashed lines represent bonds going down into the plane.

For example, the methane molecule, CH_4, which is the major component of natural gas, has four bonding pairs of electrons around the central carbon atom; the electron-pair geometry is tetrahedral, as is the molecular structure (Figure 3.7.4). On the other hand, the ammonia molecule, NH_3, also has four electron pairs associated with the nitrogen atom, and thus has a tetrahedral electron-pair geometry. One of these regions, however, is a lone pair, which is not included in the molecular structure, and this lone pair influences the shape of the molecule (Figure 3.7.5).

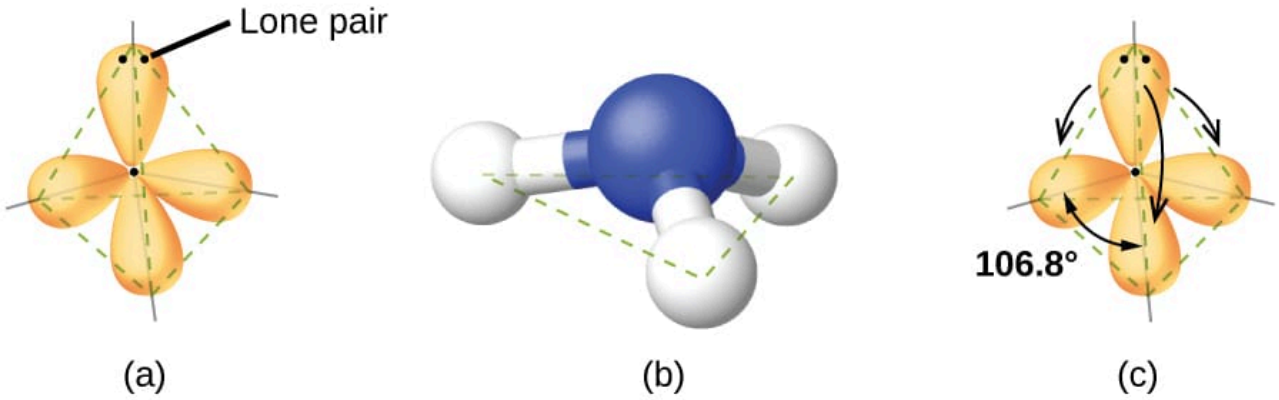


Figure 3.7.5: (a) The electron-pair geometry for the ammonia molecule is tetrahedral with one lone pair and three single bonds. (b) The trigonal pyramidal molecular structure is determined from the electron-pair geometry. (c) The actual bond angles deviate slightly from the idealized angles because the lone pair takes up a larger region of space than do the single bonds, causing the HNH angle to be slightly smaller than 109.5°.

As seen in Figure 3.7.5, small distortions from the ideal angles in Figure 3.7.3 can result from differences in repulsion between various regions of electron density. VSEPR theory predicts these distortions by establishing an order of repulsions and an order of the amount of space occupied by different kinds of electron pairs. The order of electron-pair repulsions from greatest to least repulsion is:

$$\text{lone pair-lone pair} > \text{lone pair-bonding pair} > \text{bonding pair-bonding pair}$$

This order of repulsions determines the amount of space occupied by different regions of electrons. A lone pair of electrons occupies a larger region of space than the electrons in a triple bond; in turn, electrons in a triple bond occupy more space than those in a double bond, and so on. The order of sizes from largest to smallest is:

$$\text{lone pair} > \text{triple bond} > \text{double bond} > \text{single bond}$$

Consider formaldehyde, H_2CO, which is used as a preservative for biological and anatomical specimens (Figure 3.7.1). This molecule has regions of high electron density that consist of two single bonds and one double bond. The basic geometry is trigonal planar with 120° bond angles, but we see that the double bond causes slightly larger angles (121°), and the angle between the single bonds is slightly smaller (118°).

In the ammonia molecule, the three hydrogen atoms attached to the central nitrogen are not arranged in a flat, trigonal planar molecular structure, but rather in a three-dimensional trigonal pyramid (Figure 3.7.5) with the nitrogen atom at the apex and the three hydrogen atoms forming the base. The ideal bond angles in a trigonal pyramid are based on the tetrahedral electron pair geometry. Again, there are slight deviations from the ideal because lone pairs occupy larger regions of space than do bonding electrons. The H–N–H bond angles in NH_3 are slightly smaller than the 109.5° angle in a regular tetrahedron (Figure 3.7.3) because the lone pair-bonding pair repulsion is greater than the bonding pair-bonding pair repulsion (Figure 3.7.5). Figure 3.7.6 illustrates the ideal molecular structures, which are predicted based on the electron-pair geometries for various combinations of lone pairs and bonding pairs.

Number of electron regions	Electron region geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	Linear				
3	Trigonal planar	Bent or angular			
4	Tetrahedral	Trigonal pyramid	Bent or angular		
5	Trigonal bipyramid	Sawhorse or seesaw	T-shape	Linear	
6	Octahedral	Square pyramid	Square planar	T-shape	Linear

Figure 3.7.6: The molecular structures are identical to the electron-pair geometries when there are no lone pairs present (first column). For a particular number of electron pairs (row), the molecular structures for one or more lone pairs are determined based on modifications of the corresponding electron-pair geometry.

According to VSEPR theory, the terminal atom locations (Xs in Figure 3.7.6) are equivalent within the linear, trigonal planar, and tetrahedral electron-pair geometries (the first three rows of the table). It does not matter which X is replaced with a lone pair because the molecules can be rotated to convert positions. For trigonal bipyramidal electron-pair geometries, however, there are two distinct X positions, as shown in Figure 3.7.7 an axial position (if we hold a model of a trigonal bipyramid by the two axial positions, we have an axis around which we can rotate the model) and an equatorial position (three positions form an equator around the middle of the molecule). As shown in Figure 3.7.6, the axial position is surrounded by bond angles of 90°, whereas the equatorial position has more space available because of the 120° bond angles. In a trigonal bipyramidal electron-pair geometry, lone pairs always occupy equatorial positions because these more spacious positions can more easily accommodate the larger lone pairs.

Theoretically, we can come up with three possible arrangements for the three bonds and two lone pairs for the ClF_3 molecule (Figure 3.7.7). The stable structure is the one that puts the lone pairs in equatorial locations, giving a T-shaped molecular structure.

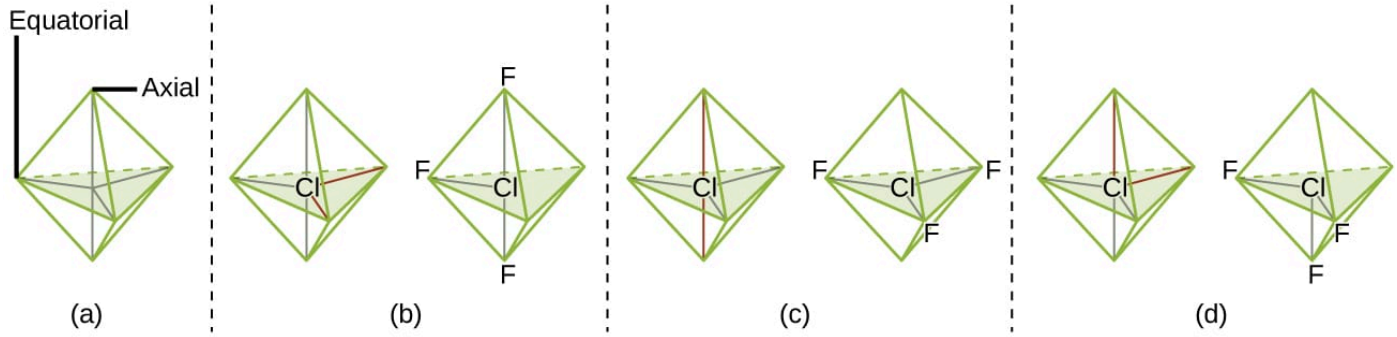


Figure 3.7.7: (a) In a trigonal bipyramid, the two axial positions are located directly across from one another, whereas the three equatorial positions are located in a triangular arrangement. (b–d) The two lone pairs (red lines) in ClF_3 have several possible arrangements, but the T-shaped molecular structure (b) is the one actually observed, consistent with the larger lone pairs both occupying equatorial positions.

When a central atom has two lone electron pairs and four bonding regions, we have an octahedral electron-pair geometry. The two lone pairs are on opposite sides of the octahedron (180° apart), giving a square planar molecular structure that minimizes lone pair-lone pair repulsions (Figure 3.7.6).

Predicting Electron Pair Geometry and Molecular Structure

The following procedure uses VSEPR theory to determine the electron pair geometries and the molecular structures:

1. Write the Lewis structure of the molecule or polyatomic ion.
2. Count the number of regions of electron density (lone pairs and bonds) around the central atom. A single, double, or triple bond counts as one region of electron density.
3. Identify the electron-pair geometry based on the number of regions of electron density: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral (Figure 3.7.6, first column).
4. Use the number of lone pairs to determine the molecular structure (Figure 3.7.6). If more than one arrangement of lone pairs and chemical bonds is possible, choose the one that will minimize repulsions, remembering that lone pairs occupy more space than multiple bonds, which occupy more space than single bonds. In trigonal bipyramidal arrangements, repulsion is minimized when every lone pair is in an equatorial position. In an octahedral arrangement with two lone pairs, repulsion is minimized when the lone pairs are on opposite sides of the central atom.

The following examples illustrate the use of VSEPR theory to predict the molecular structure of molecules or ions that have no lone pairs of electrons. In this case, the molecular structure is identical to the electron pair geometry.

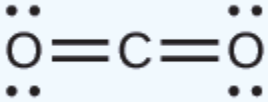
Example 3.7.1: Predicting Electron-pair Geometry and Molecular Structure: CO_2 and BCl_3

Predict the electron-pair geometry and molecular structure for each of the following:

a. carbon dioxide, CO_2, a molecule produced by the combustion of fossil fuels
b. boron trichloride, BCl_3, an important industrial chemical

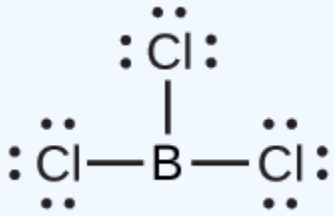
Solution

(a) We write the Lewis structure of CO_2 as:



This shows us two regions of high electron density around the carbon atom—each double bond counts as one region, and there are no lone pairs on the carbon atom. Using VSEPR theory, we predict that the two regions of electron density arrange themselves on opposite sides of the central atom with a bond angle of 180°. The electron-pair geometry and molecular structure are identical, and CO_2 molecules are linear.

(b) We write the Lewis structure of BCl_3 as:



Thus we see that BCl_3 contains three bonds, and there are no lone pairs of electrons on boron. The arrangement of three regions of high electron density gives a trigonal planar electron-pair geometry. The B–Cl bonds lie in a plane with 120° angles between them. BCl_3 also has a trigonal planar molecular structure (Figure 3.7.8).

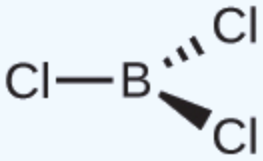


Figure 3.7.8:

The electron-pair geometry and molecular structure of BCl_3 are both trigonal planar. Note that the VSEPR geometry indicates the correct bond angles (120°), unlike the Lewis structure shown above.

Exercise 3.7.1

Carbonate, is a common polyatomic ion found in various materials from eggshells to antacids. What are the electron-pair geometry and molecular structure of this polyatomic ion?

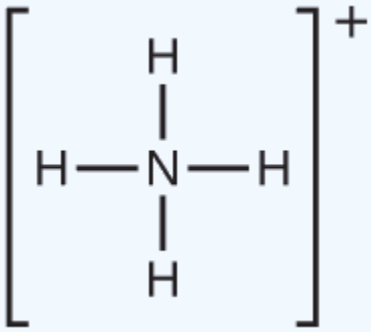
Answer available at the end of this section.

Example 3.7.2: Predicting Electron-pair Geometry and Molecular Structure: Ammonium

Two of the top 50 chemicals produced in the United States, ammonium nitrate and ammonium sulfate, both used as fertilizers, contain the ammonium ion. Predict the electron-pair geometry and molecular structure of the cation.

Solution

We write the Lewis structure of as:



We can see that NH_4^+ contains four bonds from the nitrogen atom to hydrogen atoms and no lone pairs. We expect the four regions of high electron density to arrange themselves so that they point to the corners of a tetrahedron with the central nitrogen atom in the middle (Figure 3.7.6). Therefore, the electron pair geometry of Figure 3.7.9.

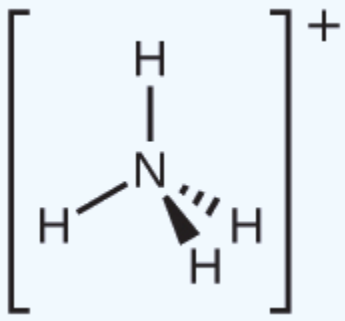


Figure 3.7.9: The ammonium ion displays a tetrahedral electron-pair geometry as well as a tetrahedral molecular structure.

Exercise 3.7.2

Identify a molecule with trigonal bipyramidal molecular structure.

Answer available at the end of this section.

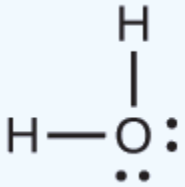
The next several examples illustrate the effect of lone pairs of electrons on molecular structure.

Example 3.7.3: Predicting Electron-pair Geometry and Molecular Structure: Lone Pairs on the Central Atom

Predict the electron-pair geometry and molecular structure of a water molecule.

Solution

The Lewis structure of H_2O indicates that there are four regions of high electron density around the oxygen atom: two lone pairs and two chemical bonds:



We predict that these four regions are arranged in a tetrahedral fashion (Figure 3.7.10), as indicated in Figure 3.7.6. Thus, the electron-pair geometry is tetrahedral and the molecular structure is bent with an angle slightly less than 109.5°. In fact, the bond angle is 104.5°.

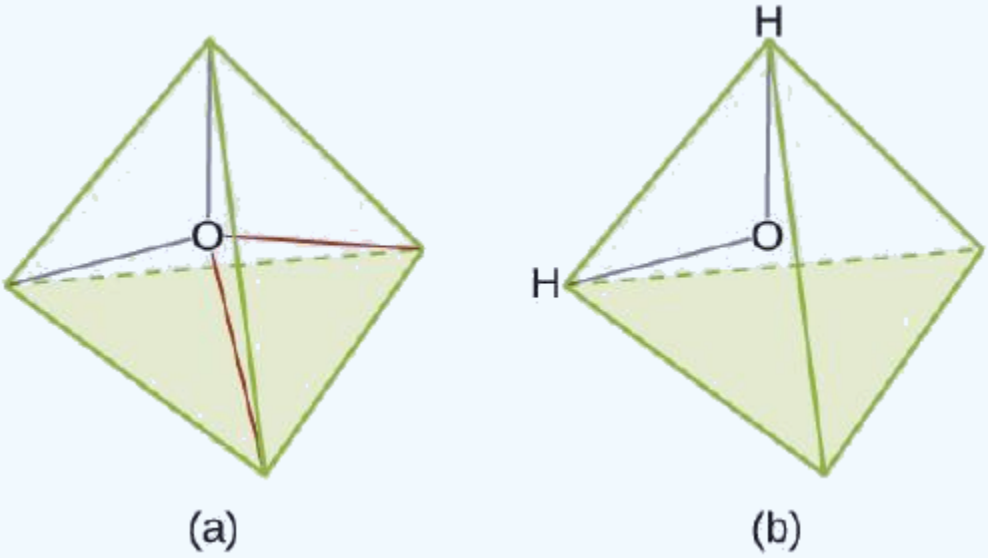


Figure 3.7.10: (a) H_2O has four regions of electron density around the central atom, so it has a tetrahedral electron-pair geometry. (b) Two of the electron regions are lone pairs, so the molecular structure is bent.

Exercise 3.7.3

The hydronium ion, H_3O^+, forms when acids are dissolved in water. Predict the electron-pair geometry and molecular structure of this cation.

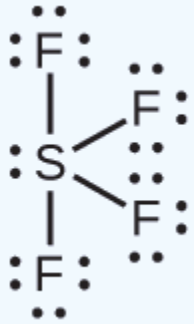
Answer available at the end of this section.

Example 3.7.4: Predicting Electron-pair Geometry and Molecular Structure: SF_4

Sulfur tetrafluoride, SF_4, is extremely valuable for the preparation of fluorine-containing compounds used as herbicides (i.e., SF_4 is used as a fluorinating agent). Predict the electron-pair geometry and molecular structure of a SF_4 molecule.

Solution

The Lewis structure of SF_4 indicates five regions of electron density around the sulfur atom: one lone pair and four bonding pairs:



We expect these five regions to adopt a trigonal bipyramidal electron-pair geometry. To minimize lone pair repulsions, the lone pair occupies one of the equatorial positions. The molecular structure (Figure 3.7.11) is that of a seesaw (Figure 3.7.6).

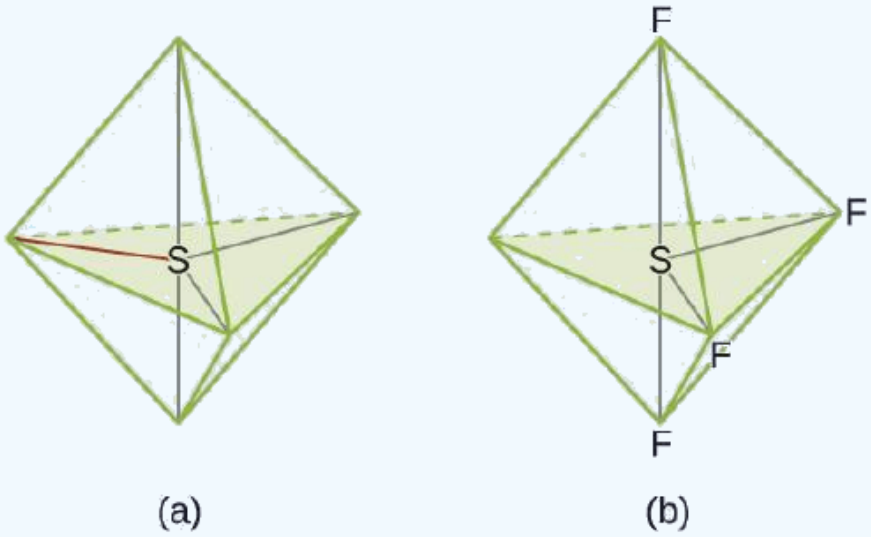


Figure 3.7.11: (a) SF4 has a trigonal bipyramidal arrangement of the five regions of electron density. (b) One of the regions is a lone pair, which results in a seesaw-shaped molecular structure.

Exercise 3.7.4

Predict the electron pair geometry and molecular structure for molecules of XeF_2.

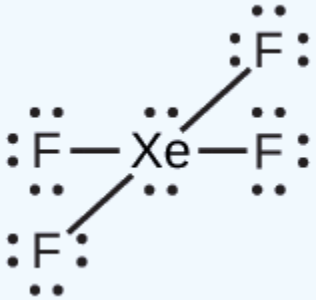
Answer available at the end of this section.

Example 3.7.5: Predicting Electron-pair Geometry and Molecular Structure: XeF_4

Of all the noble gases, xenon is the most reactive, frequently reacting with elements such as oxygen and fluorine. Predict the electron-pair geometry and molecular structure of the XeF_4 molecule.

Solution

The Lewis structure of XeF_4 indicates six regions of high electron density around the xenon atom: two lone pairs and four bonds:



These six regions adopt an octahedral arrangement (Figure 3.7.6), which is the electron-pair geometry. To minimize repulsions, the lone pairs should be on opposite sides of the central atom (Figure 3.7.12). The five atoms are all in the same plane and have a square planar molecular structure.

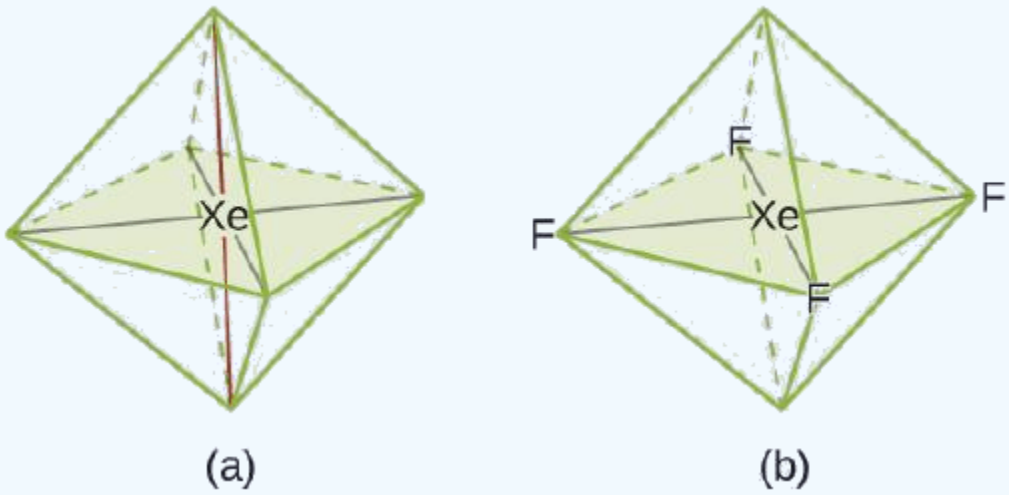


Figure 3.7.12: (a) XeF_4 adopts an octahedral arrangement with two lone pairs (red lines) and four bonds in the electron-pair geometry. (b) The molecular structure is square planar with the lone pairs directly across from one another.

Exercise 3.7.5

In a certain molecule, the central atom has three lone pairs and two bonds. What will the electron pair geometry and molecular structure be?

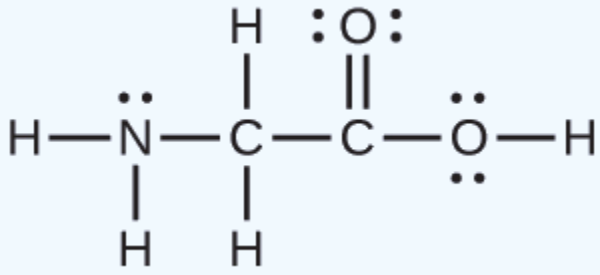
Answer available at the end of this section.

Molecular Structure for Multicenter Molecules

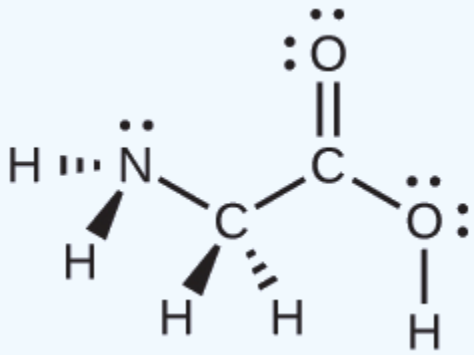
When a molecule or polyatomic ion has only one central atom, the molecular structure completely describes the shape of the molecule. Larger molecules do not have a single central atom, but are connected by a chain of interior atoms that each possess a "local" geometry. The way these local structures are oriented with respect to each other also influences the molecular shape, but such considerations are largely beyond the scope of this introductory discussion. For our purposes, we will only focus on determining the local structures.

Example 3.7.6: Predicting Structure in Multicenter Molecules

The Lewis structure for the simplest amino acid, glycine, $H_2NCH_2CO_2H$, is shown here. Predict the local geometry for the nitrogen atom, the two carbon atoms, and the oxygen atom with a hydrogen atom attached:



Solution



Consider each central atom independently. The electron-pair geometries:

- nitrogen––four regions of electron density; tetrahedral
- carbon ($\underline{C}H_2$)––four regions of electron density; tetrahedral
- carbon ($\underline{C}O_2$)—three regions of electron density; trigonal planar
- oxygen ($\underline{O}H$)—four regions of electron density; tetrahedral

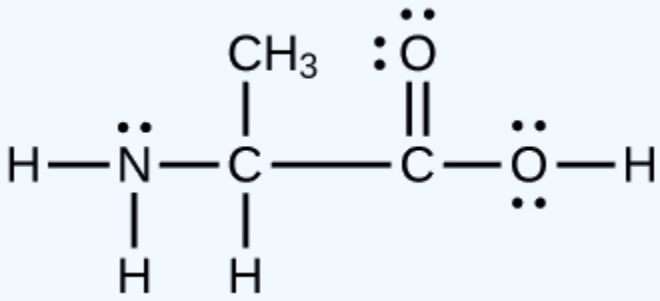
The local structures:

- nitrogen––three bonds, one lone pair; trigonal pyramidal

- carbon (CH_2)—four bonds, no lone pairs; tetrahedral
- carbon (CO_2)—three bonds (double bond counts as one bond), no lone pairs; trigonal planar
- oxygen (OH)—two bonds, two lone pairs; bent (109°)

Exercise 3.7.6

Another amino acid is alanine, which has the Lewis structure shown here. Predict the electron-pair geometry and local structure of the nitrogen atom, the three carbon atoms, and the oxygen atom with hydrogen attached:



Answer available at the end of this section.

Link to Learning

The molecular shape simulator lets you build various molecules and practice naming their electron-pair geometries and molecular structures.

Example 3.7.7: Molecular Simulation

Using molecular shape simulator allows us to control whether bond angles and/or lone pairs are displayed by checking or unchecking the boxes under "Options" on the right. We can also use the "Name" checkboxes at bottom-left to display or hide the electron pair geometry (called "electron geometry" in the simulator) and/or molecular structure (called "molecular shape" in the simulator).

Build the molecule HCN in the simulator based on the following Lewis structure:

$$\mathrm{H{-}C{\equiv}N}$$

Click on each bond type or lone pair at right to add that group to the central atom. Once you have the complete molecule, rotate it to examine the predicted molecular structure. What molecular structure is this?

Solution

The molecular structure is linear.

Exercise 3.7.7

Build a more complex molecule in the simulator. Identify the electron-group geometry, molecular structure, and bond angles. Then try to find a chemical formula that would match the structure you have drawn.

Answer available at the end of this section.

Molecular Polarity and Dipole Moment

As discussed previously, polar covalent bonds connect two atoms with differing electronegativities, leaving one atom with a partial positive charge (δ+) and the other atom with a partial negative charge (δ–), as the electrons are pulled toward the more electronegative atom. This separation of charge gives rise to a bond dipole moment. The magnitude of a bond dipole moment is represented by the Greek letter mu (μ) and is given by the formula shown here, where Q is the magnitude of the partial charges (determined by the electronegativity difference) and r is the distance between the charges:

$$\mu = Qr$$

This bond moment can be represented as a vector, a quantity having both direction and magnitude (Figure 3.7.13). Dipole vectors are shown as arrows pointing along the bond from the less electronegative atom toward the more electronegative atom. A small plus sign is drawn on the less electronegative end to indicate the partially positive end of the bond. The length of the arrow is proportional to the magnitude of the electronegativity difference between the two atoms.

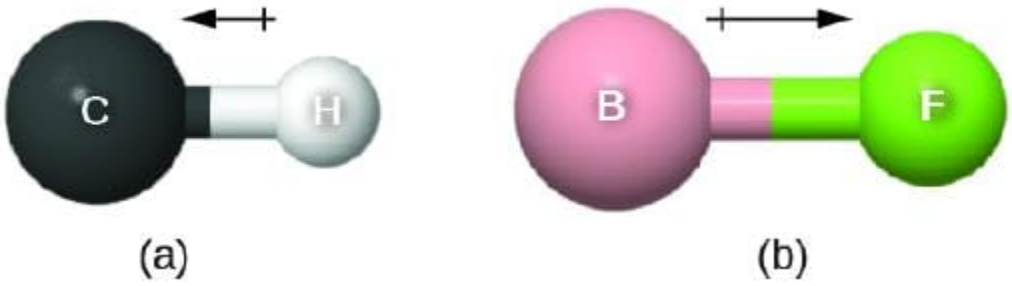


Figure 3.7.13: (a) There is a small difference in electronegativity between C and H, represented as a short vector. (b) The electronegat difference between B and F is much larger, so the vector representing the bond moment is much longer.

A whole molecule may also have a separation of charge, depending on its molecular structure and the polarity of each of its bonds. If such a charge separation exists, the molecule is said to be a polar molecule (or dipole); otherwise the molecule is said to be nonpolar. The dipole moment measures the extent of net charge separation in the molecule as a whole. We determine the dipole moment by adding the bond moments in three-dimensional space, taking into account the molecular structure.

For diatomic molecules, there is only one bond, so its bond dipole moment determines the molecular polarity. Homonuclear diatomic molecules such as Br_2 and N_2 have no difference in electronegativity, so their dipole moment is zero. For heteronuclear molecules such as CO, there is a small dipole moment. For HF, there is a larger dipole moment because there is a larger difference in electronegativity.

When a molecule contains more than one bond, the geometry must be taken into account. If the bonds in a molecule are arranged such that their bond moments cancel (vector sum equals zero), then the molecule is nonpolar. This is the situation in CO_2 (Figure 3.7.14). Each of the bonds is polar, but the molecule as a whole is nonpolar. From the Lewis structure, and using VSEPR theory, we determine that the CO_2 molecule is linear with polar C=O bonds on opposite sides of the carbon atom. The bond moments cancel because they are pointed in opposite directions. In the case of the water molecule (Figure 3.7.14), the Lewis structure again shows that there are two bonds to a central atom, and the electronegativity difference again shows that each of these bonds has a nonzero bond moment. In this case, however, the molecular structure is bent because of the lone pairs on O, and the two bond moments do not cancel. Therefore, water does have a net dipole moment and is a polar molecule (dipole).

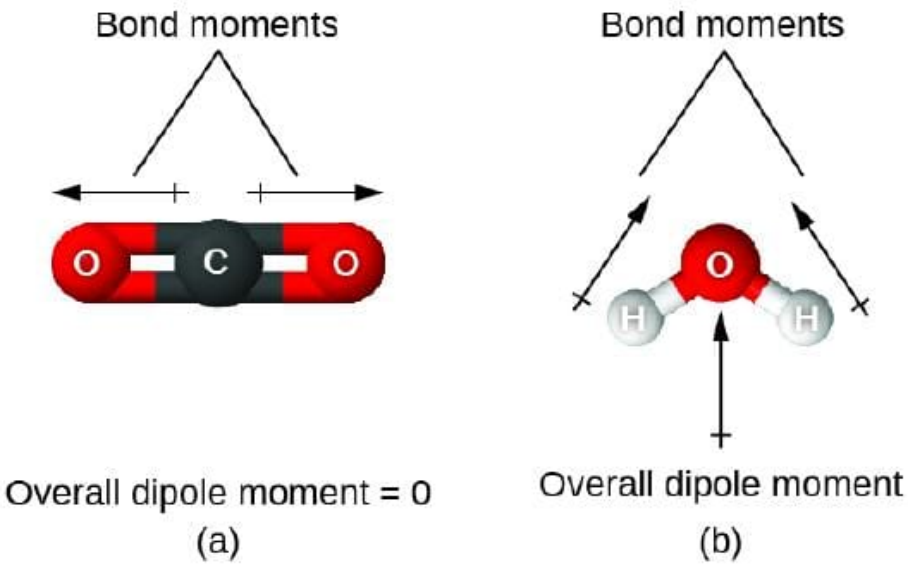
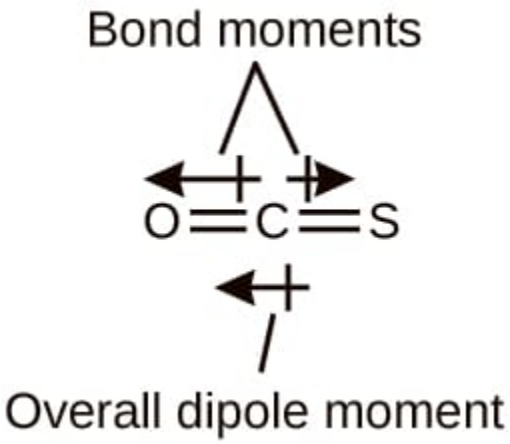


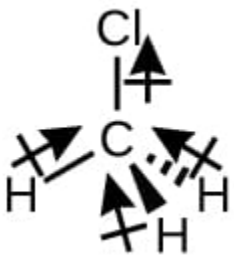
Figure 3.7.14: The overall dipole moment of a molecule depends on the individual bond dipole moments and how they are arranged. (a) Each CO bond has a bond dipole moment, but they point in opposite directions so that the net CO_2 molecule is nonpolar. (b) In contrast, water is polar because the OH bond moments do not cancel out.

The OCS molecule has a structure similar to CO_2, but a sulfur atom has replaced one of the oxygen atoms. To determine if this molecule is polar, we draw the molecular structure. VSEPR theory predicts a linear molecule:

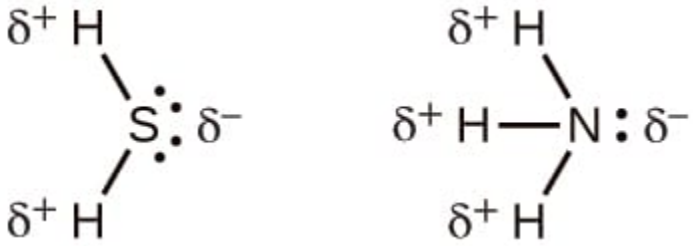


The C-O bond is considerably polar. Although C and S have very similar electronegativity values, S is slightly more electronegative than C, and so the C-S bond is just slightly polar. Because oxygen is more electronegative than sulfur, the oxygen end of the molecule is the negative end.

Chloromethane, CH_3Cl, is a tetrahedral molecule with three slightly polar C-H bonds and a more polar C-Cl bond. The relative electronegativities of the bonded atoms is H < C < Cl, and so the bond moments all point toward the Cl end of the molecule and sum to yield a considerable dipole moment (the molecules are relatively polar).



For molecules of high symmetry such as BF_3 (trigonal planar), CH_4 (tetrahedral), PF_5 (trigonal bipyramidal), and SF_6 (octahedral), all the bonds are of identical polarity (same bond moment) and they are oriented in geometries that yield nonpolar molecules (dipole moment is zero). Molecules of less geometric symmetry, however, may be polar even when all bond moments are identical. For these molecules, the directions of the equal bond moments are such that they sum to give a nonzero dipole moment and a polar molecule. Examples of such molecules include hydrogen sulfide, H_2S (nonlinear), and ammonia, NH_3 (trigonal pyramidal).



To summarize, to be polar, a molecule must:

1. Contain at least one polar covalent bond.
2. Have a molecular structure such that the sum of the vectors of each bond dipole moment does not cancel.

Properties of Polar Molecules

Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate (Figure 3.7.15). We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted. Also, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.

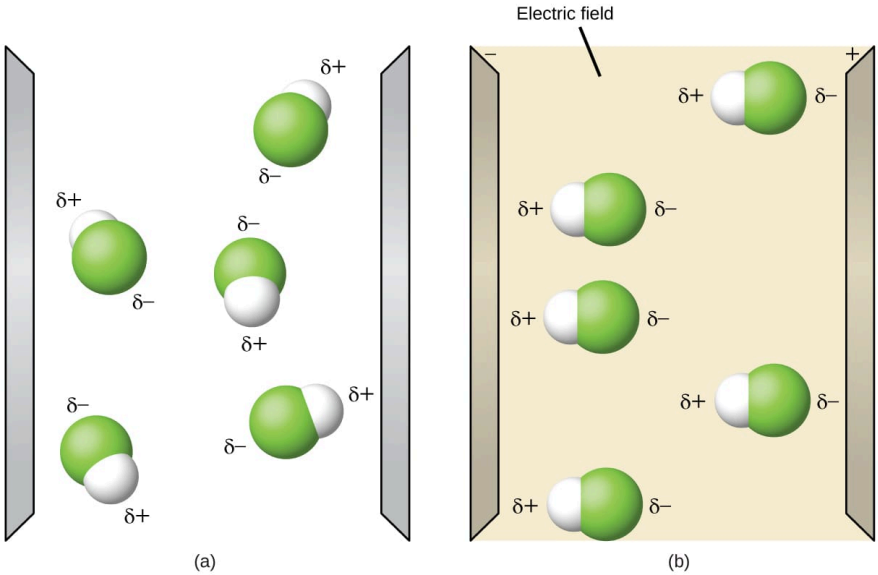


Figure 3.7.15: (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction.

Link to Learning

The molecule polarity simulation provides many ways to explore dipole moments of bonds and molecules.

Example 3.7.8: Polarity Simulations

Open the molecule polarity simulation and select the “Three Atoms” tab at the top. This should display a molecule ABC with three electronegativity adjustors. You can display or hide the bond moments, molecular dipoles, and partial charges at the right. Turning on the Electric Field will show whether the molecule moves when exposed to a field, similar to Figure 3.7.15.

Use the electronegativity controls to determine how the molecular dipole will look for the starting bent molecule if:

a. A and C are very electronegative and B is in the middle of the range.
b. A is very electronegative, and B and C are not.

Solution

a. Molecular dipole moment points immediately between A and C.
b. Molecular dipole moment points along the A–B bond, toward A.

Exercise 3.7.8

Determine the partial charges that will give the largest possible bond dipoles.

Answer available at the end of this section.

Answers

Exercise 3.7.1

The electron-pair geometry is trigonal planar and the molecular structure is trigonal planar. Due to resonance, all three C–O bonds are identical. Whether they are single, double, or an average of the two, each bond counts as one region of electron density.

Exercise 3.7.2

Any molecule with five electron pairs around the central atoms including no lone pairs will be trigonal bipyramidal. PF_5 is a common example.

Exercise 3.7.3

electron pair geometry: tetrahedral; molecular structure: trigonal pyramidal

Exercise 3.7.4

The electron-pair geometry is trigonal bipyramidal. The molecular structure is linear.

Exercise 3.7.5

electron pair geometry: trigonal bipyramidal; molecular structure: linear

Exercise 3.7.6

electron-pair geometries: nitrogen––tetrahedral; carbon (C<u>H</u>)—tetrahedral; carbon ($C\underline{H}_3$)—tetrahedral; carbon ($C\underline{O}_2$)—trigonal planar; oxygen (O<u>H</u>)—tetrahedral; local structures: nitrogen—trigonal pyramidal; carbon (C<u>H</u>)—tetrahedral; carbon ($C\underline{H}_3$)—tetrahedral; carbon ($C\underline{O}_2$)—trigonal planar; oxygen (O<u>H</u>)—bent (109°)

Exercise 3.7.7

Answers will vary. For example, an atom with four single bonds, a double bond, and a lone pair has an octahedral electron-group geometry and a square pyramidal molecular structure. $XeOF_4$ is a molecule that adopts this structure.

Exercise 3.7.8

The largest bond moments will occur with the largest partial charges. The two solutions above represent how unevenly the electrons are shared in the bond. The bond moments will be maximized when the electronegativity difference is greatest. The controls for A and C should be set to one extreme, and B should be set to the opposite extreme. Although the magnitude of the bond moment will not change based on whether B is the most electronegative or the least, the direction of the bond moment will.

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3.8: Key Terms

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

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.

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 length
distance between the nuclei of two bonded atoms at which the lowest potential energy is achieved

covalent bond
bond formed when electrons are shared between atoms

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

double bond
covalent bond in which two pairs of electrons are shared between two atoms

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

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

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)

free radical
molecule that contains an odd number of electrons

hypervalent molecule
molecule containing at least one main group element that has more than eight electrons in its valence shell

inert pair effect
tendency of heavy atoms to form ions in which their valence s electrons are not lost

ionic bond
strong electrostatic force of attraction between cations and anions in an ionic compound

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

linear
shape in which two outside groups are placed on opposite sides of a central atom

lone pair
two (a pair of) valence electrons that are not used to form a covalent bond

molecular structure
arrangement of atoms in a molecule or ion

molecular structure
structure that includes only the placement of the atoms in the molecule

nomenclature
system of rules for naming objects of interest

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

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

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)

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

pure covalent bond
(also, nonpolar covalent bond) covalent bond between atoms of identical electronegativities

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

single bond
bond in which a single pair of electrons is shared between two atoms

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

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

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

vector
quantity having magnitude and direction

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3.9: Key Equations

$$\text{formal charge} = \#\text{ valence shell electrons (free atom)} - \#\text{ lone pair electrons} - \tfrac{1}{2}\#\text{ bonding}$$

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3.10: Summary

Atoms gain or lose electrons to form ions with particularly stable electron configurations. The charges of cations formed by the representative metals may be determined readily because, with few exceptions, the electronic structures of these ions have either a noble gas configuration or a completely filled electron shell. The charges of anions formed by the nonmetals may also be readily determined because these ions form when nonmetal atoms gain enough electrons to fill their valence shells.

Covalent bonds form when electrons are shared between atoms and are attracted by the nuclei of both atoms. In pure covalent bonds, the electrons are shared equally. In polar covalent bonds, the electrons are shared unequally, as one atom exerts a stronger force of attraction on the electrons than the other. The ability of an atom to attract a pair of electrons in a chemical bond is called its electronegativity. The difference in electronegativity between two atoms determines how polar a bond will be. In a diatomic molecule with two identical atoms, there is no difference in electronegativity, so the bond is nonpolar or pure covalent. When the electronegativity difference is very large, as is the case between metals and nonmetals, the bonding is characterized as ionic.

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.

Valence electronic structures can be visualized by drawing Lewis symbols (for atoms and monatomic ions) and Lewis structures (for molecules and polyatomic ions). Lone pairs, unpaired electrons, and single, double, or triple bonds are used to indicate where the valence electrons are located around each atom in a Lewis structure. Most structures—especially those containing second row elements—obey the octet rule, in which every atom (except H) is surrounded by eight electrons. Exceptions to the octet rule occur for odd-electron molecules (free radicals), electron-deficient molecules, and hypervalent molecules.

In a Lewis structure, formal charges can be assigned to each atom by treating each bond as if one-half of the electrons are assigned to each atom. These hypothetical formal charges are a guide to determining the most appropriate Lewis structure. A structure in which the formal charges are as close to zero as possible is preferred. Resonance occurs in cases where two or more Lewis structures with identical arrangements of atoms but different distributions of electrons can be written. The actual distribution of electrons (the resonance hybrid) is an average of the distribution indicated by the individual Lewis structures (the resonance forms).

VSEPR theory predicts the three-dimensional arrangement of atoms in a molecule. It states that valence electrons will assume an electron-pair geometry that minimizes repulsions between areas of high electron density (bonds and/or lone pairs). Molecular structure, which refers only to the placement of atoms in a molecule and not the electrons, is equivalent to electron-pair geometry only when there are no lone electron pairs around the central atom. A dipole moment measures a separation of charge. For one bond, the bond dipole moment is determined by the difference in electronegativity between the two atoms. For a molecule, the overall dipole moment is determined by both the individual bond moments and how these dipoles are arranged in the molecular structure. Polar molecules (those with an appreciable dipole moment) interact with electric fields, whereas nonpolar molecules do not.

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3.11: Exercises

1.

Does a cation gain protons to form a positive charge or does it lose electrons?

2.

Iron(III) sulfate $[\mathrm{Fe_2\,(SO_4)_3}]$ is composed of $\mathrm{Fe^{3+}}$ and $\mathrm{{SO_4}^{2-}}$ ions. Explain why a sample of iron(III) sulfate is uncharged.

3.

Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions: P, I, Mg, Cl, In, Cs, O, Pb, Co?

4.

Which of the following atoms would be expected to form negative ions in binary ionic compounds and which would be expected to form positive ions: Br, Ca, Na, N, F, Al, Sn, S, Cd?

5.

Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:

(a) P

(b) Mg

(c) Al

(d) O

(e) Cl

(f) Cs

6.

Predict the charge on the monatomic ions formed from the following atoms in binary ionic compounds:

(a) I

(b) Sr

(c) K

(d) N

(e) S

(f) In

7.

Write the electron configuration for each of the following ions:

(a) As^{3-}

(b) I^{-}

(c) Be^{2+}

(d) Cd^{2+}

(e) O^{2-}

(f) Ga^{3+}

(g) Li^{+}

(h) N^{3-}

(i) Sn^{2+}

(j) Co^{2+}

(k) Fe^{2+}

(l) As^{3+}

8.

Write the electron configuration for the monatomic ions formed from the following elements (which form the greatest concentration of monatomic ions in seawater):

(a) Cl

(b) Na

(c) Mg

(d) Ca

(e) K

(f) Br

(g) Sr

(h) F

9.

Write out the full electron configuration for each of the following atoms and for the monatomic ion found in binary ionic compounds containing the element:

(a) Al

(b) Br

(c) Sr

(d) Li

(e) As

(f) S

10.

From the labels of several commercial products, prepare a list of six ionic compounds in the products. For each compound, write the formula. (You may need to look up some formulas in a suitable reference.)

11.

Why is it incorrect to speak of a molecule of solid NaCl?

12.

What information can you use to predict whether a bond between two atoms is covalent or ionic?

13.

Predict which of the following compounds are ionic and which are covalent, based on the location of their constituent atoms in the periodic table:

(a) Cl_2CO

(b) MnO

(c) NCl_3

(d) $CoBr_2$

(e) K_2S

(f) CO

(g) CaF_2

(h) HI

(i) CaO

(j) IBr

(k) CO_2

14.

Explain the difference between a nonpolar covalent bond, a polar covalent bond, and an ionic bond.

15.

From its position in the periodic table, determine which atom in each pair is more electronegative:

(a) Br or Cl

(b) N or O

(c) S or O

(d) P or S

(e) Si or N

(f) Ba or P

(g) N or K

16.

From its position in the periodic table, determine which atom in each pair is more electronegative:

(a) N or P

(b) N or Ge

(c) S or F

(d) Cl or S

(e) H or C

(f) Se or P

(g) C or Si

17.

From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:

(a) C, F, H, N, O

(b) Br, Cl, F, H, I

(c) F, H, O, P, S

(d) Al, H, Na, O, P

(e) Ba, H, N, O, As

18.

From their positions in the periodic table, arrange the atoms in each of the following series in order of increasing electronegativity:

(a) As, H, N, P, Sb

(b) Cl, H, P, S, Si

(c) Br, Cl, Ge, H, Sr

(d) Ca, H, K, N, Si

(e) Cl, Cs, Ge, H, Sr

19.

Which atoms can bond to sulfur so as to produce a positive partial charge on the sulfur atom?

20.

Which is the most polar bond?

(a) C–C

(b) C–H

(c) N–H

(d) O–H

(e) Se–H

21.

Identify the more polar bond in each of the following pairs of bonds:

(a) HF or HCl

(b) NO or CO

(c) SH or OH

(d) PCl or SCl

(e) CH or NH

(f) SO or PO

(g) CN or NN

22.

Which of the following molecules or ions contain polar bonds?

(a) O_3

(b) S_8

(c) O_2^{2-}

(d) NO_3^-

(e) CO_2

(f) $H_2 S$

(g) BH_4^-

23.

Name the following compounds:

(a) CsCl

(b) BaO

(c) K_2S

(d) $BeCl_2$

(e) HBr

(f) AlF_3

24.

Name the following compounds:

(a) NaF

(b) Rb_2O

(c) BCl_3

(d) H_2Se

(e) P_4O_6

(f) ICl_3

25.

Write the formulas of the following compounds:

(a) rubidium bromide

(b) magnesium selenide

(c) sodium oxide

(d) calcium chloride

(e) hydrogen fluoride

(f) gallium phosphide

(g) aluminum bromide

(h) ammonium sulfate

26.

Write the formulas of the following compounds:

(a) lithium carbonate

(b) sodium perchlorate

(c) barium hydroxide

(d) ammonium carbonate

(e) sulfuric acid

(f) calcium acetate

(g) magnesium phosphate

(h) sodium sulfite

27.

Write the formulas of the following compounds:

(a) chlorine dioxide

(b) dinitrogen tetraoxide

(c) potassium phosphide

(d) silver(I) sulfide

(e) aluminum fluoride trihydrate

(f) silicon dioxide

28.

Write the formulas of the following compounds:

(a) barium chloride

(b) magnesium nitride

(c) sulfur dioxide

(d) nitrogen trichloride

(e) dinitrogen trioxide

(f) tin(IV) chloride

29.

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

(a) Cr_2O_3

(b) $FeCl_2$

(c) CrO_3

(d) $TiCl_4$

(e) $CoCl_2 \cdot 6H_2O$

(f) MoS_2

30.

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

(a) $NiCO_3$

(b) MoO_3

(c) $Co(NO_3)_2$

(d) V_2O_5

(e) MnO_2

(f) Fe_2O_3

31.

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

(a) potassium phosphate

(b) copper(II) sulfate

(c) calcium chloride

(d) titanium(IV) oxide

(e) ammonium nitrate

(f) sodium bisulfate (the common name for sodium hydrogen sulfate)

32.

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

(a) $Ca(H_2PO_4)_2$

(b) $FeSO_4$

(c) $CaCO_3$

(d) MgO

(e) $NaNO_2$

(f) KI

33.

What are the IUPAC names of the following compounds?

(a) manganese dioxide

(b) mercurous chloride (Hg_2Cl_2)

(c) ferric nitrate [$Fe(NO_3)_3$]

(d) titanium tetrachloride

(e) cupric bromide ($CuBr_2$)

34.

Write the Lewis symbols for each of the following ions:

(a) As^{3-}

(b) I^-

(c) Be^{2+}

(d) O^{2-}

(e) Ga^{3+}

(f) Li^+

(g) N^{3-}

35.

Many monatomic ions are found in seawater, including the ions formed from the following list of elements. Write the Lewis symbols for the monatomic ions formed from the following elements:

(a) Cl

(b) Na

(c) Mg

(d) Ca

(e) K

(f) Br

(g) Sr

(h) F

36.

Write the Lewis symbols of the ions in each of the following ionic compounds and the Lewis symbols of the atom from which they are formed:

(a) MgS

(b) Al_2O_3

(c) $GaCl_3$

(d) K_2O

(e) Li_3N

(f) KF

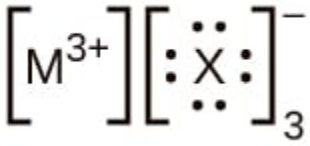
37.

In the Lewis structures listed here, M and X represent various elements in the third period of the periodic table. Write the formula of each compound using the chemical symbols of each element:

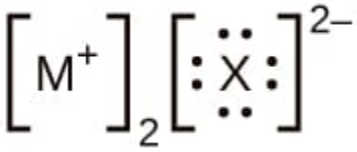
(a)



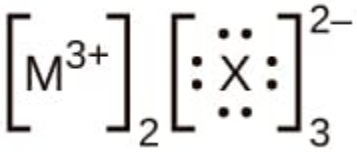
(b)



(c)



(d)



38.

Write the Lewis structure for the diatomic molecule P_2, an unstable form of phosphorus found in high-temperature phosphorus vapor.

39.

Write Lewis structures for the following:

(a) H_2

(b) HBr

(c) PCl_3

(d) SF_2

(e) H_2CCH_2

(f) HNNH

(g) H_2CNH

(h) NO^-

(i) N_2

(j) CO

(k) CN^-

40.

Write Lewis structures for the following:

(a) O_2

(b) H_2CO

(c) AsF_3

(d) ClNO

(e) $SiCl_4$

(f) H_3O^+

(g) NH_4^+

(h) BF_4^-

(i) HCCH

(j) ClCN

(k) C_2^{2+}

41.

Write Lewis structures for the following:

(a) ClF_3

(b) PCl_5

(c) BF_3

(d) PF_6^-

42.

Write Lewis structures for the following:

(a) SeF_6

(b) XeF_4

(c) $SeCl_3^+$

(d) Cl_2BBCl_2 (contains a B–B bond)

43.

Write Lewis structures for:

(a) PO_4^{3-}

(b) ICl_4^-

(c) SO_3^{2}[redacted]

(d) HONO

44.

Correct the following statement: “The bonds in solid $PbCl_2$ are ionic; the bond in a HCl molecule is covalent. Thus, all of the valence electrons in $PbCl_2$ are located on the Cl^- ions, and all of the valence electrons in a HCl molecule are shared between the H and Cl atoms.”

45.

Write Lewis structures for the following molecules or ions:

(a) SbH_3

(b) XeF_2

(c) Se_8 (a cyclic molecule with a ring of eight Se atoms)

46.

Methanol, H_3COH, is used as the fuel in some race cars. Ethanol, C_2H_5OH, is used extensively as motor fuel in Brazil. Both methanol and ethanol produce CO_2 and H_2O when they burn. Write the chemical equations for these combustion reactions using

Lewis structures instead of chemical formulas.

47.

Many planets in our solar system contain organic chemicals including methane (CH_4) and traces of ethylene (C_2H_4), ethane (C_2H_6), propyne (H_3CCCH), and diacetylene (HCCCCH). Write the Lewis structures for each of these molecules.

48.

Carbon tetrachloride was formerly used in fire extinguishers for electrical fires. It is no longer used for this purpose because of the formation of the toxic gas phosgene, Cl_2CO. Write the Lewis structures for carbon tetrachloride and phosgene.

49.

Identify the atoms that correspond to each of the following electron configurations. Then, write the Lewis symbol for the common ion formed from each atom:

(a) $1s^2 2s^2 2p^5$

(b) $1s^2 2s^2 2p^6 3s^2$

(c) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$

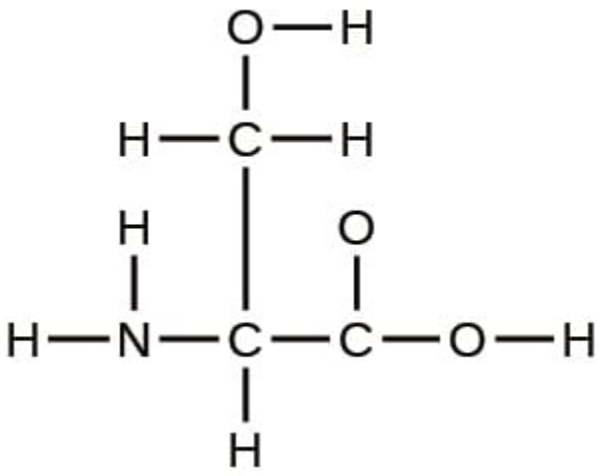
(d) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^4$

(e) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$

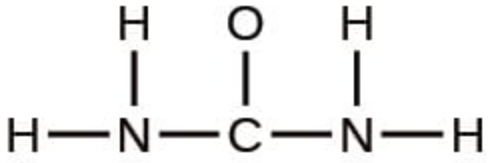
50.

The arrangement of atoms in several biologically important molecules is given here. Complete the Lewis structures of these molecules by adding multiple bonds and lone pairs. Do not add any more atoms.

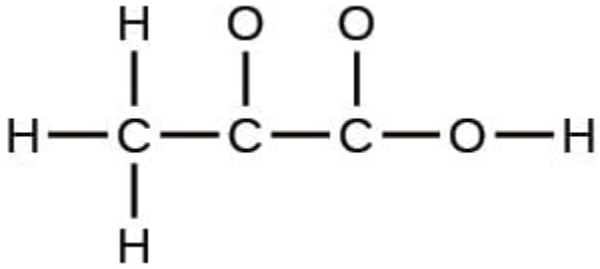
(a) the amino acid serine:



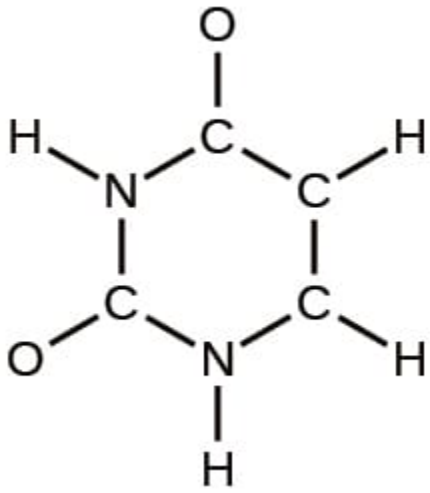
(b) urea:



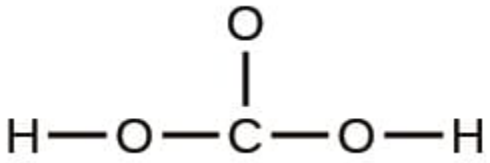
(c) pyruvic acid:



(d) uracil:



(e) carbonic acid:



51.

A compound with a molar mass of about 28 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.

52.

A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.

53.

Two arrangements of atoms are possible for a compound with a molar mass of about 45 g/mol that contains 52.2% C, 13.1% H, and 34.7% O by mass. Write the Lewis structures for the two molecules.

54.

How are single, double, and triple bonds similar? How do they differ?

55.

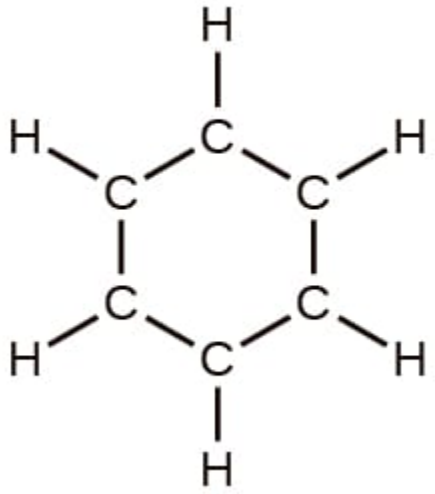
Write resonance forms that describe the distribution of electrons in each of these molecules or ions.

(a) selenium dioxide, OSeO

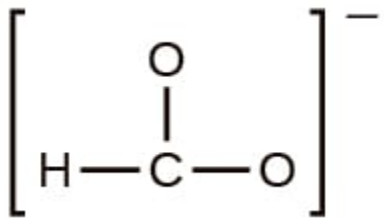
(b) nitrate ion, NO_3^-

(c) nitric acid, HNO_3 (N is bonded to an OH group and two O atoms)

(d) benzene, C_6H_6:



(e) the formate ion:



56.

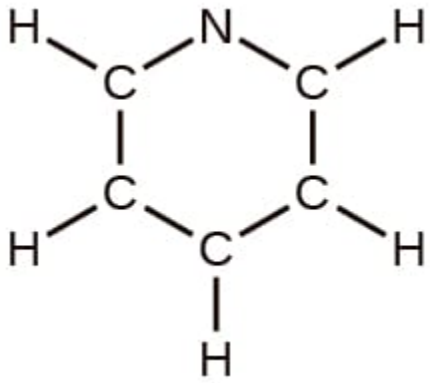
Write resonance forms that describe the distribution of electrons in each of these molecules or ions.

(a) sulfur dioxide, SO_2

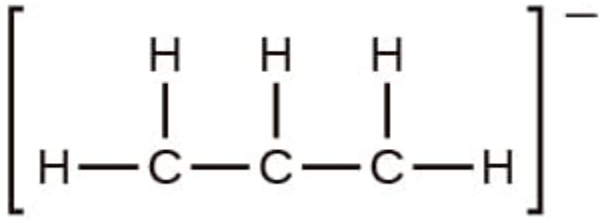
(b) carbonate ion, CO_3^{2}[redacted]

(c) hydrogen carbonate ion, HCO_3^- (C is bonded to an OH group and two O atoms)

(d) pyridine:



(e) the allyl ion:



57.

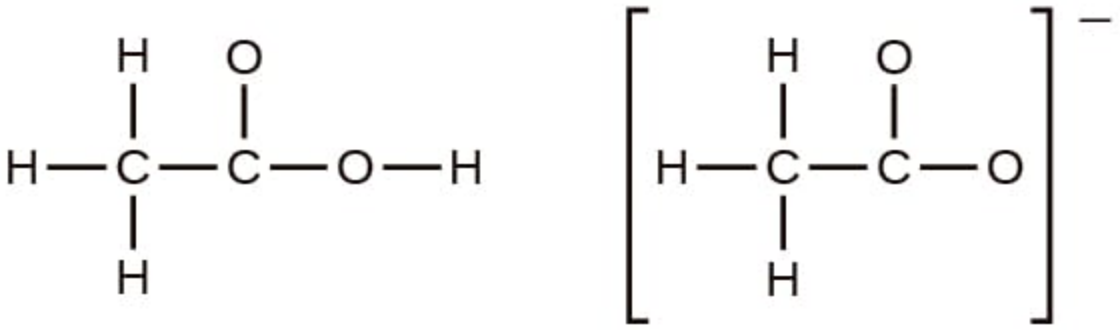
Write the resonance forms of ozone, O_3, the component of the upper atmosphere that protects the Earth from ultraviolet radiation.

58.

Sodium nitrite, which has been used to preserve bacon and other meats, is an ionic compound. Write the resonance forms of the nitrite ion, NO_2^-.

59.

In terms of the bonds present, explain why acetic acid, CH_3CO_2H, contains two distinct types of carbon-oxygen bonds, whereas the acetate ion, formed by loss of a hydrogen ion from acetic acid, only contains one type of carbon-oxygen bond. The skeleton structures of these species are shown:



60.

Write the Lewis structures for the following, and include resonance structures where appropriate. Indicate which has the strongest carbon-oxygen bond.

(a) CO_2

(b) CO

61.

Toothpastes containing sodium hydrogen carbonate (sodium bicarbonate) and hydrogen peroxide are widely used. Write Lewis structures for the hydrogen carbonate ion and hydrogen peroxide molecule, with resonance forms where appropriate.

62.

Determine the formal charge of each element in the following:

(a) HCl

(b) CF_4

(c) PCl_3

(d) PF_5

63.

Determine the formal charge of each element in the following:

(a) H_3O^+

(b) SO_4^{2}[redacted]

(c) NH_3

(d) O_2^{2-}

(e) H_2O_2

64.

Calculate the formal charge of chlorine in the molecules Cl_2, $BeCl_2$, and ClF_5.

65.

Calculate the formal charge of each element in the following compounds and ions:

(a) F_2CO

(b) NO^-

(c) BF_4^-

(d) $SnCl_3^-$

(e) H_2CCH_2

(f) ClF_3

(g) SeF_6

(h) PO_4^{3-}

66.

Draw all possible resonance structures for each of these compounds. Determine the formal charge on each atom in each of the resonance structures:

(a) O_3

(b) SO_2

(c) NO_2^-

(d) NO_3^-

67.

Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in nitrosyl chloride: ClNO or ClON?

68.

Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in hypochlorous acid: HOCl or OClH?

69.

Based on formal charge considerations, which of the following would likely be the correct arrangement of atoms in sulfur dioxide: OSO or SOO?

70.

Draw the structure of hydroxylamine, H_3NO, and assign formal charges; look up the structure. Is the actual structure consistent with the formal charges?

71.

Iodine forms a series of fluorides (listed here). Write Lewis structures for each of the four compounds and determine the formal charge of the iodine atom in each molecule:

(a) IF

(b) IF_3

(c) IF_5

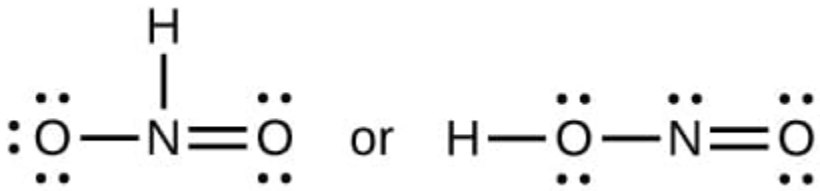
(d) IF_7

72.

Write the Lewis structure and chemical formula of the compound with a molar mass of about 70 g/mol that contains 19.7% nitrogen and 80.3% fluorine by mass, and determine the formal charge of the atoms in this compound.

73.

Which of the following structures would we expect for nitrous acid? Determine the formal charges:



74.

Sulfuric acid is the industrial chemical produced in greatest quantity worldwide. About 90 billion pounds are produced each year in the United States alone. Write the Lewis structure for sulfuric acid, H_2SO_4, which has two oxygen atoms and two OH groups bonded to the sulfur.

75.

Explain why the HOH molecule is bent, whereas the HBeH molecule is linear.

76.

What feature of a Lewis structure can be used to tell if a molecule's (or ion's) electron-pair geometry and molecular structure will be identical?

77.

Explain the difference between electron-pair geometry and molecular structure.

78.

Why is the H–N–H angle in NH_3 smaller than the H–C–H bond angle in CH_4? Why is the H–N–H angle in NH_4^+ identical to the H–C–H bond angle in CH_4?

79.

Explain how a molecule that contains polar bonds can be nonpolar.

80.

As a general rule, MX_n molecules (where M represents a central atom and X represents terminal atoms; n = 2 – 5) are polar if there is one or more lone pairs of electrons on M. NH_3 (M = N, X = H, n = 3) is an example. There are two molecular structures with lone pairs that are exceptions to this rule. What are they?

81.

Predict the electron pair geometry and the molecular structure of each of the following molecules or ions:

(a) SF_6

(b) PCl_5

(c) BeH_2

(d) CH_3^+

82.

Identify the electron pair geometry and the molecular structure of each of the following molecules or ions:

(a) IF_6^+

(b) CF_4

(c) BF_3

(d) SiF_5^-

(e) $BeCl_2$

83.

What are the electron-pair geometry and the molecular structure of each of the following molecules or ions?

(a) ClF_5

(b) ClO_2^-

(c) $TeCl_4^2$[redacted]

(d) PCl_3

(e) SeF_4

(f) PH_2^-

84.

Predict the electron pair geometry and the molecular structure of each of the following ions:

(a) H_3O^+

(b) PCl_4^-

(c) $SnCl_3^+$

(d) $BrCl_4^-$

(e) ICl_3

(f) XeF_4

(g) SF_2

85.

Identify the electron pair geometry and the molecular structure of each of the following molecules:

(a) ClNO (N is the central atom)

(b) CS_2

(c) Cl_2CO (C is the central atom)

(d) Cl_2SO (S is the central atom)

(e) SO_2F_2 (S is the central atom)

(f) XeO_2F_2 (Xe is the central atom)

(g) $ClOF_2^+$ (Cl is the central atom)

86.

Predict the electron pair geometry and the molecular structure of each of the following:

(a) IOF_5 (I is the central atom)

(b) $POCl_3$ (P is the central atom)

(c) Cl_2SeO (Se is the central atom)

(d) $ClSO^+$ (S is the central atom)

(e) F_2SO (S is the central atom)

(f) NO_2^-

(g) SiO_4^{4-}

87.

Which of the following molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?

(a) ClF_5

(b) ClO_2^-

(c) $TeCl_4^{2}$[redacted]

(d) PCl_3

(e) SeF_4

(f) PH_2^-

(g) XeF_2

88.

Which of these molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?

(a) H_3O^+

(b) PCl_4^-

(c) $SnCl_3^-$

(d) $BrCl_4^-$

(e) ICl_3

(f) XeF_4

(g) SF_2

89.

Which of the following molecules have dipole moments?

(a) CS_2

(b) SeS_2

(c) CCl_2F_2

(d) PCl_3 (P is the central atom)

(e) ClNO (N is the central atom)

90.

Identify the molecules with a dipole moment:

(a) SF_4

(b) CF_4

(c) Cl_2CCBr_2

(d) CH_3Cl

(e) H_2CO

91.

The molecule XF_3 has a dipole moment. Is X boron or phosphorus?

92.

The molecule XCl_2 has a dipole moment. Is X beryllium or sulfur?

93.

Is the Cl_2BBCl_2 molecule polar or nonpolar?

94.

There are three possible structures for PCl_2F_3 with phosphorus as the central atom. Draw them and discuss how measurements of dipole moments could help distinguish among them.

95.

Describe the molecular structure around the indicated atom or atoms:

(a) the sulfur atom in sulfuric acid, H_2SO_4 [$(HO)_2SO_2$]

(b) the chlorine atom in chloric acid, $HClO_3$ [$HOClO_2$]

(c) the oxygen atom in hydrogen peroxide, HOOH

(d) the nitrogen atom in nitric acid, HNO_3 [$HONO_2$]

(e) the oxygen atom in the OH group in nitric acid, HNO_3 [$HONO_2$]

(f) the central oxygen atom in the ozone molecule, O_3

(g) each of the carbon atoms in propyne, CH_3CCH

(h) the carbon atom in Freon, CCl_2F_2

(i) each of the carbon atoms in allene, H_2CCCH_2

96.

Draw the Lewis structures and predict the shape of each compound or ion:

(a) CO_2

(b) NO_2^-

(c) SO_3

(d) SO_3^{2-}

97.

A molecule with the formula AB_2, in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion for each shape.

98.

A molecule with the formula AB_3, in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion that has each shape.

99.

Draw the Lewis electron dot structures for these molecules, including resonance structures where appropriate:

(a) CS_3^{2-}

(b) CS_2

(c) CS

(d) predict the molecular shapes for CS_3^{2-} and CS_2 and explain how you arrived at your predictions

100.

What is the molecular structure of the stable form of FNO_2? (N is the central atom.)

101.

A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen. What is its molecular structure?

102.

Use the simulation to perform the following exercises for a two-atom molecule:

(a) Adjust the electronegativity value so the bond dipole is pointing toward B. Then determine what the electronegativity values must be to switch the dipole so that it points toward A.

(b) With a partial positive charge on A, turn on the electric field and describe what happens.

(c) With a small partial negative charge on A, turn on the electric field and describe what happens.

(d) Reset all, and then with a large partial negative charge on A, turn on the electric field and describe what happens.

103.

Use the simulation to perform the following exercises for a real molecule. You may need to rotate the molecules in three dimensions to see certain dipoles.

(a) Sketch the bond dipoles and molecular dipole (if any) for O_3. Explain your observations.

(b) Look at the bond dipoles for NH_3. Use these dipoles to predict whether N or H is more electronegative.

(c) Predict whether there should be a molecular dipole for NH_3 and, if so, in which direction it will point. Check the molecular dipole box to test your hypothesis.

104.

Use the Molecule Shape simulator to build a molecule. Starting with the central atom, click on the double bond to add one double bond. Then add one single bond and one lone pair. Rotate the molecule to observe the complete geometry. Name the electron group geometry and molecular structure and predict the bond angle. Then click the check boxes at the bottom and right of the simulator to check your answers.

105.

Use the Molecule Shape simulator to explore real molecules. On the Real Molecules tab, select H_2O. Switch between the “real” and “model” modes. Explain the difference observed.

106.

Use the Molecule Shape simulator to explore real molecules. On the Real Molecules tab, select “model” mode and S_2O. What is the model bond angle? Explain whether the “real” bond angle should be larger or smaller than the ideal model angle.

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4: ADVANCED THEORIES OF COVALENT BONDING

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4.3: Hybrid Atomic Orbitals

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4.1: Introduction

We have examined the basic ideas of bonding, showing that atoms share electrons to form molecules with stable Lewis structures and that we can predict the shapes of those molecules by valence shell electron pair repulsion (VSEPR) theory. These ideas provide an important starting point for understanding chemical bonding. But these models sometimes fall short in their abilities to predict the behavior of real substances. How can we reconcile the geometries of *s*, *p*, and *d* atomic orbitals with molecular shapes that show angles like 120° and 109.5°? Furthermore, we know that electrons and magnetic behavior are related through electromagnetic fields. Both N_2 and O_2 have fairly similar Lewis structures that contain lone pairs of electrons.

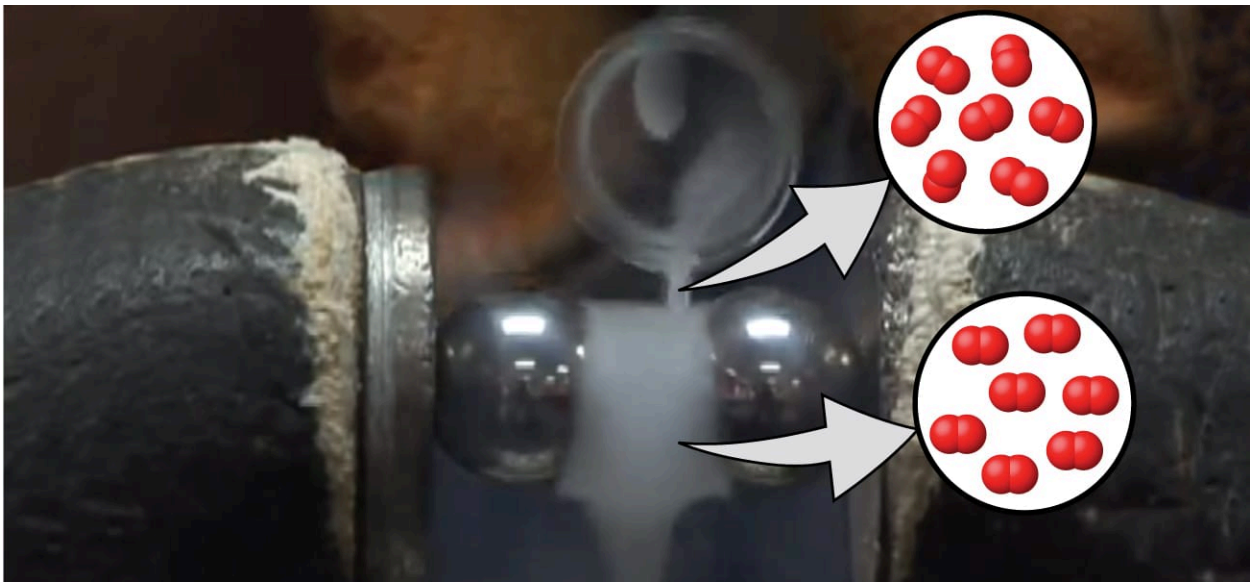


Figure 4.1.1: Oxygen molecules orient randomly most of the time, as shown in the top magnified view. However, when we pour liquid oxygen through a magnet, the molecules line up with the magnetic field, and the attraction allows them to stay suspended between the poles of the magnet where the magnetic field is strongest. Other diatomic molecules (like N_2) flow past the magnet. The detailed explanation of bonding described in this chapter allows us to understand this phenomenon. (credit: modification of work by Jefferson Lab)

Yet oxygen demonstrates very different magnetic behavior than nitrogen. We can pour liquid nitrogen through a magnetic field with no visible interactions, while liquid oxygen (shown in Figure 4.1.1) is attracted to the magnet and floats in the magnetic field. We need to understand the additional concepts of valence bond theory, orbital hybridization, and molecular orbital theory to understand these observations.



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4.2: Valence Bond Theory

Learning Objectives

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

- Describe the formation of covalent bonds in terms of atomic orbital overlap
- Define and give examples of σ and π bonds

As we know, a scientific theory is a strongly supported explanation for observed natural laws or large bodies of experimental data. For a theory to be accepted, it must explain experimental data and be able to predict behavior. For example, VSEPR theory has gained widespread acceptance because it predicts three-dimensional molecular shapes that are consistent with experimental data collected for thousands of different molecules. However, VSEPR theory does not provide an explanation of chemical bonding.

Atomic Orbital Overlap

There are successful theories that describe the electronic structure of atoms. We can use quantum mechanics to predict the specific regions around an atom where electrons are likely to be located: A spherical shape for an *s* orbital, a dumbbell shape for a *p* orbital, and so forth. However, these predictions only describe the orbitals around free atoms. When atoms bond to form molecules, atomic orbitals are not sufficient to describe the regions where electrons will be located in the molecule. A more complete understanding of electron distributions requires a model that can account for the electronic structure of molecules. One popular theory holds that a covalent bond forms when a pair of electrons is shared by two atoms and is simultaneously attracted by the nuclei of both atoms. In the following sections, we will discuss how such bonds are described by valence bond theory and hybridization.

Valence bond theory describes a covalent bond as the overlap of half-filled atomic orbitals (each containing a single electron) that yield a pair of electrons shared between the two bonded atoms. We say that orbitals on two different atoms overlap when a portion of one orbital and a portion of a second orbital occupy the same region of space. According to valence bond theory, a covalent bond results when two conditions are met: (1) an orbital on one atom overlaps an orbital on a second atom and (2) the single electrons in each orbital combine to form an electron pair. The mutual attraction between this negatively charged electron pair and the two atoms' positively charged nuclei serves to physically link the two atoms through a force we define as a covalent bond. The strength of a covalent bond depends on the extent of overlap of the orbitals involved. Orbitals that overlap extensively form bonds that are stronger than those that have less overlap.

The energy of the system depends on how much the orbitals overlap. Figure 4.2 illustrates how the sum of the energies of two hydrogen atoms (the colored curve) changes as they approach each other. When the atoms are far apart there is no overlap, and by convention we set the sum of the energies at zero. As the atoms move together, their orbitals begin to overlap. Each electron begins to feel the attraction of the nucleus in the other atom. In addition, the electrons begin to repel each other, as do the nuclei. While the atoms are still widely separated, the attractions are slightly stronger than the repulsions, and the energy of the system decreases. (A bond begins to form.) As the atoms move closer together, the overlap increases, so the attraction of the nuclei for the electrons continues to increase (as do the repulsions among electrons and between the nuclei). At some specific distance between the atoms, which varies depending on the atoms involved, the energy reaches its lowest (most stable) value. This optimum distance between the two bonded nuclei is the bond distance between the two atoms. The bond is stable because at this point, the attractive and repulsive forces combine to create the lowest possible energy configuration. If the distance between the nuclei were to decrease further, the repulsions between nuclei and the repulsions as electrons are confined in closer proximity to each other would become stronger than the attractive forces. The energy of the system would then rise (making the system destabilized), as shown at the far left of Figure 4.2.

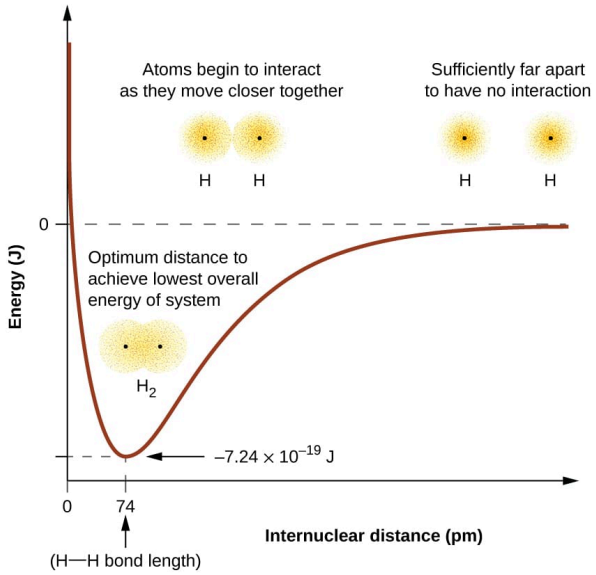


Figure 4.2 (a) The interaction of two hydrogen atoms changes as a function of distance. (b) The energy of the system changes as the atoms interact. The lowest (most stable) energy occurs at a distance of 74 pm, which is the bond length observed for the H_2 molecule.

In addition to the distance between two orbitals, the orientation of orbitals also affects their overlap (other than for two s orbitals, which are spherically symmetric). Greater overlap is possible when orbitals are oriented such that they overlap on a direct line between the two nuclei. Figure 4.3 illustrates this for two *p* orbitals from different atoms; the overlap is greater when the orbitals overlap end to end rather than at an angle.

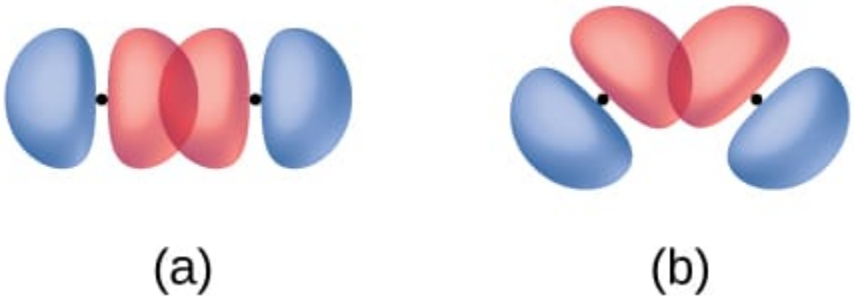


Figure 4.3 (a) The overlap of two *p* orbitals is greatest when the orbitals are directed end to end. (b) Any other arrangement results in less overlap. The dots indicate the locations of the nuclei.

The overlap of two s orbitals (as in H_2), the overlap of an s orbital and a *p* orbital (as in HCl), and the end-to-end overlap of two *p* orbitals (as in Cl_2) all produce sigma bonds (σ bonds), as illustrated in Figure 4.4. A σ bond is a covalent bond in which the electron density is concentrated in the region along the internuclear axis; that is, a line between the nuclei would pass through the center of the overlap region. Single bonds in Lewis structures are described as σ bonds in valence bond theory.

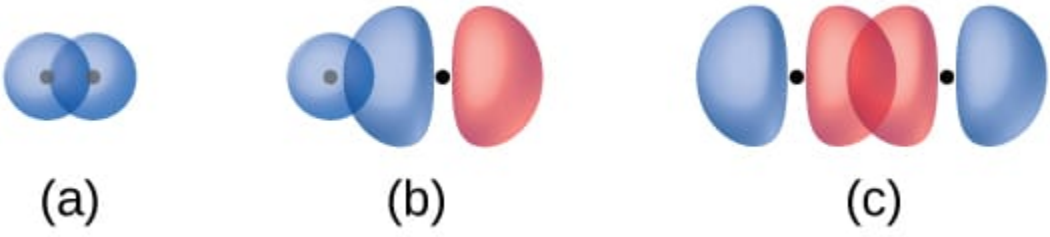


Figure 4.4 Sigma (σ) bonds form from the overlap of the following: (a) two s orbitals, (b) an s orbital and a *p* orbital, and (c) two *p* orbitals. The dots indicate the locations of the nuclei.

A pi bond (π bond) is a type of covalent bond that results from the side-by-side overlap of two *p* orbitals, as illustrated in Figure 4.5. In a π bond, the regions of orbital overlap lie on opposite sides of the internuclear axis. Along the axis itself, there is a node, that is, a plane with no probability of finding an electron.

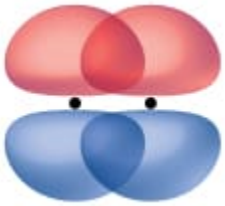
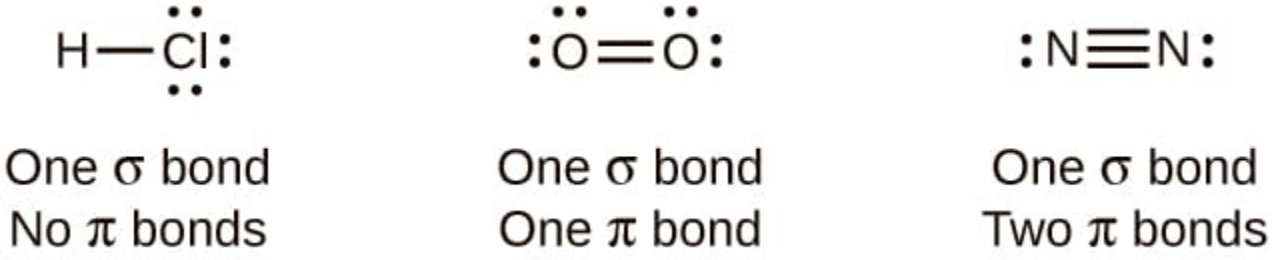


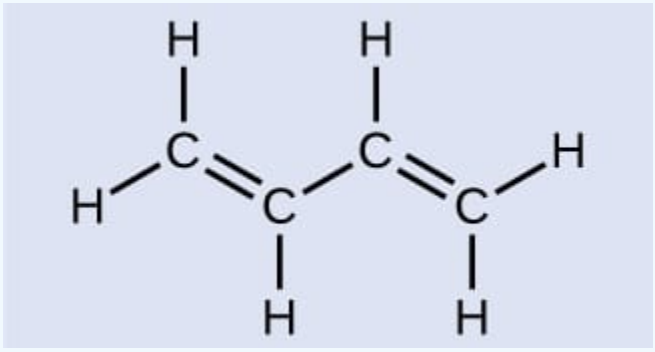
Figure 4.5 Pi (π) bonds form from the side-by-side overlap of two *p* orbitals. The dots indicate the location of the nuclei.

While all single bonds are σ bonds, multiple bonds consist of both σ and π bonds. As the Lewis structures below suggest, O_2 contains a double bond, and N_2 contains a triple bond. The double bond consists of one σ bond and one π bond, and the triple bond consists of one σ bond and two π bonds. Between any two atoms, the first bond formed will always be a σ bond, but there can only be one σ bond in any one location. In any multiple bond, there will be one σ bond, and the remaining one or two bonds will be π bonds. These bonds are described in more detail later in this chapter.



Example 4.1

Counting σ and π Bonds



Butadiene, C_4H_6, is used to make synthetic rubber. Identify the number of σ and π bonds contained in this molecule.

Solution

There are six σ C–H bonds and one σ C–C bond, for a total of seven from the single bonds. There are two double bonds that each have a π bond in addition to the σ bond. This gives a total nine σ and two π bonds overall.

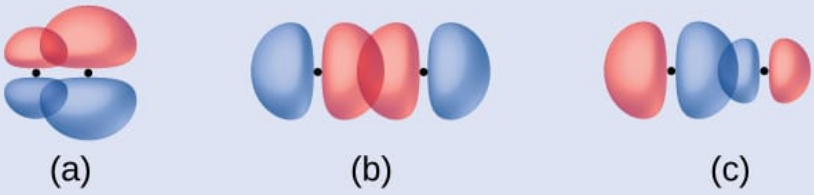
Check Your Learning

Identify each illustration as depicting a σ or π bond:

(a) side-by-side overlap of a 4*p* and a 2*p* orbital

(b) end-to-end overlap of a 4*p* and 4*p* orbital

(c) end-to-end overlap of a 4*p* and a 2*p* orbital



Answer:

(a) is a π bond with a node along the axis connecting the nuclei while (b) and (c) are σ bonds that overlap along the axis.

Dipole Moments and Ionic Character

Now that we have seen the importance of understanding the connection between the location of electrons in atoms and the properties of elements, we can expand our understanding of the connection between atoms. This will be an introduction to more advanced aspects of the chemical bond, which is the very heart of chemistry itself. With the sole exception of the noble gases, atoms by themselves do not possess the most stable possible electron configuration. That is where the concept of chemical bonding comes into its own: atoms can attain a stable configuration by exchanging electrons with another atom, resulting in the formation of ions.

Ions, in turn, can associate by charge – simple Coulombic attraction – resulting in the formation of compounds we call ionic compounds. We will look at the ionic nature of bonds first, from a simple positive-negative attraction standpoint. Just as important is that some atoms bond by sharing rather than exchanging electrons; the sharing of electrons gives rise to the covalent bond. To add just one more dimension, some chemical species are neither completely ionic nor completely covalent; these species possess a permanent dipole, and are classified as polar.

In your introductory physics course, you will likely discuss the concept of Coulombic interactions in much more rigorous detail than we will do here. We are interested primarily in the differences in properties between species that arise from their relative covalent, ionic, or polar nature – not in a rigorous model of those properties. We are concerned with the connection between potential energy and force and the relative separation (or lack of separation) between charges. We begin by defining the electric or Coulomb force as the product of the charges divided by the square of the distance between those charges:

$$F =$$

Here, Q is taken to be the fundamental constant of electron charge: one electron has a charge of 1.60218×10^{-19} C. (We will work exclusively in the SI system, so distances will be measured in meters (m)).

And as you may recall, energy is force times distance, so

$$E =$$

To illustrate the trend in attractive force, we will consider first the attractive force between two ions of single charge separated by a distance of 2*d*:

$$F = \frac{(1)(-1)}{(2d)^2} = -$$

And then the attractive force between two ions of double charge separated by a distance *d*:

$$F = \frac{(2)(-2)}{(d)^2} = -$$

The force of attraction increases with the charge and decreases with increased distance. If all matter were composed of ions that would be the end of the story, but it clearly is not. There are molecules for which the charge – either positive or negative – is

permanently concentrated more on one atom than the other. Notice we say atom, because these compounds are not composed of ions but rather of atoms sharing electrons through covalent bonds.

Bond Dipole Moments

The concept of a bond dipole moment allows us to examine the partial separation of charge between atoms. It is a simple model when applied to diatomic molecules, which will be more than sufficient for our purposes. The dipole moment of a bond is defined as the charge times the distance – charge once again being measured in multiples of the charge on an electron, or coulombs. The distance will always be in meters. Because we are considering very small charges and distances, and because it is the relative separation of charge rather than the actual value for it that we are interested in, we will introduce a new unit called the Debye, named after the physical chemist Peter Debye:

$$1\,\text{Debye (D)} = 3.336 \times 10^{-\blacksquare}\,\text{C-m} \qquad \mu =$$

The usefulness of the Debye unit will be shown by example:
For HCl, the bond dipole moment is known to be 1.08 D
For HI, the bond dipole moment is known to be 0.44 D

Comparing the two, we can see that HI is less polar than HCl, which is what we would expect based on electronegativity values.

We have now made a transition between the concept of an ionic compound and a partially ionic one. Of course, the partially ionic compound must also by definition be partially covalent.

Partial Ionic Character

The concept of the bond dipole moment helps bridge the concepts of ionic and covalent bonding. Because there is a separation of charge that is less complete than it is in an ionic bond, we can refer to polar bonds as being partially ionic in nature. In contrast to sodium chloride, hydrogen chloride shows partial charges (indicated with a delta notation) on the hydrogen and chlorine. As you would expect from the electronegativity values, hydrogen carries a partial positive charge, while chlorine carries a partial negative charge. Where do these charges come from?

It is easy to come up with the partial charges by comparing the actual dipole moments (which can be obtained experimentally, using spectroscopy) with the dipole expected in the limiting case (that is, if we were to consider the molecule ionic). The actual dipole moment is 1.03 D.

Example 4.2

Finding the Partial Ionic Character

What are the partial charges of an HCl molecule, whose bond length is 0.127 nm?

Solution

The bond dipole moment is $(1.60218 \times 10^{-\blacksquare}\text{C})\left(0.127 \times 10^{-9}\text{m}\right)$ or $2.03 \times 10^{-\blacksquare}$C-m. Converted to D, this is $(2.03 \times 10^{-\blacksquare}\text{C-m})\left(\frac{1\,\text{Debye}}{3.336\times10^{-\blacksquare}\text{C-m}}\right)$ or 6.09 D. Were HCl completely ionic, this would be its molecular dipole moment. To get the partial ionic character, we divide the experimentally measured bond moment by this limiting value: $\%\text{ionic character} = \frac{\mu_{\text{exp}}}{\blacksquare} \times 100\% = \frac{(1.03\ \ \text{D}}{(6.09\ \ \text{D})} \times 100\% = 17\%$. This means the bond is about 17% ionic – or, put another way, the positive charge in H is +0.17 and the partial negative charge on chlorine, –0.17.

Check Your Learning

Repeat the calculation for HI, which has a dipole moment of 0.42 D and a bond length of 0.161 nm.

Answer: Calculated 7.73, percent 5.43

What does the result suggest about the relative polarity of the HI bond vs. that of the HCl bond? Does the calculated dipole and percent ionic character reconcile with the difference in electronegativity between Cl and I?

The electron configuration of an atom or ion is key to understanding the chemical behavior of an element. The atoms that make up the element combine in various ways, ranging from the mostly ionic (NaCl) to the partially ionic (HCl) to what we will call purely covalent. At the most fundamental level, all chemical bonds involve electrons, and a significant percentage of chemical and physical properties can be explained by considering the location and separation of charge in a species. By understanding the structure of matter at the atomic level, we can begin to build an understanding of the behavior of matter at both the microscopic and macroscopic levels.

An understanding of dipoles and partial ionic character is fundamental to understanding the interactions between particles, which we will examine in the chapter on liquids and solids. These intermolecular forces become important in the liquid and solid states of matter.

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4.3: Hybrid Atomic Orbitals

Learning Objectives

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

- Explain the concept of atomic orbital hybridization
- Determine the hybrid orbitals associated with various molecular geometries

Thinking in terms of overlapping atomic orbitals is one way for us to explain how chemical bonds form in diatomic molecules. However, to understand how molecules with more than two atoms form stable bonds, we require a more detailed model. As an example, let us consider the water molecule, in which we have one oxygen atom bonding to two hydrogen atoms. Oxygen has the electron configuration $1s^2 2s^2 2p^4$, with two unpaired electrons (one in each of the two 2*p* orbitals). Valence bond theory would predict that the two O–H bonds form from the overlap of these two 2*p* orbitals with the 1s orbitals of the hydrogen atoms. If this were the case, the bond angle would be 90°, as shown in Figure 4.3.1, because *p* orbitals are perpendicular to each other. Experimental evidence shows that the bond angle is 104.5°, not 90°. The prediction of the valence bond theory model does not match the real-world observations of a water molecule; a different model is needed.

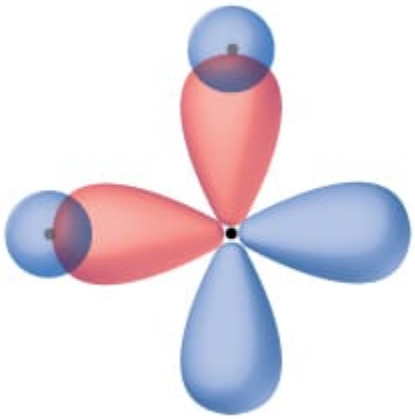


Figure 4.3.1: The hypothetical overlap of two of the 2*p* orbitals on an oxygen atom (red) with the 1s orbitals of two hydrogen atoms (blue) would produce a bond angle of 90°. This is not consistent with experimental evidence.[1]

Quantum-mechanical calculations suggest why the observed bond angles in H_2O differ from those predicted by the overlap of the 1s orbital of the hydrogen atoms with the 2*p* orbitals of the oxygen atom. The mathematical expression known as the wave function, ψ, contains information about each orbital and the wavelike properties of electrons in an isolated atom. When atoms are bound together in a molecule, the wave functions combine to produce new mathematical descriptions that have different shapes. This process of combining the wave functions for atomic orbitals is called **hybridization** and is mathematically accomplished by the *linear combination of atomic orbitals*, LCAO, (a technique that we will encounter again later). The new orbitals that result are called **hybrid orbitals**. The valence orbitals in an *isolated* oxygen atom are a 2*s* orbital and three 2*p* orbitals. The valence orbitals in an oxygen atom in a water molecule differ; they consist of four equivalent hybrid orbitals that point approximately toward the corners of a tetrahedron (Figure 4.3.2). Consequently, the overlap of the O and H orbitals should result in a tetrahedral bond angle (109.5°). The observed angle of 104.5° is experimental evidence for which quantum-mechanical calculations give a useful explanation: Valence bond theory must include a hybridization component to give accurate predictions.

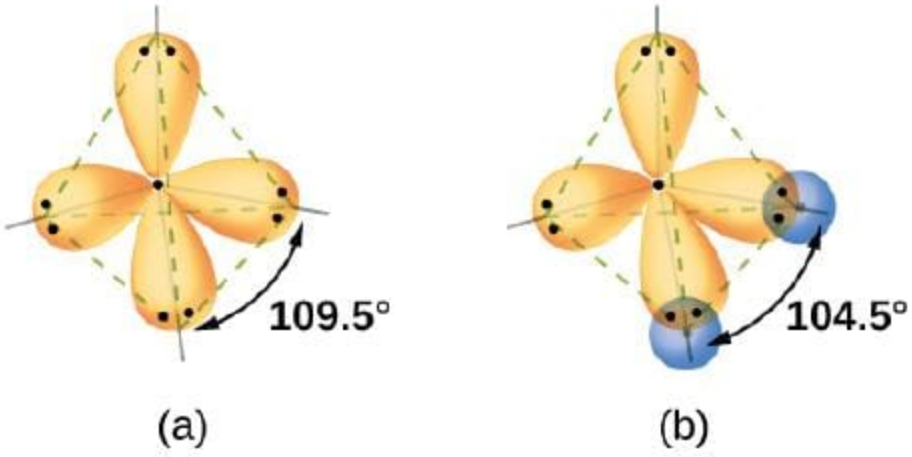


Figure 4.3.2: (a) A water molecule has four regions of electron density, so VSEPR theory predicts a tetrahedral arrangement of hybrid orbitals. (b) Two of the hybrid orbitals on oxygen contain lone pairs, and the other two overlap with the 1s orbitals of hydrogen atoms to form the O–H bonds in H_2O. This description is more consistent with the experimental structure.

The following ideas are important in understanding hybridization:

1. Hybrid orbitals do not exist in isolated atoms. They are formed only in covalently bonded atoms.
2. Hybrid orbitals have shapes and orientations that are very different from those of the atomic orbitals in isolated atoms.
3. A set of hybrid orbitals is generated by combining atomic orbitals. The number of hybrid orbitals in a set is equal to the number of atomic orbitals that were combined to produce the set.
4. All orbitals in a set of hybrid orbitals are equivalent in shape and energy.
5. The type of hybrid orbitals formed in a bonded atom depends on its electron-pair geometry as predicted by the VSEPR theory.
6. Hybrid orbitals overlap to form σ bonds. Unhybridized orbitals overlap to form π bonds.

In the following sections, we shall discuss the common types of hybrid orbitals.

sp Hybridization

The beryllium atom in a gaseous $BeCl_2$ molecule is an example of a central atom with no lone pairs of electrons in a linear arrangement of three atoms. There are two regions of valence electron density in the $BeCl_2$ molecule that correspond to the two covalent Be–Cl bonds. To accommodate these two electron domains, two of the Be atom's four valence orbitals will mix to yield two hybrid orbitals. This hybridization process involves mixing of the valence *s* orbital with one of the valence *p* orbitals to yield two equivalent ***sp* hybrid orbitals** that are oriented in a linear geometry (Figure 4.3.3). In this figure, the set of *sp* orbitals appears similar in shape to the original *p* orbital, but there is an important difference. The number of atomic orbitals combined always equals the number of hybrid orbitals formed. The *p* orbital is one orbital that can hold up to two electrons. The *sp* set is two equivalent orbitals that point 180° from each other. The two electrons that were originally in the *s* orbital are now distributed to the two *sp* orbitals, which are half filled. In gaseous $BeCl_2$, these half-filled hybrid orbitals will overlap with orbitals from the chlorine atoms to form two identical σ bonds.

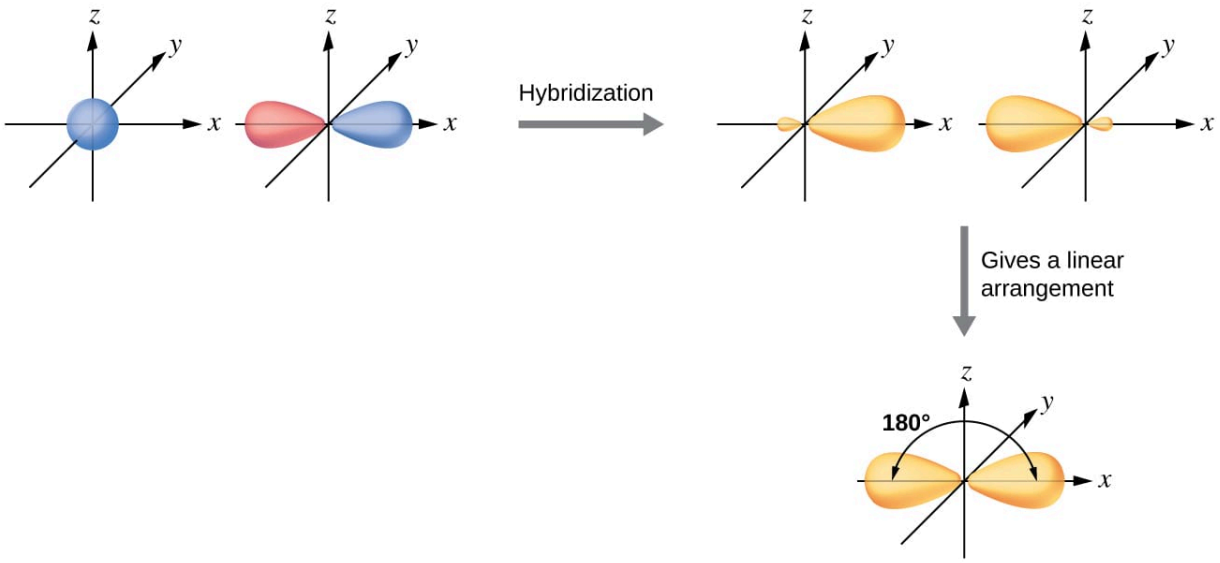


Figure 4.3.3: Hybridization of an s orbital (blue) and a *p* orbital (red) of the same atom produces two *sp* hybrid orbitals (yellow). Each hybrid orbital is oriented primarily in just one direction. Note that each *sp* orbital contains one lobe that is significantly larger than the other. The set of two *sp* orbitals are oriented at 180°, which is consistent with the geometry for two domains.

We illustrate the electronic differences in an isolated Be atom and in the bonded Be atom in the orbital energy-level diagram in Figure 4.3.4. These diagrams represent each orbital by a horizontal line (indicating its energy) and each electron by an arrow. Energy increases toward the top of the diagram. We use one upward arrow to indicate one electron in an orbital and two arrows (up and down) to indicate two electrons of opposite spin.

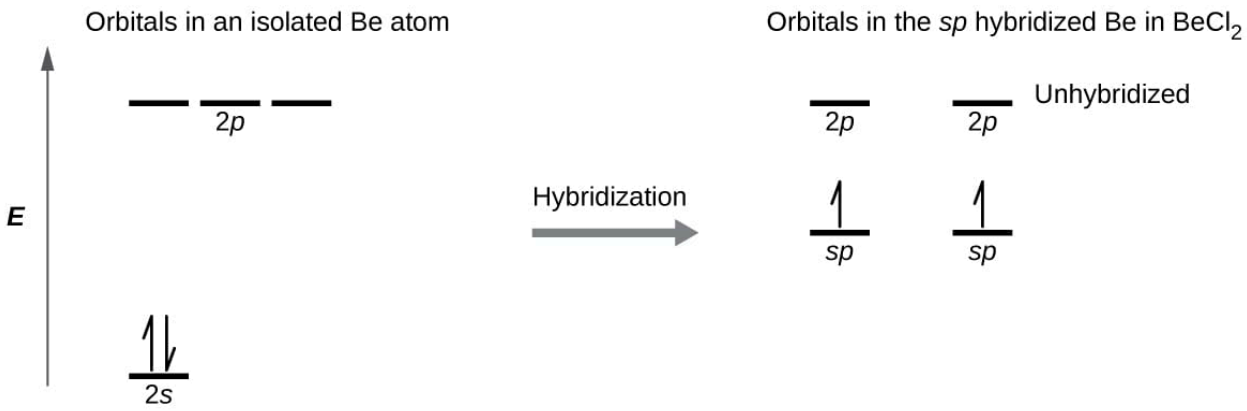


Figure 4.3.4: This orbital energy-level diagram shows the *sp* hybridized orbitals on Be in the linear $BeCl_2$ molecule. Each of the two *sp* hybrid orbitals holds one electron and is thus half filled and available for bonding via overlap with a Cl 3*p* orbital.

When atomic orbitals hybridize, the valence electrons occupy the newly created orbitals. The Be atom had two valence electrons, so each of the *sp* orbitals gets one of these electrons. Each of these electrons pairs up with the unpaired electron on a chlorine atom when a hybrid orbital and a chlorine orbital overlap during the formation of the Be–Cl bonds.

Any central atom surrounded by just two regions of valence electron density in a molecule will exhibit *sp* hybridization. Other examples include the mercury atom in the linear $HgCl_2$ molecule, the zinc atom in $Zn(CH_3)_2$, which contains a linear C–Zn–C arrangement, and the carbon atoms in HCCH and CO_2.

Link to Learning

Check out the University of Wisconsin-Oshkosh website to learn about visualizing hybrid orbitals in three dimensions.

sp^2 Hybridization

The valence orbitals of a central atom surrounded by three regions of electron density consist of a set of three **sp^2 hybrid orbitals** and one unhybridized *p* orbital. This arrangement results from sp^2 hybridization, the mixing of one s orbital and two *p* orbitals to produce three identical hybrid orbitals oriented in a trigonal planar geometry (Figure 4.3.5).

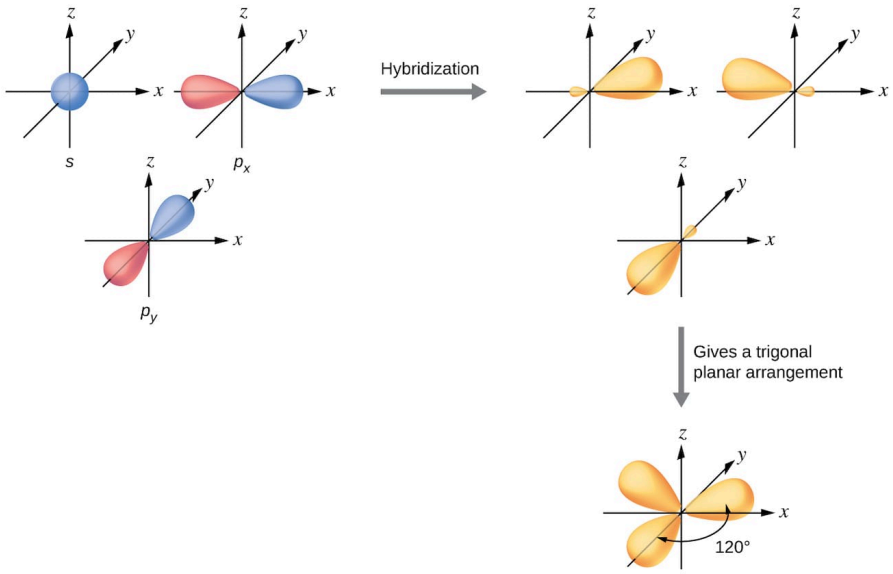


Figure 4.3.5: The hybridization of an s orbital (blue) and two *p* orbitals (red) produces three equivalent sp^2 hybridized orbitals (yellow) oriented at 120° with respect to each other. The remaining unhybridized *p* orbital is not shown here, but is located along the z axis.

Although quantum mechanics yields the "plump" orbital lobes as depicted in Figure 4.3.5, sometimes for clarity these orbitals are drawn thinner and without the minor lobes, as in Figure 4.3.6, to avoid obscuring other features of a given illustration. We will use these "thinner" representations whenever the true view is too crowded to easily visualize.

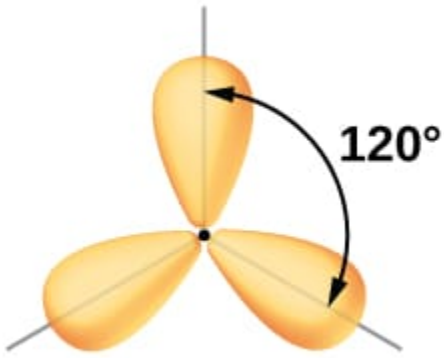


Figure 4.3.6: This alternate way of drawing the trigonal planar sp^2 hybrid orbitals is sometimes used in more crowded figures.

The observed structure of the borane molecule, BH_3, suggests sp^2 hybridization for boron in this compound. The molecule is trigonal planar, and the boron atom is involved in three bonds to hydrogen atoms (Figure 4.3.7). We can illustrate the comparison of orbitals and electron distribution in an isolated boron atom and in the bonded atom in BH_3 as shown in the orbital energy level diagram in Figure 4.3.8. We redistribute the three valence electrons of the boron atom in the three sp^2 hybrid orbitals, and each boron electron pairs with a hydrogen electron when B–H bonds form.

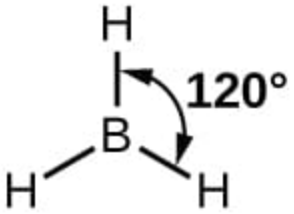


Figure 4.3.7: BH_3 is an electron-deficient molecule with a trigonal planar structure.

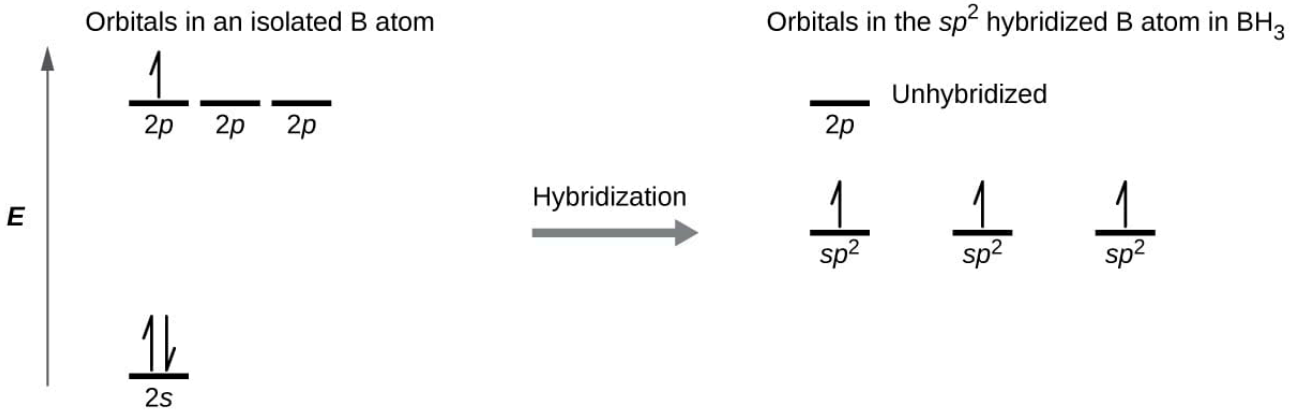


Figure 4.3.8: In an isolated B atom, there are one 2*s* and three 2*p* valence orbitals. When boron is in a molecule with three regions of electron density, three of the orbitals hybridize and create a set of three sp^2 orbitals and one unhybridized 2*p* orbital. The three half-filled hybrid orbitals each overlap with an orbital from a hydrogen atom to form three σ bonds in BH_3.

Any central atom surrounded by three regions of electron density will exhibit sp^2 hybridization. This includes molecules with a lone pair on the central atom, such as ClNO (Figure 4.3.9), or molecules with two single bonds and a double bond connected to the central atom, as in formaldehyde, CH_2O, and ethene, H_2CCH_2.

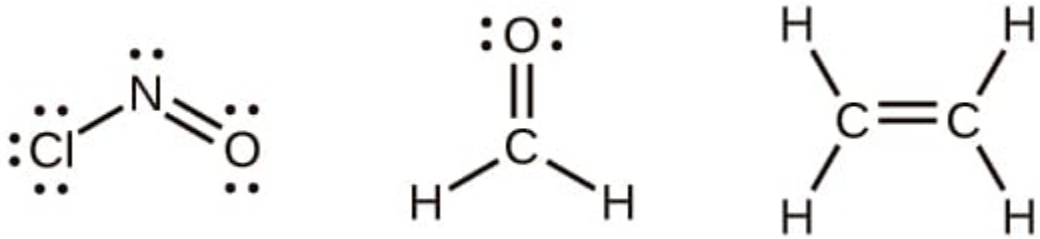


Figure 4.3.9: The central atom(s) in each of the structures shown contain three regions of electron density and are sp^2 hybridized. As we know from the discussion of VSEPR theory, a region of electron density contains all of the electrons that point in one direction. A lone pair, an unpaired electron, a single bond, or a multiple bond would each count as one region of electron density.

sp^3 Hybridization

The valence orbitals of an atom surrounded by a tetrahedral arrangement of bonding pairs and lone pairs consist of a set of four **sp^3 hybrid orbitals**. The hybrids result from the mixing of one *s* orbital and all three *p* orbitals that produces four identical sp^3 hybrid orbitals (Figure 4.3.10). Each of these hybrid orbitals points toward a different corner of a tetrahedron.

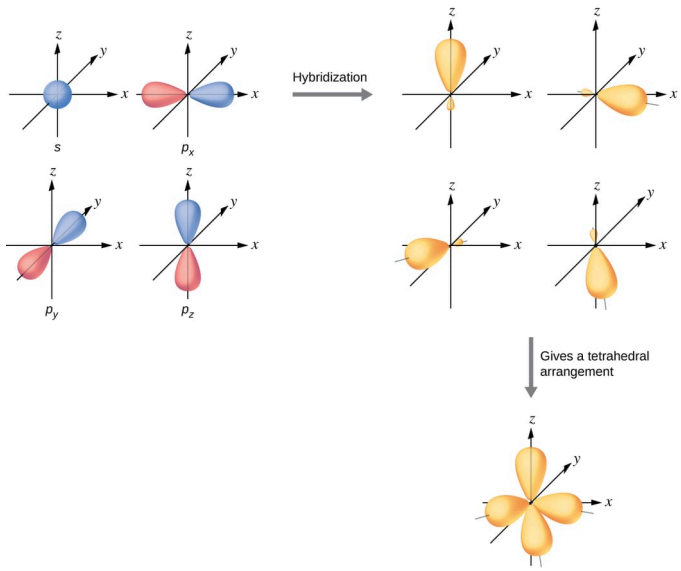


Figure 4.3.10: The hybridization of an s orbital (blue) and three *p* orbitals (red) produces four equivalent sp^3 hybridized orbitals (yellow) oriented at 109.5° with respect to each other.

A molecule of methane, CH_4, consists of a carbon atom surrounded by four hydrogen atoms at the corners of a tetrahedron. The carbon atom in methane exhibits sp^3 hybridization. We illustrate the orbitals and electron distribution in an isolated carbon atom and in the bonded atom in CH_4 in Figure 4.3.11. The four valence electrons of the carbon atom are distributed equally in the hybrid orbitals, and each carbon electron pairs with a hydrogen electron when the C–H bonds form.

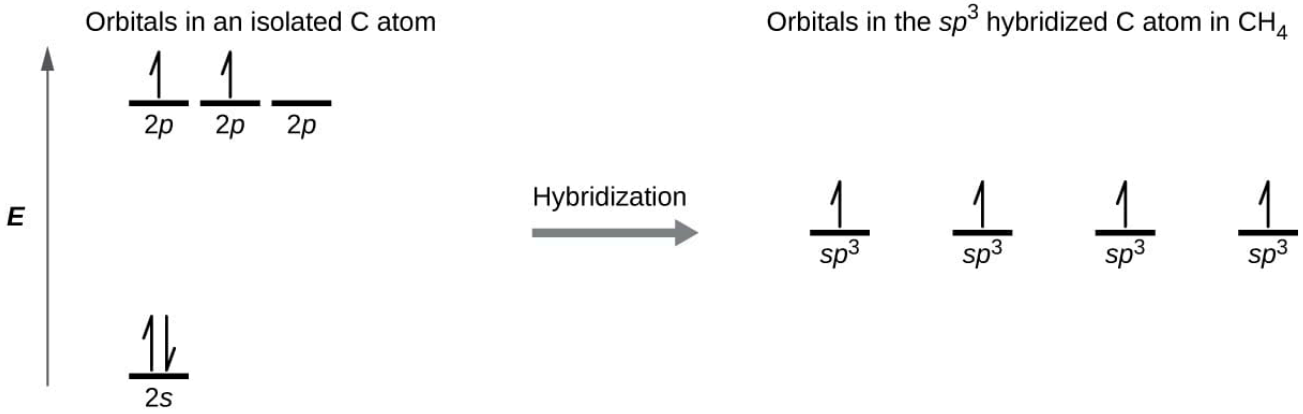


Figure 4.3.11: The four valence atomic orbitals from an isolated carbon atom all hybridize when the carbon bonds in a molecule like CH_4 with four regions of electron density. This creates four equivalent sp^3 hybridized orbitals. Overlap of each of the hybrid orbitals with a hydrogen orbital creates a C–H σ bond.

In a methane molecule, the 1s orbital of each of the four hydrogen atoms overlaps with one of the four sp^3 orbitals of the carbon atom to form a sigma (σ) bond. This results in the formation of four strong, equivalent covalent bonds between the carbon atom and each of the hydrogen atoms to produce the methane molecule, CH_4.

The structure of ethane, C_2H_6, is similar to that of methane in that each carbon in ethane has four neighboring atoms arranged at the corners of a tetrahedron—three hydrogen atoms and one carbon atom (Figure 4.3.12). However, in ethane an sp^3 orbital of one carbon atom overlaps end to end with an sp^3 orbital of a second carbon atom to form a σ bond between the two carbon atoms. Each of the remaining sp^3 hybrid orbitals overlaps with an s orbital of a hydrogen atom to form carbon–hydrogen σ bonds. The structure and overall outline of the bonding orbitals of ethane are shown in Figure 4.3.12. The orientation of the two CH_3 groups is not fixed relative to each other. Experimental evidence shows that rotation around σ bonds occurs easily.

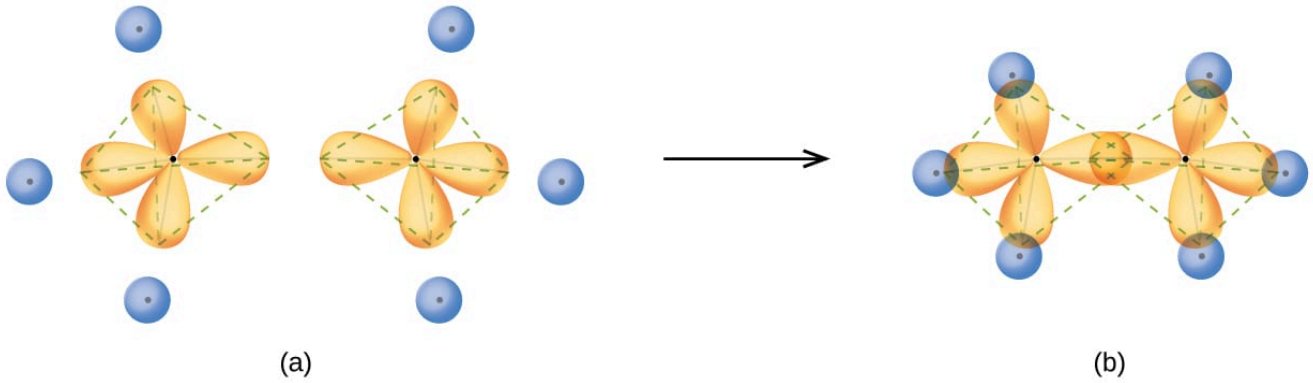


Figure 4.3.12: (a) In the ethane molecule, C_2H_6, each carbon has four sp^3 orbitals. (b) These four orbitals overlap to form seven σ bonds.

An sp^3 hybrid orbital can also hold a lone pair of electrons. For example, the nitrogen atom in ammonia is surrounded by three bonding pairs and a lone pair of electrons directed to the four corners of a tetrahedron. The nitrogen atom is sp^3 hybridized with one hybrid orbital occupied by the lone pair.

The molecular structure of water is consistent with a tetrahedral arrangement of two lone pairs and two bonding pairs of electrons. Thus we say that the oxygen atom is sp^3 hybridized, with two of the hybrid orbitals occupied by lone pairs and two by bonding pairs. Since lone pairs occupy more space than bonding pairs, structures that contain lone pairs have bond angles slightly distorted from the ideal. Perfect tetrahedra have angles of 109.5°, but the observed angles in ammonia (107.3°) and water (104.5°) are slightly smaller. Other examples of sp^3 hybridization include CCl_4, PCl_3, and NCl_3.

sp^3d and sp^3d^2 Hybridization

To describe the five bonding orbitals in a trigonal bipyramidal arrangement, we must use five of the valence shell atomic orbitals (the s orbital, the three *p* orbitals, and one of the *d* orbitals), which gives five **sp^3d hybrid orbitals**. With an octahedral arrangement of six hybrid orbitals, we must use six valence shell atomic orbitals (the s orbital, the three *p* orbitals, and two of the *d* orbitals in its valence shell), which gives six **sp^3d^2 hybrid orbitals**. These hybridizations are only possible for atoms that have *d* orbitals in their valence subshells (that is, not those in the first or second period).

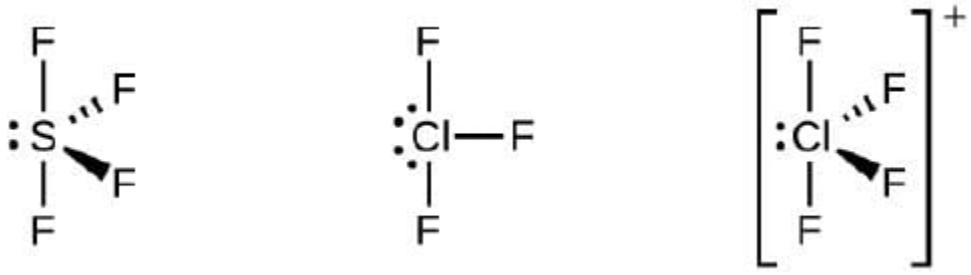


Figure 4.3.13: The three compounds pictured exhibit sp^3d hybridization in the central atom and a trigonal bipyramid form. SF_4 and have one lone pair of electrons on the central atom, and ClF_3 has two lone pairs giving it the T-shape shown.

In a molecule of phosphorus pentachloride, PCl_5, there are five P–Cl bonds (thus five pairs of valence electrons around the phosphorus atom) directed toward the corners of a trigonal bipyramid. We use the 3*s* orbital, the three 3*p* orbitals, and one of the 3*d* orbitals to form the set of five sp^3d hybrid orbitals (Figure 4.3.14) that are involved in the P–Cl bonds. Other atoms that exhibit sp^3d hybridization include the sulfur atom in SF_4 and the chlorine atoms in ClF_3 and in (The electrons on fluorine atoms are omitted for clarity.)

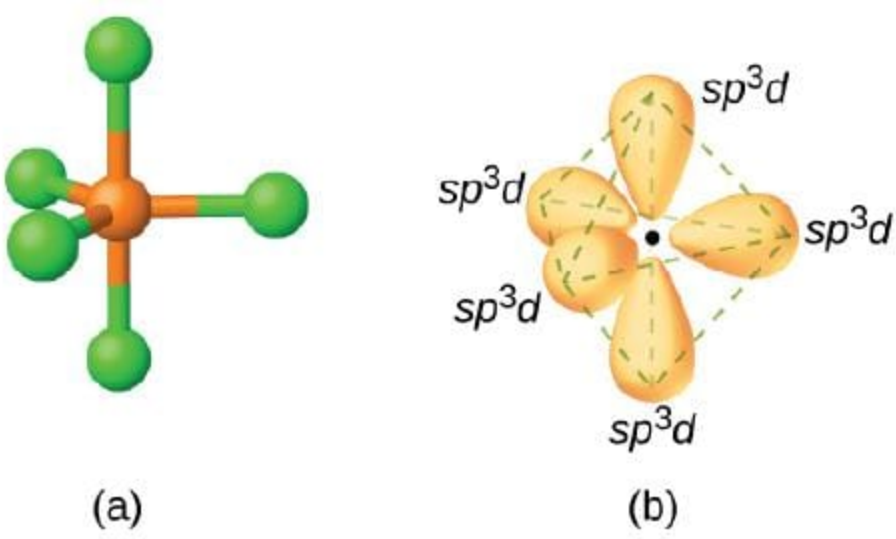


Figure 4.3.14: (a) The five regions of electron density around phosphorus in PCl_5 require five hybrid sp^3d orbitals. (b) These orbitals combine to form a trigonal bipyramidal structure with each large lobe of the hybrid orbital pointing at a vertex. As before, there are also small lobes pointing in the opposite direction for each orbital (not shown for clarity).

The sulfur atom in sulfur hexafluoride, SF_6, exhibits sp^3d^2 hybridization. A molecule of sulfur hexafluoride has six bonding pairs of electrons connecting six fluorine atoms to a single sulfur atom. There are no lone pairs of electrons on the central atom. To bond six fluorine atoms, the 3s orbital, the three 3*p* orbitals, and two of the 3*d* orbitals form six equivalent sp^3d^2 hybrid orbitals, each directed toward a different corner of an octahedron. Other atoms that exhibit sp^3d^2 hybridization include the phosphorus atom in the iodine atom in the interhalogens IF_5, and the xenon atom in XeF_4.

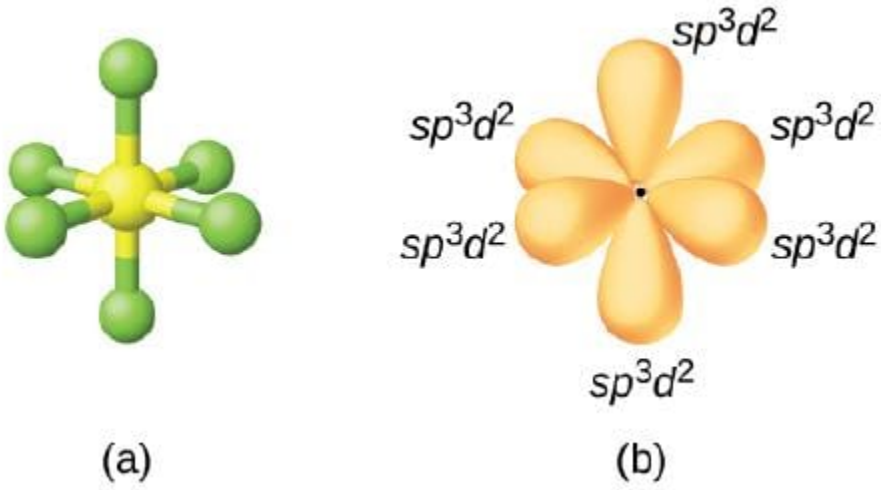


Figure 4.3.15: (a) Sulfur hexafluoride, SF_6, has an octahedral structure that requires sp^3d^2 hybridization. (b) The six sp^3d^2 orbitals form an octahedral structure around sulfur. Again, the minor lobe of each orbital is not shown for clarity.

Assignment of Hybrid Orbitals to Central Atoms

The hybridization of an atom is determined based on the number of regions of electron density that surround it. The geometrical arrangements characteristic of the various sets of hybrid orbitals are shown in Figure 4.3.16. These arrangements are identical to those of the electron-pair geometries predicted by VSEPR theory. VSEPR theory predicts the shapes of molecules, and hybrid orbital theory provides an explanation for how those shapes are formed. To find the hybridization of a central atom, we can use the following guidelines:

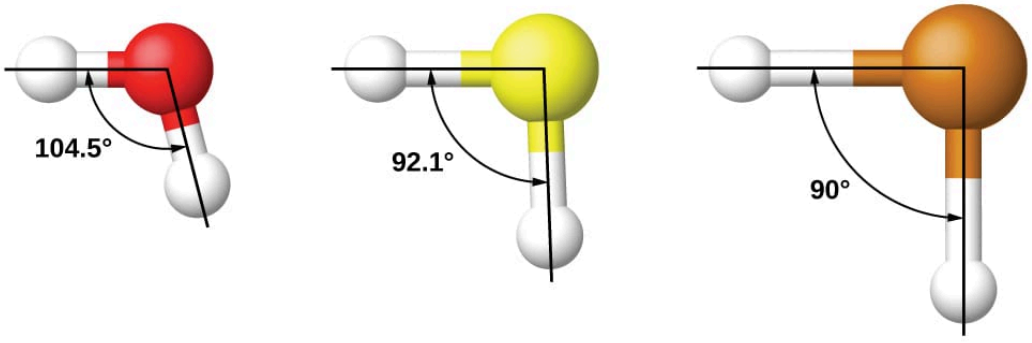
1. Determine the Lewis structure of the molecule.

2. Determine the number of regions of electron density around an atom using VSEPR theory, in which single bonds, multiple bonds, radicals, and lone pairs each count as one region.
3. Assign the set of hybridized orbitals from Figure 4.3.16 that corresponds to this geometry.

Regions of Electron Density	Arrangement		Hybridization	
2		linear	*sp*	180°
3		trigonal planar	sp^2	120°
4		tetrahedral	sp^3	109.5°
5		trigonal bipyramidal	sp^3d	90°, 120°
6		octahedral	sp^3d^2	90°, 90°

Figure 4.3.16: The shapes of hybridized orbital sets are consistent with the electron-pair geometries. For example, an atom surrounded by three regions of electron density is sp^2 hybridized, and the three sp^2 orbitals are arranged in a trigonal planar fashion.

It is important to remember that hybridization was devised to rationalize experimentally observed molecular geometries. The model works well for molecules containing small central atoms, in which the valence electron pairs are close together in space. However, for larger central atoms, the valence-shell electron pairs are farther from the nucleus, and there are fewer repulsions. Their compounds exhibit structures that are often not consistent with VSEPR theory, and hybridized orbitals are not necessary to explain the observed data. For example, we have discussed the H–O–H bond angle in H_2O, 104.5°, which is more consistent with sp^3 hybrid orbitals (109.5°) on the central atom than with 2*p* orbitals (90°). Sulfur is in the same group as oxygen, and H_2S has a similar Lewis structure. However, it has a much smaller bond angle (92.1°), which indicates much less hybridization on sulfur than oxygen. Continuing down the group, tellurium is even larger than sulfur, and for H_2Te, the observed bond angle (90°) is consistent with overlap of the 5*p* orbitals, without invoking hybridization. We invoke hybridization where it is necessary to explain the observed structures.

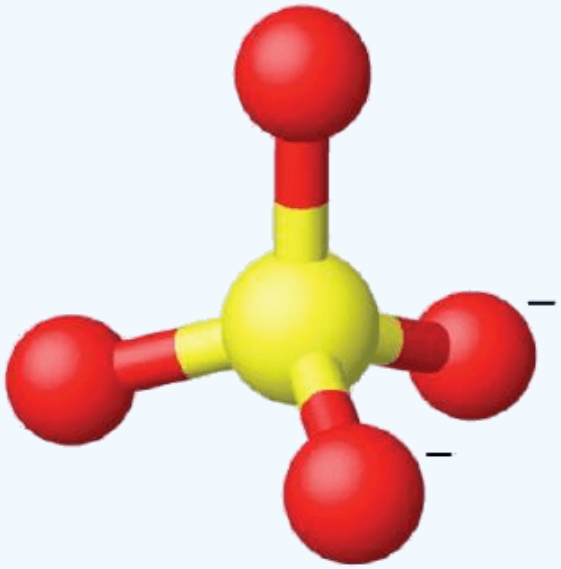


Example 4.3.1: Assigning Hybridization

Ammonium sulfate is important as a fertilizer. What is the hybridization of the sulfur atom in the sulfate ion,

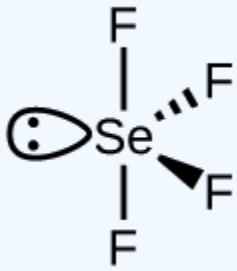
Solution

The Lewis structure of sulfate shows there are four regions of electron density. The hybridization is sp^3.



Exercise 4.3.1

What is the hybridization of the selenium atom in SeF_4?



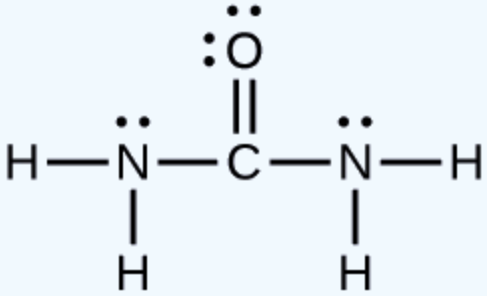
Answer available at the end of this section.

Example 4.3.2: Assigning Hybridization

Urea, $NH_2C(O)NH_2$, is sometimes used as a source of nitrogen in fertilizers. What is the hybridization of the carbon atom in urea?

Solution

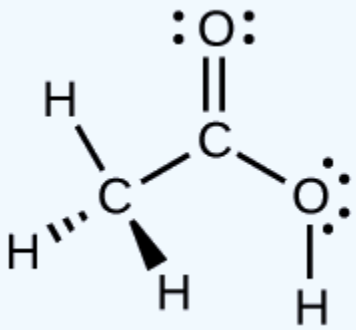
The Lewis structure of urea is



The carbon atom is surrounded by three regions of electron density, positioned in a trigonal planar arrangement. The hybridization in a trigonal planar electron pair geometry is sp^2 (Figure 4.3.16), which is the hybridization of the carbon atom in urea.

Exercise 4.3.1

Acetic acid, $H_3CC(O)OH$, is the molecule that gives vinegar its odor and sour taste. What is the hybridization of the two carbon atoms in acetic acid?



Answer available at the end of this section.

Footnotes

- 1Note that orbitals may sometimes be drawn in an elongated “balloon” shape rather than in a more realistic “plump” shape in order to make the geometry easier to visualize.

Answers

Exercise 4.3.1

The selenium atom is sp^3d hybridized.

Exercise 4.3.1

$H_3\underline{C}$, sp^3; $\underline{C}(O)OH$, sp^2

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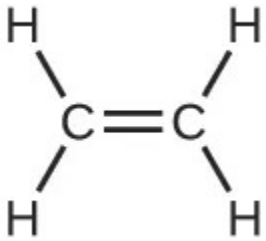
4.4: Multiple Bonds formed between Hybridized Atoms

Learning Objectives

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

- Describe multiple covalent bonding in terms of atomic orbital overlap
- Relate the concept of resonance to π-bonding and electron delocalization

The hybrid orbital model appears to account well for the geometry of molecules involving single covalent bonds. Is it also capable of describing molecules containing double and triple bonds? We have already discussed that multiple bonds consist of σ and π bonds. Next we can consider how we visualize these components and how they relate to hybrid orbitals. The Lewis structure of ethene, C_2H_4, shows us that each carbon atom is surrounded by one other carbon atom and two hydrogen atoms.



The three bonding regions form a trigonal planar electron-pair geometry. Thus we expect the σ bonds from each carbon atom are formed using a set of sp^2 hybrid orbitals that result from hybridization of two of the 2*p* orbitals and the 2*s* orbital (Figure 4.4.1).

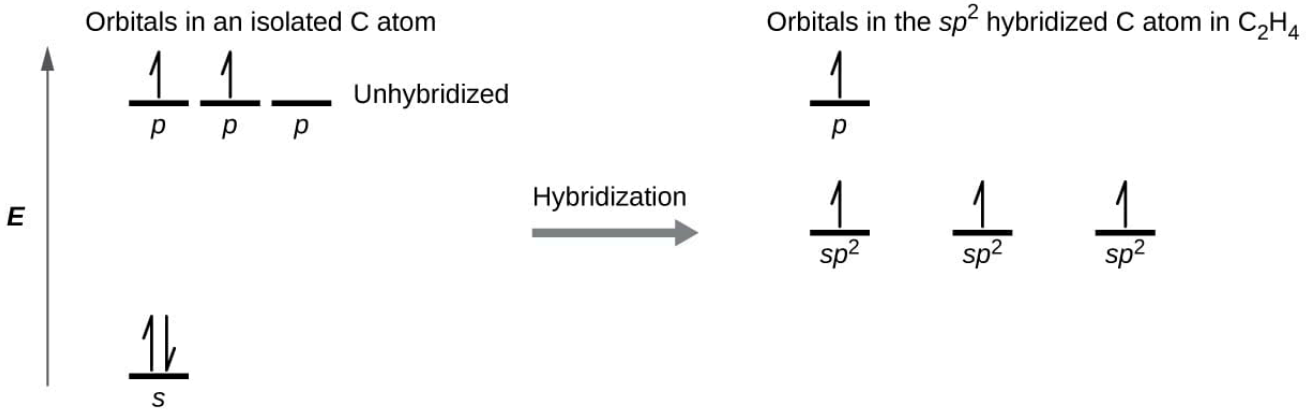


Figure 4.4.1: In ethene, each carbon atom is sp^2 hybridized, and the sp^2 orbitals and the *p* orbital are singly occupied. The hybrid orbitals overlap to form σ bonds, while the *p* orbitals on each carbon atom overlap to form a π bond.

These orbitals form the C–H single bonds and the σ bond in the Figure 4.4.2. The π bond in the C=C double bond results from the overlap of the third (remaining) 2p orbital on each carbon atom that is not involved in hybridization. This unhybridized p orbital (lobes shown in red and blue in Figure 4.4.2) is perpendicular to the plane of the sp2 hybrid orbitals. Thus the unhybridized 2p orbitals overlap in a side-by-side fashion, above and below the internuclear axis (Figure 4.4.2) and form a π bond.

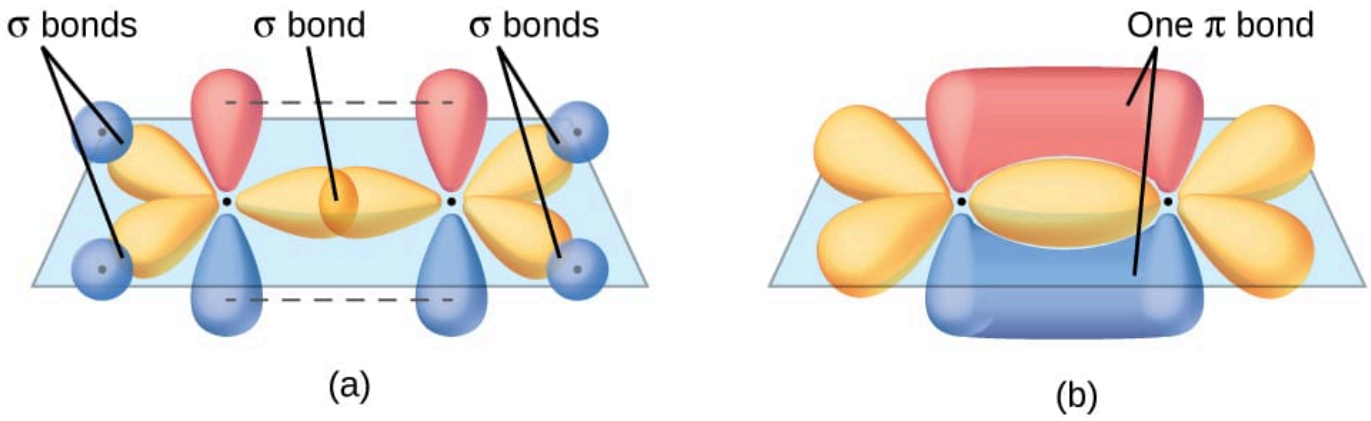


Figure 4.4.2: In the ethene molecule, C_2H_4, there are (a) five σ bonds. One C–C σ bond results from overlap of sp^2 hybrid orbitals on the carbon atom with one sp^2 hybrid orbital on the other carbon atom. Four C–H bonds result from the overlap between the C atoms' sp^2 orbitals with *s* orbitals on the hydrogen atoms. (b) The π bond is formed by the side-by-side overlap of the two unhybridized *p* orbitals in the two carbon atoms. The two lobes of the π bond are above and below the plane of the σ system.

In an ethene molecule, the four hydrogen atoms and the two carbon atoms are all in the same plane. If the two planes of sp^2 hybrid orbitals tilted relative to each other, the *p* orbitals would not be oriented to overlap efficiently to create the π bond. The planar configuration for the ethene molecule occurs because it is the most stable bonding arrangement. This is a significant difference between σ and π bonds; rotation around single (σ) bonds occurs easily because the end-to-end orbital overlap does not depend on the relative orientation of the orbitals on each atom in the bond. In other words, rotation around the internuclear axis does not change the extent to which the σ bonding orbitals overlap because the bonding electron density is symmetric about the axis. Rotation about the internuclear axis is much more difficult for multiple bonds; however, this would drastically alter the off-axis overlap of the π bonding orbitals, essentially breaking the π bond.

In molecules with *sp* hybrid orbitals, two unhybridized *p* orbitals remain on the atom (Figure 4.4.3). We find this situation in acetylene, $\mathrm{H{-}C{\equiv}C{-}H}$ (Figure 4.4.4), The remaining sp orbitals form σ bonds with hydrogen atoms. The two unhybridized *p* orbitals per carbon are positioned such that they overlap side by side and, hence, form two π bonds. The two carbon atoms of acetylene are thus bound together by one σ bond and two π bonds, giving a triple bond.

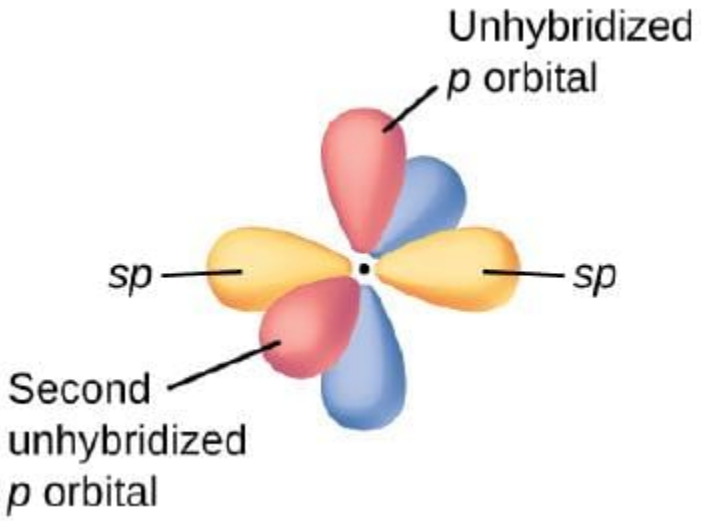


Figure 4.4.3: Diagram of the two linear *sp* hybrid orbitals of a carbon atom, which lie in a straight line, and the two unhybridized *p* orbitals at perpendicular angles.

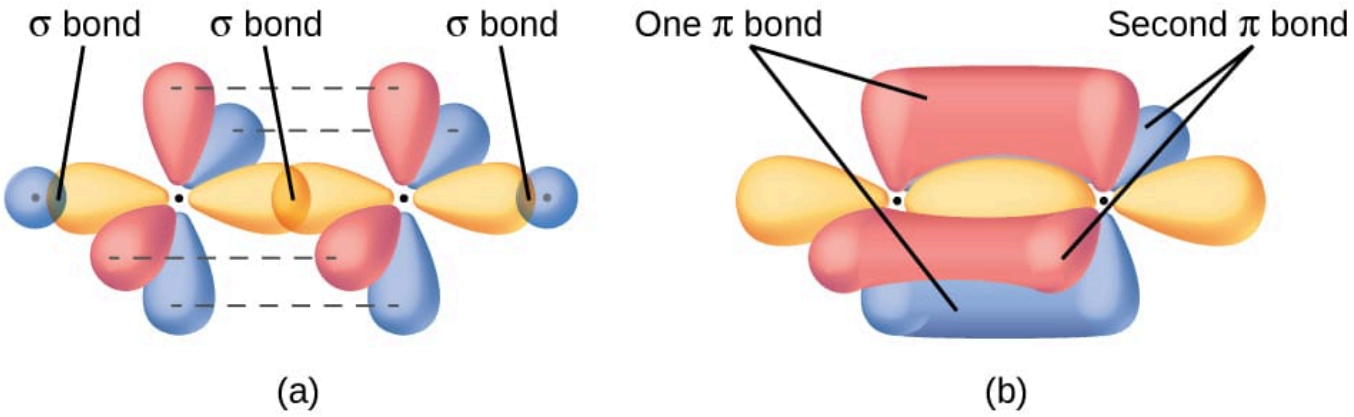


Figure 4.4.4: (a) In the acetylene molecule, C_2H_2, there are two C–H σ bonds and a triple bond involving one C–C σ bond and two C–C π bonds. The dashed lines, each connecting two lobes, indicate the side-by-side overlap of the four unhybridized *p* orbitals. (b) This shows the overall outline of the bonds in C_2H_2. The two lobes of each of the π bonds are positioned across from each other around the line of the C–C σ bond.

Hybridization involves only σ bonds, lone pairs of electrons, and single unpaired electrons (radicals). Structures that account for these features describe the correct hybridization of the atoms. However, many structures also include resonance forms. Remember that resonance forms occur when various arrangements of π bonds are possible. Since the arrangement of π bonds involves only the unhybridized orbitals, resonance does not influence the assignment of hybridization.

For example, molecule benzene has two resonance forms (Figure 4.4.5). We can use either of these forms to determine that each of the carbon atoms is bonded to three other atoms with no lone pairs, so the correct hybridization is sp^2. The electrons in the unhybridized *p* orbitals form π bonds. Neither resonance structure completely describes the electrons in the π bonds. They are not located in one position or the other, but in reality are delocalized throughout the ring. Valence bond theory does not easily address delocalization. Bonding in molecules with resonance forms is better described by molecular orbital theory. (See the next module.)

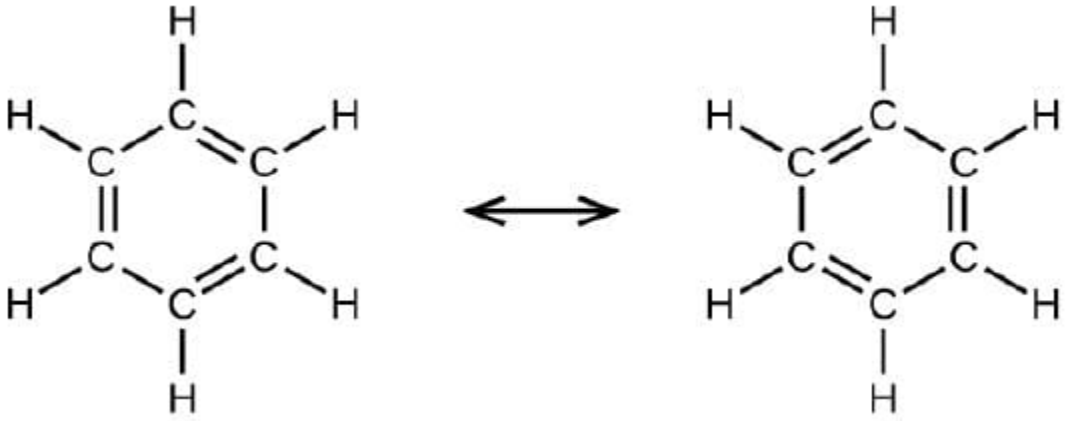


Figure 4.4.5: Each carbon atom in benzene, C_6H_6, is sp^2 hybridized, independently of which resonance form is considered. The electrons in the π bonds are not located in one set of *p* orbitals or the other, but rather delocalized throughout the molecule.

Example 4.4.1: Assignment of Hybridization Involving Resonance

Some acid rain results from the reaction of sulfur dioxide with atmospheric water vapor, followed by the formation of sulfuric acid. Sulfur dioxide, SO_2, is a major component of volcanic gases as well as a product of the combustion of sulfur-containing coal. What is the hybridization of the S atom in SO_2?

Solution

The resonance structures of SO_2 are



The sulfur atom is surrounded by two bonds and one lone pair of electrons in either resonance structure. Therefore, the electron-pair geometry is trigonal planar, and the hybridization of the sulfur atom is sp^2.

Exercise 4.4.1

Another acid in acid rain is nitric acid, HNO_3, which is produced by the reaction of nitrogen dioxide, NO_2, with atmospheric water vapor. What is the hybridization of the nitrogen atom in NO_2? (Note: the lone electron on nitrogen occupies a hybridized orbital just as a lone pair would.)

Answer available at the end of this section.

Answers

Exercise 4.4.1

sp^2

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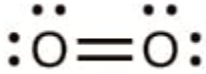
4.5: Molecular Orbital Theory

Learning Objectives

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

- Outline the basic quantum-mechanical approach to deriving molecular orbitals from atomic orbitals
- Describe traits of bonding and antibonding molecular orbitals
- Calculate bond orders based on molecular electron configurations
- Write molecular electron configurations for first- and second-row diatomic molecules
- Relate these electron configurations to the molecules' stabilities and magnetic properties

For almost every covalent molecule that exists, we can now draw the Lewis structure, predict the electron-pair geometry, predict the molecular geometry, and come close to predicting bond angles. However, one of the most important molecules we know, the oxygen molecule O_2, presents a problem with respect to its Lewis structure. We would write the following Lewis structure for O_2:



This electronic structure adheres to all the rules governing Lewis theory. There is an O=O double bond, and each oxygen atom has eight electrons around it. However, this picture is at odds with the magnetic behavior of oxygen. By itself, O_2 is not magnetic, but it is attracted to magnetic fields. Thus, when we pour liquid oxygen past a strong magnet, it collects between the poles of the magnet and defies gravity. Such attraction to a magnetic field is called **paramagnetism**, and it arises in molecules that have unpaired electrons. And yet, the Lewis structure of O_2 indicates that all electrons are paired. How do we account for this discrepancy?

Magnetic susceptibility measures the force experienced by a substance in a magnetic field. When we compare the weight of a sample to the weight measured in a magnetic field (Figure 4.5.1), paramagnetic samples that are attracted to the magnet will appear heavier because of the force exerted by the magnetic field. We can calculate the number of unpaired electrons based on the increase in weight.

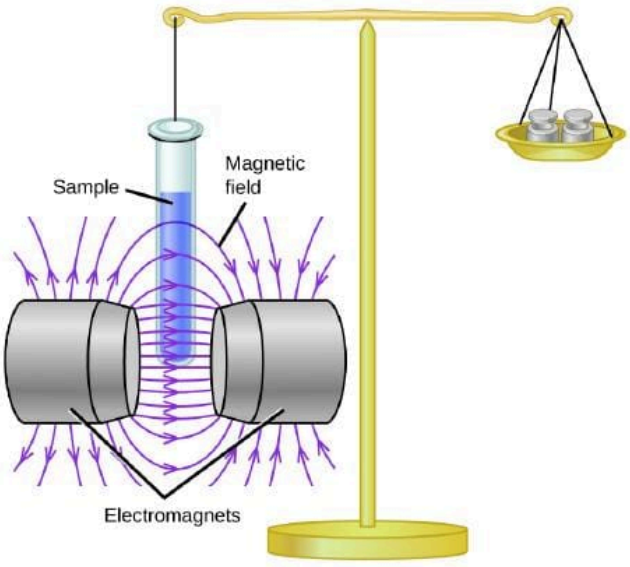


Figure 4.5.1: A Gouy balance compares the mass of a sample in the presence of a magnetic field with the mass with the electromagnet turned off to determine the number of unpaired electrons in a sample.

Experiments show that each O_2 molecule has two unpaired electrons. The Lewis-structure model does not predict the presence of these two unpaired electrons. Unlike oxygen, the apparent weight of most molecules decreases slightly in the presence of an inhomogeneous magnetic field. Materials in which all of the electrons are paired are diamagnetic and weakly repel a magnetic field. Paramagnetic and diamagnetic materials do not act as permanent magnets. Only in the presence of an applied magnetic field do they demonstrate attraction or repulsion.

Link to Learning

Water, like most molecules, contains all paired electrons. Living things contain a large percentage of water, so they demonstrate diamagnetic behavior. If you place a frog near a sufficiently large magnet, it will levitate. You can see videos of diamagnetic floating frogs, strawberries, and more.

Molecular orbital theory (MO theory) provides an explanation of chemical bonding that accounts for the paramagnetism of the oxygen molecule. It also explains the bonding in a number of other molecules, such as violations of the octet rule and more molecules with more complicated bonding (beyond the scope of this text) that are difficult to describe with Lewis structures. Additionally, it provides a model for describing the energies of electrons in a molecule and the probable location of these electrons. Unlike valence bond theory, which uses hybrid orbitals that are assigned to one specific atom, MO theory uses the combination of atomic orbitals to yield molecular orbitals that are *delocalized* over the entire molecule rather than being localized on its constituent atoms. MO theory also helps us understand why some substances are electrical conductors, others are semiconductors, and still others are insulators. Table $4.5.1$ summarizes the main points of the two complementary bonding theories. Both theories provide different, useful ways of describing molecular structure.

Molecular orbital theory describes the distribution of electrons in molecules in much the same way that the distribution of electrons in atoms is described using atomic orbitals. Using quantum mechanics, the behavior of an electron in a molecule is still described by a wave function, Ψ, analogous to the behavior in an atom. Just like electrons around isolated atoms, electrons around atoms in molecules are limited to discrete (quantized) energies. The region of space in which a valence electron in a molecule is likely to be found is called a molecular orbital (Ψ^2). Like an atomic orbital, a molecular orbital is full when it contains two electrons with opposite spin.

We will consider the molecular orbitals in molecules composed of two identical atoms (H_2 or Cl_2, for example). Such molecules are called homonuclear diatomic molecules. In these diatomic molecules, several types of molecular orbitals occur.

The mathematical process of combining atomic orbitals to generate molecular orbitals is called the **linear combination of atomic orbitals** (LCAO). The wave function describes the wavelike properties of an electron. Molecular orbitals are combinations of atomic orbital wave functions. Combining waves can lead to constructive interference, in which peaks line up with peaks, or destructive interference, in which peaks line up with troughs (Figure $4.5.2$). In orbitals, the waves are three dimensional, and they combine with in-phase waves producing regions with a higher probability of electron density and out-of-phase waves producing nodes, or regions of no electron density.

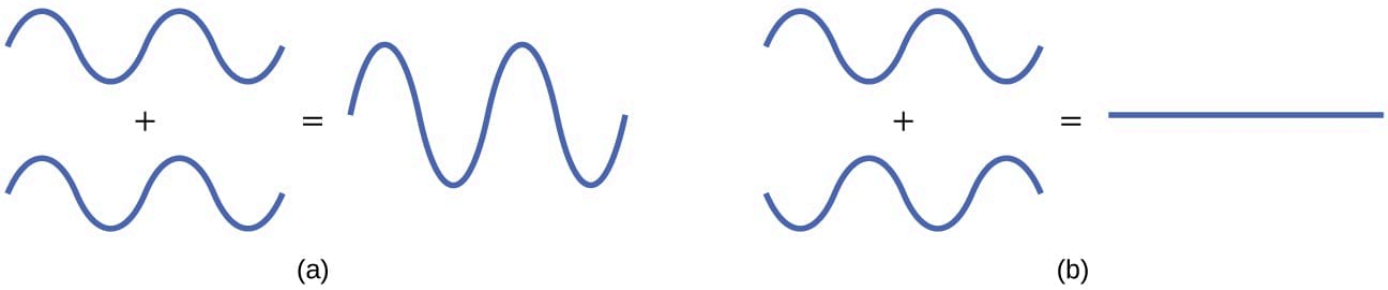


Figure $4.5.2$: (a) When in-phase waves combine, constructive interference produces a wave with greater amplitude. (b) When out-of-phase waves combine, destructive interference produces a wave with less (or no) amplitude.

There are two types of molecular orbitals that can form from the overlap of two atomic *s* orbitals on adjacent atoms. The two types are illustrated in Figure $4.5.3$. The in-phase combination produces a lower energy σ_s molecular orbital (read as "sigma-s") in which most of the electron density is directly between the nuclei. The out-of-phase addition (which can also be thought of as subtracting the wave functions) produces a higher energy molecular orbital (read as "sigma-s-star") molecular orbital in which there is a node between the nuclei. The asterisk signifies that the orbital is an antibonding orbital. Electrons in a σ_s orbital are

attracted by both nuclei at the same time and are more stable (of lower energy) than they would be in the isolated atoms. Adding electrons to these orbitals creates a force that holds the two nuclei together, so we call these orbitals bonding orbitals. Electrons in the orbitals are located well away from the region between the two nuclei. The attractive force between the nuclei and these electrons pulls the two nuclei apart. Hence, these orbitals are called antibonding orbitals. Electrons fill the lower-energy bonding orbital before the higher-energy antibonding orbital, just as they fill lower-energy atomic orbitals before they fill higher-energy atomic orbitals.

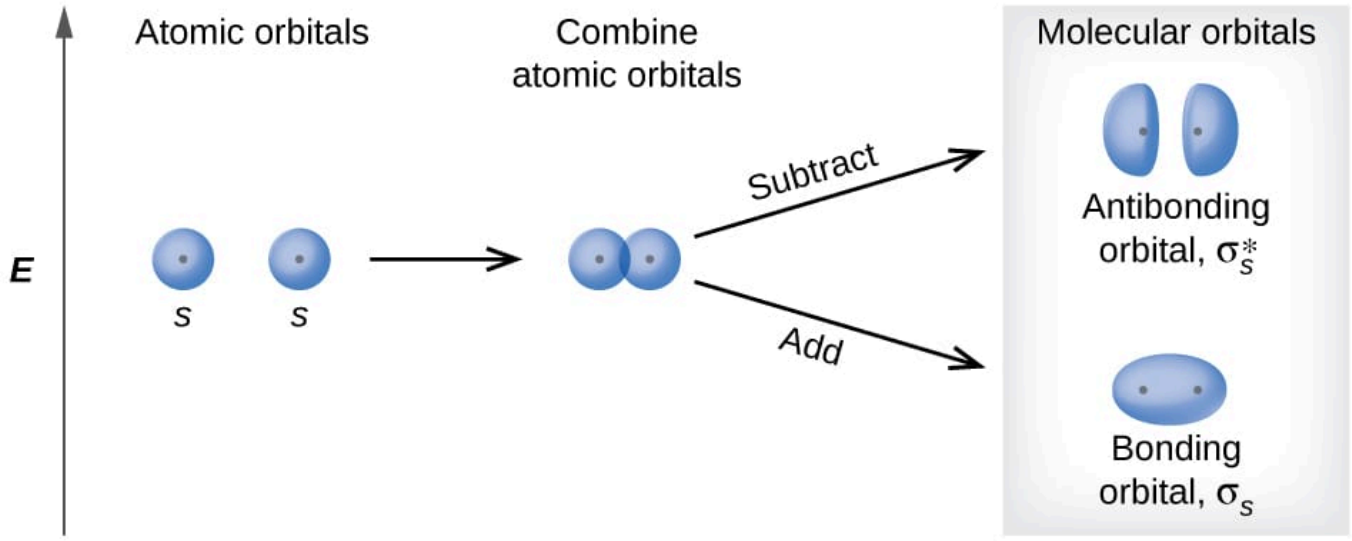


Figure 4.5.3: Sigma (σ) and sigma-star (σ*) molecular orbitals are formed by the combination of two s atomic orbitals. The dots (·) indicate the locations of nuclei.

Link to Learning

You can watch animations visualizing the calculated atomic orbitals combining to form various molecular orbitals at the Orbitron website.

In *p* orbitals, the wave function gives rise to two lobes with opposite phases, analogous to how a two-dimensional wave has both parts above and below the average. We indicate the phases by shading the orbital lobes different colors. When orbital lobes of the same phase overlap, constructive wave interference increases the electron density. When regions of opposite phase overlap, the destructive wave interference decreases electron density and creates nodes. When *p* orbitals overlap end to end, they create σ and σ* orbitals (Figure 4.5.4). If two atoms are located along the *x*-axis in a Cartesian coordinate system, the two p_x orbitals overlap end to end and form σ_{px} (bonding) and (antibonding) (read as "sigma-p-x" and "sigma-p-x star," respectively). Just as with s-orbital overlap, the asterisk indicates the orbital with a node between the nuclei, which is a higher-energy, antibonding orbital.

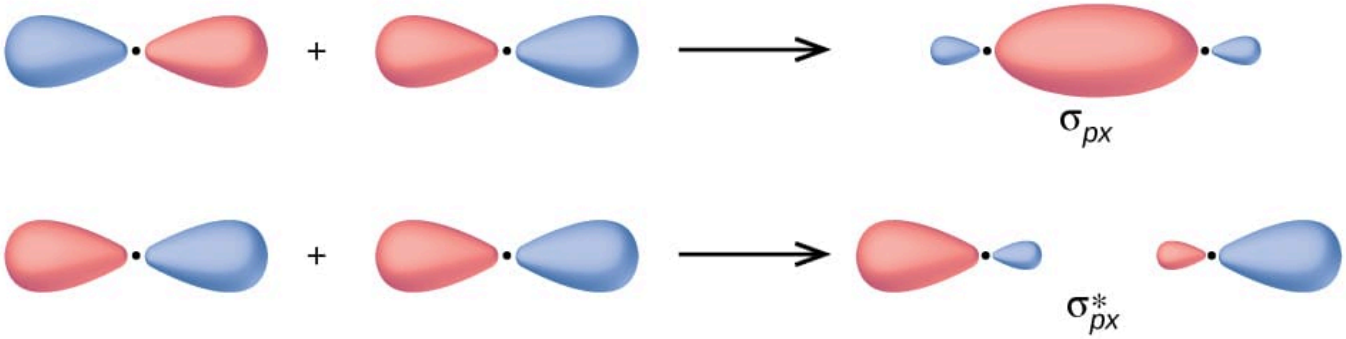


Figure 4.5.4: Combining wave functions of two *p* atomic orbitals along the internuclear axis creates two molecular orbitals, σ_p and σ^*_p

The side-by-side overlap of two *p* orbitals gives rise to a **pi (π) bonding molecular orbital** and a **π* antibonding molecular**

orbital, as shown in Figure 4.5.5. In valence bond theory, we describe π bonds as containing a nodal plane containing the internuclear axis and perpendicular to the lobes of the *p* orbitals, with electron density on either side of the node. In molecular orbital theory, we describe the π orbital by this same shape, and a π bond exists when this orbital contains electrons. Electrons in this orbital interact with both nuclei and help hold the two atoms together, making it a bonding orbital. For the out-of-phase combination, there are two nodal planes created, one along the internuclear axis and a perpendicular one between the nuclei.

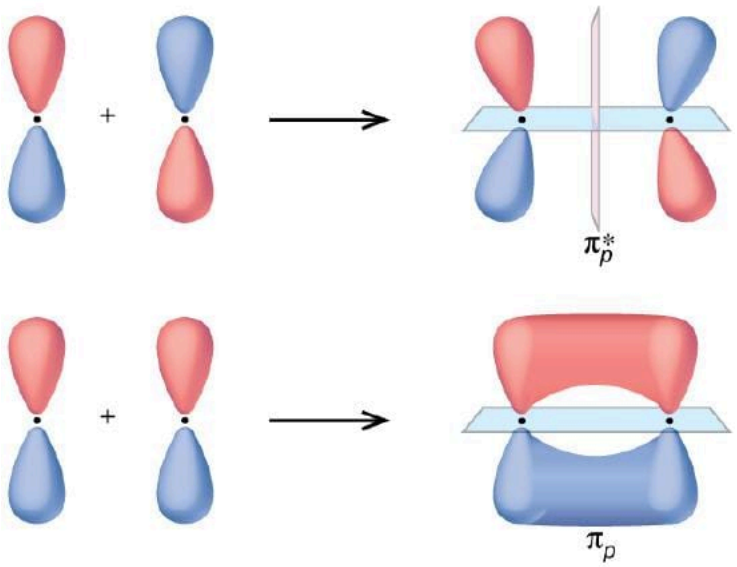
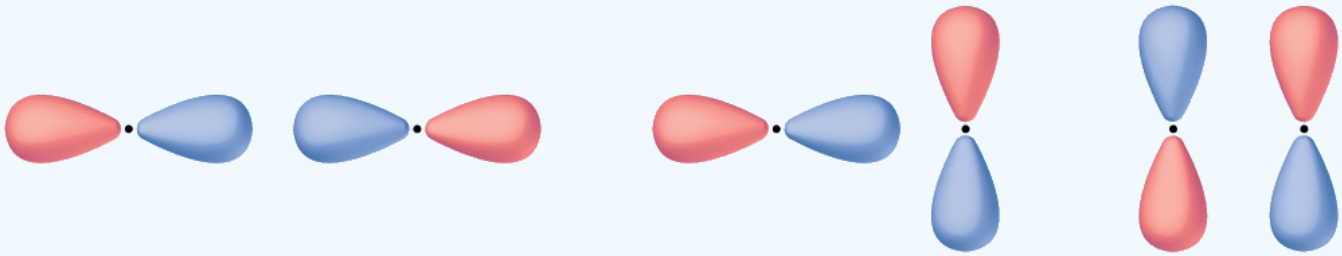


Figure 4.5.5: Side-by-side overlap of each two *p* orbitals results in the formation of two π molecular orbitals. Combining the out-of-phase orbitals results in an antibonding molecular orbital with two nodes. One contains the internuclear axis, and one is perpendicular to the axis. Combining the in-phase orbitals results in a bonding orbital. There is a node (blue) containing the internuclear axis with the two lobes of the orbital located above and below this node.

In the molecular orbitals of diatomic molecules, each atom also has two sets of *p* orbitals oriented side by side (p_y and p_z), so these four atomic orbitals combine pairwise to create two π orbitals and two π* orbitals. The π_{py} and orbitals are oriented at right angles to the π_{pz} and π^*_{pz} orbitals. Except for their orientation, the \(π_{py}\) and \(π_{pz}\) orbitals are identical and have the same energy; they are **degenerate orbitals**. The π^*_{py} and π^*_{pz} antibonding orbitals are also degenerate and identical except for their orientation. A total of six molecular orbitals results from the combination of the six atomic p orbitals in two atoms: σ_{px} and σ^*_{px}, π_{py} and π^*_{py}, π_{pz} and π^*_{pz}.

Example 4.5.1: Molecular Orbitals

Predict what type (if any) of molecular orbital would result from adding the wave functions so each pair of orbitals shown overlap. The orbitals are all similar in energy.



$3p_x$ and $3p_x$ (a)

$3p_x$ and $3p_y$ (b)

$3p_y$ and $3p_y$ (c)

Solution

a. is an in-phase combination, resulting in a σ_{3p} orbital
b. will not result in a new orbital because the in-phase component (bottom) and out-of-phase component (top) cancel out. Only orbitals with the correct alignment can combine.
c. is an out-of-phase combination, resulting in a \(\pi_{3 p}^*) orbital.

Exercise 4.5.1

Label the molecular orbital shown as σ or π, bonding or antibonding and indicate where the node occurs.



Answer available at the end of this section.

Portrait of a Chemist: Walter Kohn: Nobel Laureate

Walter Kohn (Figure 4.5.6) is a theoretical physicist who studies the electronic structure of solids. His work combines the principles of quantum mechanics with advanced mathematical techniques. This technique, called density functional theory, makes it possible to compute properties of molecular orbitals, including their shape and energies. Kohn and mathematician John Pople were awarded the Nobel Prize in Chemistry in 1998 for their contributions to our understanding of electronic structure. Kohn also made significant contributions to the physics of semiconductors.

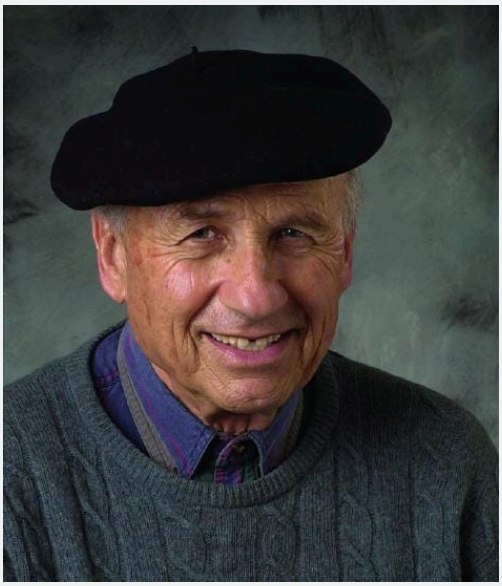


Figure 4.5.6: Walter Kohn developed methods to describe molecular orbitals. (credit: image courtesy of Walter Kohn)

Kohn's biography has been remarkable outside the realm of physical chemistry as well. He was born in Austria, and during World War II he was part of the Kindertransport program that rescued 10,000 children from the Nazi regime. His summer jobs included discovering gold deposits in Canada and helping Polaroid explain how its instant film worked. Dr. Kohn passed away in 2016 at the age of 93.

How Sciences Interconnect: Computational Chemistry in Drug Design

While the descriptions of bonding described in this chapter involve many theoretical concepts, they also have many practical, real-world applications. For example, drug design is an important field that uses our understanding of chemical bonding to develop pharmaceuticals. This interdisciplinary area of study uses biology (understanding diseases and how they operate) to identify specific targets, such as a binding site that is involved in a disease pathway. By modeling the structures of the binding site and potential drugs, computational chemists can predict which structures can fit together and how effectively they will bind (see Figure 4.5.7). Thousands of potential candidates can be narrowed down to a few of the most promising candidates. These candidate molecules are then carefully tested to determine side effects, how effectively they can be transported through the body, and other factors. Dozens of important new pharmaceuticals have been discovered with the aid of computational chemistry, and new research projects are underway.

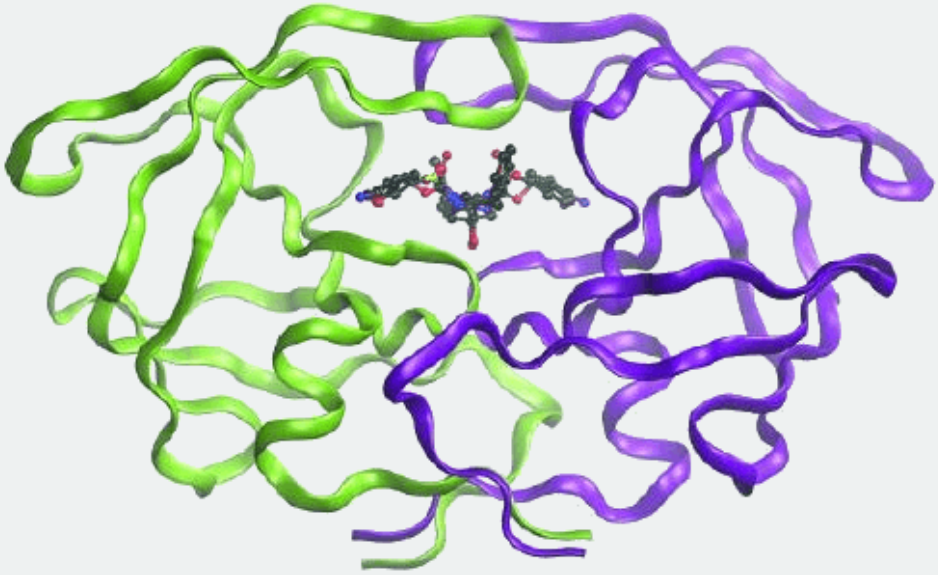


Figure 4.5.7: The molecule shown, HIV-1 protease, is an important target for pharmaceutical research. By designing molecules that bind to this protein, scientists are able to drastically inhibit the progress of the disease.

Molecular Orbital Energy Diagrams

The relative energy levels of atomic and molecular orbitals are typically shown in a molecular orbital diagram (Figure 4.5.8). For a diatomic molecule, the atomic orbitals of one atom are shown on the left, and those of the other atom are shown on the right. Each horizontal line represents one orbital that can hold two electrons. The molecular orbitals formed by the combination of the atomic orbitals are shown in the center. Dashed lines show which of the atomic orbitals combine to form the molecular orbitals. For each pair of atomic orbitals that combine, one lower-energy (bonding) molecular orbital and one higher-energy (antibonding) orbital result. Thus we can see that combining the six 2*p* atomic orbitals results in three bonding orbitals (one σ and two π) and three antibonding orbitals (one σ* and two π*).

We predict the distribution of electrons in these molecular orbitals by filling the orbitals in the same way that we fill atomic orbitals, by the Aufbau principle. Lower-energy orbitals fill first, electrons spread out among degenerate orbitals before pairing, and each orbital can hold a maximum of two electrons with opposite spins (Figure 4.5.8). Just as we write electron configurations for atoms, we can write the molecular electronic configuration by listing the orbitals with superscripts indicating the number of electrons present. For clarity, we place parentheses around molecular orbitals with the same energy. In this case, each orbital is at a different energy, so parentheses separate each orbital. Thus we would expect a diatomic molecule or ion containing seven electrons (such as $\mathrm{Be_2}^+$) would have the molecular electron configuration $(\sigma_{1s})^2 (\sigma^*_{1s})^2 (\sigma_{2s})^2 (\sigma^*_{2s})^1$. It is common to omit the core electrons from molecular orbital diagrams and configurations and include only the valence electrons.

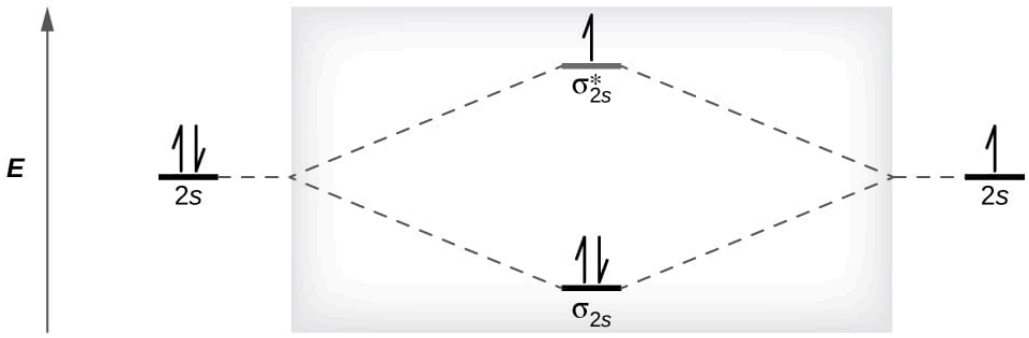


Figure 4.5.8: This is the molecular orbital diagram for the homonuclear diatomic showing the molecular orbitals of the valence shell only. The molecular orbitals are filled in the same manner as atomic orbitals, using the Aufbau principle and Hund's rule.

Bond Order

The filled molecular orbital diagram shows the number of electrons in both bonding and antibonding molecular orbitals. The net contribution of the electrons to the bond strength of a molecule is identified by determining the **bond order** that results from the filling of the molecular orbitals by electrons.

When using Lewis structures to describe the distribution of electrons in molecules, we define bond order as the number of bonding pairs of electrons between two atoms. Thus a single bond has a bond order of 1, a double bond has a bond order of 2, and a triple bond has a bond order of 3. We define bond order differently when we use the molecular orbital description of the distribution of electrons, but the resulting bond order is usually the same. The MO technique is more accurate and can handle cases when the Lewis structure method fails, but both methods describe the same phenomenon.

In the molecular orbital model, an electron contributes to a bonding interaction if it occupies a bonding orbital and it contributes to an antibonding interaction if it occupies an antibonding orbital. The bond order is calculated by subtracting the destabilizing (antibonding) electrons from the stabilizing (bonding) electrons. Since a bond consists of two electrons, we divide by two to get the bond order. We can determine bond order with the following equation:

$$\text{bond order } = \frac{(\text{number of bonding electrons }) - (\text{ number of antibonding electrons })}{2}$$

The order of a covalent bond is a guide to its strength; a bond between two given atoms becomes stronger as the bond order increases (Table 8.1). If the distribution of electrons in the molecular orbitals between two atoms is such that the resulting bond would have a bond order of zero, a stable bond does not form. We next look at some specific examples of MO diagrams and bond orders.

Bonding in Diatomic Molecules

A dihydrogen molecule (H_2) forms from two hydrogen atoms. When the atomic orbitals of the two atoms combine, the electrons occupy the molecular orbital of lowest energy, the σ_{1s} bonding orbital. A dihydrogen molecule, H_2, readily forms because the energy of a H_2 molecule is lower than that of two H atoms. The σ_{1s} orbital that contains both electrons is lower in energy than either of the two 1s atomic orbitals.

A molecular orbital can hold two electrons, so both electrons in the H_2 molecule are in the σ1s bonding orbital; the electron configuration is $(\sigma_{1s})^2$. We represent this configuration by a molecular orbital energy diagram (Figure 4.5.9) in which a single upward arrow indicates one electron in an orbital, and two (upward and downward) arrows indicate two electrons of opposite spin.

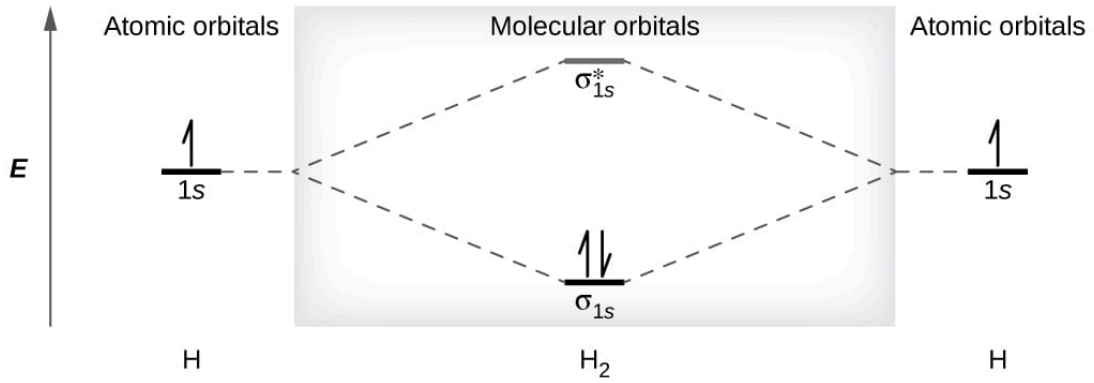


Figure 4.5.9: The molecular orbital energy diagram predicts that H_2 will be a stable molecule with lower energy than the separated atoms.

A dihydrogen molecule contains two bonding electrons and no antibonding electrons so we have

$$\text{bond order in } H_2 = \frac{(2-0)}{2} = 1$$

Because the bond order for the H–H bond is equal to 1, the bond is a single bond.

A helium atom has two electrons, both of which are in its 1s orbital. Two helium atoms do not combine to form a dihelium molecule, He_2, with four electrons, because the stabilizing effect of the two electrons in the lower-energy bonding orbital would be offset by the destabilizing effect of the two electrons in the higher-energy antibonding molecular orbital. We would write the hypothetical electron configuration of He_2 as

$$\text{bond order in } He_2 = \frac{(2-2)}{2} = 0$$

A bond order of zero indicates that no bond is formed between two atoms.

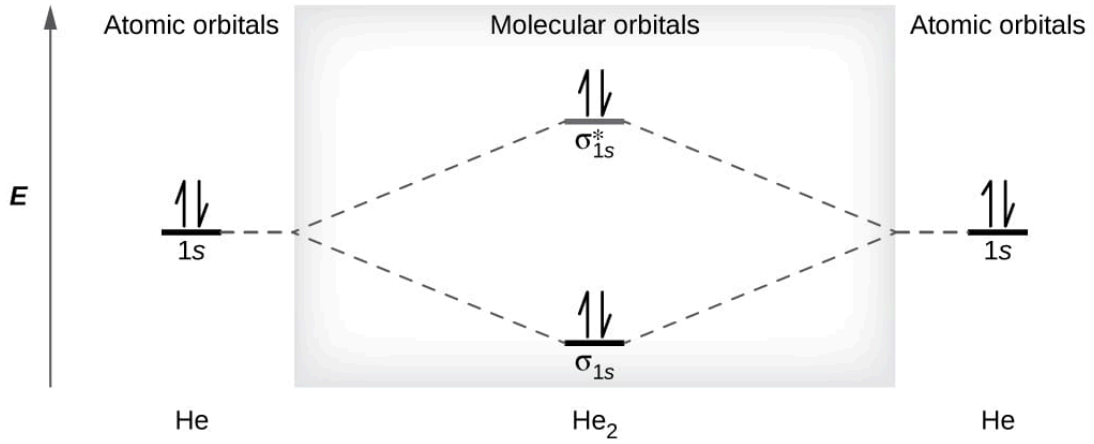


Figure 4.5.10: The molecular orbital energy diagram predicts that He_2 will not be a stable molecule, since it has equal numbers of bonding and antibonding electrons.

The Diatomic Molecules of the Second Period

Eight possible homonuclear diatomic molecules might be formed by the atoms of the second period of the periodic table: Li_2, Be_2, B_2, C_2, N_2, O_2, F_2, and Ne_2. However, we can predict that the Be_2 molecule and the Ne_2 molecule would not be stable. We can see this by a consideration of the molecular electron configurations (Table 4.5.2).

We predict valence molecular orbital electron configurations just as we predict electron configurations of atoms. Valence electrons are assigned to valence molecular orbitals with the lowest possible energies. Consistent with Hund's rule, whenever

there are two or more degenerate molecular orbitals, electrons fill each orbital of that type singly before any pairing of electrons takes place.

As we saw in valence bond theory, σ bonds are generally more stable than π bonds formed from degenerate atomic orbitals. Similarly, in molecular orbital theory, σ orbitals are usually more stable than π orbitals. However, this is not always the case. The MOs for the valence orbitals of the second period are shown in Figure 4.5.11. Looking at Ne_2 molecular orbitals, we see that the order is consistent with the generic diagram shown in the previous section. However, for atoms with three or fewer electrons in the *p* orbitals (Li through N) we observe a different pattern, in which the σ_p orbital is higher in energy than the π_p set. Obtain the molecular orbital diagram for a homonuclear diatomic ion by adding or subtracting electrons from the diagram for the neutral molecule.

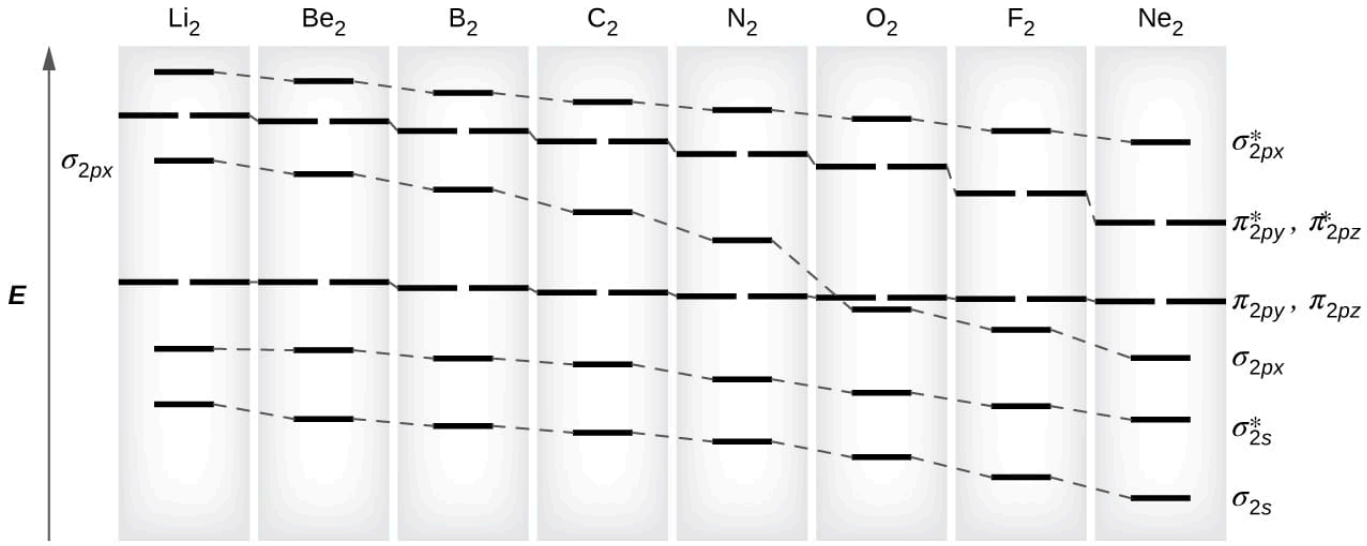


Figure 4.5.11: This shows the MO diagrams for each homonuclear diatomic molecule in the second period. The orbital energies decrease across the period as the effective nuclear charge increases and atomic radius decreases. Between N_2 and O_2, the order of the orbitals changes due to mixing.

This switch in orbital ordering occurs because of a phenomenon called s-p mixing. s-p mixing does not create new orbitals; it merely influences the energies of the existing molecular orbitals. The σ_s wavefunction mathematically combines with the σ_p wavefunction, with the result that the σ_s orbital becomes more stable, and the σ_p orbital becomes less stable (Figure 4.5.12). Similarly, the antibonding orbitals also undergo s-p mixing, with the σ_{s^*} becoming more stable and the σ_{p^*} becoming less stable.

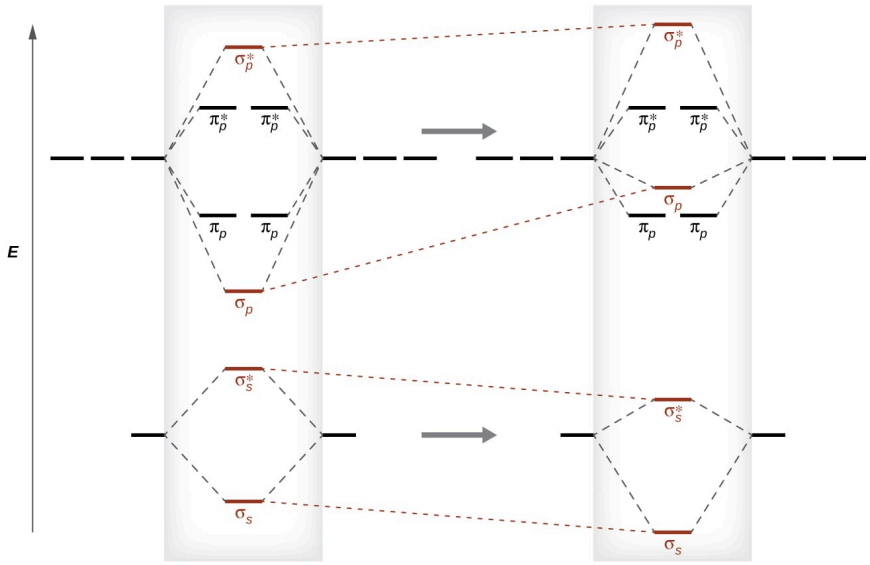


Figure 4.5.12: Without mixing, the MO pattern occurs as expected, with the σ_p orbital lower in energy than the π_p orbitals. When s-p mixing occurs, the orbitals shift as shown, with the σ_p orbital higher in energy than the π_p orbitals.

s-p mixing occurs when s and *p* orbitals on each side of the diagram have similar energies. The energy difference between 2*s* and 2*p* orbitals in O, F, and Ne is greater than that in Li, Be, B, C, and N. Because of this, O_2, F_2, and Ne_2 exhibit negligible s-p mixing (not sufficient to change the energy ordering), and their MO diagrams follow the normal pattern, as shown in Figure 4.5.11 . All of the other period 2 diatomic molecules do have s-p mixing, which leads to the pattern where the σ_p orbital is raised above the π_p set.

Using the MO diagrams shown in Figure 4.5.11: , we can add in the electrons and determine the molecular electron configuration and bond order for each of the diatomic molecules. As shown in Table 4.5.2, Be_2 and Ne_2 molecules would have a bond order of 0, and these molecules do not exist.

Table 4.5.2: Electron Configuration and Bond Order for Molecular Orbitals in Homonuclear Diatomic Molecules of Period Two Elements

Molecule	Electron Configuration	Bond Order
Li_2	$(\sigma_{2s})^2$	1
Be_2 (unstable)	$(\sigma_{2s})^2 (\sigma^*_{2s})^2$	0
B_2	$(\sigma_{2s})^2 (\sigma^*_{2s})^2 (\pi_{2py}, \pi_{2pz})^2$	1
C_2	$(\sigma_{2s})^2 (\sigma^*_{2s})^2 (\pi_{2py}, \pi_{2pz})^4$	2
N_2	$(\sigma_{2s})^2 (\sigma^*_{2s})^2 (\pi_{2py}, \pi_{2pz})^4 (\sigma_{2px})^2$	3
O_2	$(\sigma_{2s})^2 (\sigma^*_{2s})^2 (\sigma_{2px})^2 (\pi_{2py}, \pi_{2pz})^4 (\pi^*_{2py}, \pi^*_{2pz})^2$	2
F_2	$(\sigma_{2s})^2 (\sigma^*_{2s})^2 (\sigma_{2px})^2 (\pi_{2py}, \pi_{2pz})^4 (\pi^*_{2py}, \pi^*_{2pz})^4$	1
Ne_2 (unstable)	$(\sigma_{2s})^2 (\sigma^*_{2s})^2 (\sigma_{2px})^2 (\pi_{2py}, \pi_{2pz})^4 (\pi^*_{2py}, \pi^*_{2pz})^4 (\sigma^*_{2px})^2$	0

The combination of two lithium atoms to form a lithium molecule, Li_2, is analogous to the formation of H_2, but the atomic orbitals involved are the valence 2*s* orbitals. Each of the two lithium atoms has one valence electron. Hence, we have two valence electrons available for the σ_{2s} bonding molecular orbital. Because both valence electrons would be in a bonding orbital, we would predict the Li_2 molecule to be stable. The molecule is, in fact, present in appreciable concentration in lithium vapor at temperatures near the boiling point of the element. All of the other molecules in Table 4.5.2 with a bond order greater than zero are also known.

The O_2 molecule has enough electrons to half fill the $(\pi^*_{2py}, \pi^*_{2pz})$ level. We expect the two electrons that occupy these two degenerate orbitals to be unpaired, and this molecular electronic configuration for O_2 is in accord with the fact that the oxygen

molecule has two unpaired electrons (Figure 8.40). The presence of two unpaired electrons has proved to be difficult to explain using Lewis structures, but the molecular orbital theory explains it quite well. In fact, the unpaired electrons of the oxygen molecule provide a strong piece of support for the molecular orbital theory.

How Sciences Interconnect: Band Theory

When two identical atomic orbitals on different atoms combine, two molecular orbitals result (see Figure 4.5.3). The bonding orbital is lower in energy than the original atomic orbitals because the atomic orbitals are in-phase in the molecular orbital. The antibonding orbital is higher in energy than the original atomic orbitals because the atomic orbitals are out-of-phase.

In a solid, similar things happen, but on a much larger scale. Remember that even in a small sample there are a huge number of atoms (typically > 10^{23} atoms), and therefore a huge number of atomic orbitals that may be combined into molecular orbitals. When *N* valence atomic orbitals, all of the same energy and each containing one (1) electron, are combined, *N*/2 (filled) bonding orbitals and *N*/2 (empty) antibonding orbitals will result. Each bonding orbital will show an energy lowering as the atomic orbitals are *mostly* in-phase, but each of the bonding orbitals will be a little different and have slightly different energies. The antibonding orbitals will show an increase in energy as the atomic orbitals are *mostly* out-of-phase, but each of the antibonding orbitals will also be a little different and have slightly different energies. The allowed energy levels for all the bonding orbitals are so close together that they form a band, called the valence band. Likewise, all the antibonding orbitals are very close together and form a band, called the conduction band. Figure 4.5.13 shows the bands for three important classes of materials: insulators, semiconductors, and conductors.

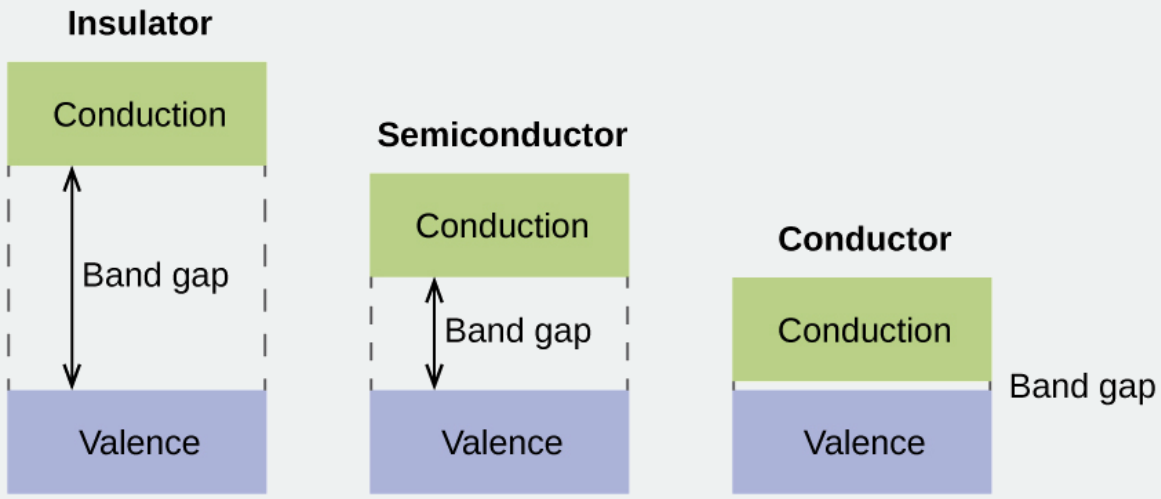


Figure 4.5.13: Molecular orbitals in solids are so closely spaced that they are described as bands. The valence band is lower in energy and the conduction band is higher in energy. The type of solid is determined by the size of the "band gap" between the valence and conduction bands. Only a very small amount of energy is required to move electrons from the valence band to the conduction band in a conductor, and so they conduct electricity well. In an insulator, the band gap is large, so that very few electrons move, and they are poor conductors of electricity. Semiconductors are in between: they conduct electricity better than insulators, but not as well as conductors.

In order to conduct electricity, electrons must move from the filled valence band to the empty conduction band where they can move throughout the solid. The size of the band gap, or the energy difference between the top of the valence band and the bottom of the conduction band, determines how easy it is to move electrons between the bands. Only a small amount of energy is required in a conductor because the band gap is very small. This small energy difference is "easy" to overcome, so they are good conductors of electricity. In an insulator, the band gap is so "large" that very few electrons move into the conduction band; as a result, insulators are poor conductors of electricity. Semiconductors conduct electricity when "moderate" amounts of energy are provided to move electrons out of the valence band and into the conduction band. Semiconductors, such as silicon, are found in many electronics.

Semiconductors are used in devices such as computers, smartphones, and solar cells. Solar cells produce electricity when light provides the energy to move electrons out of the valence band. The electricity that is generated may then be used to power a light or tool, or it can be stored for later use by charging a battery. As of December 2014, up to 46% of the energy in sunlight could be converted into electricity using solar cells.

Example 4.5.2: Molecular Orbital Diagrams, Bond Order, and Number of Unpaired Electrons

Draw the molecular orbital diagram for the oxygen molecule, O_2. From this diagram, calculate the bond order for O_2. How does this diagram account for the paramagnetism of O_2?

Solution

We draw a molecular orbital energy diagram similar to that shown in Figure 4.5.11. Each oxygen atom contributes six electrons, so the diagram appears as shown in Figure 4.5.14.

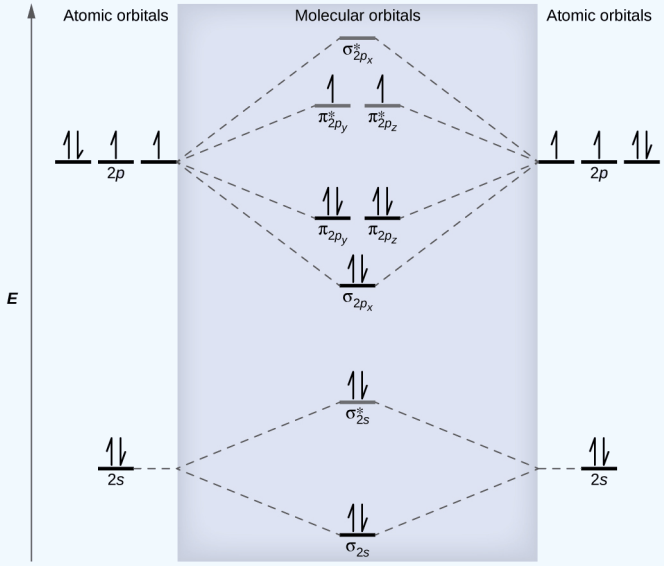


Figure 4.5.14: The molecular orbital energy diagram for O_2 predicts two unpaired electrons.

We calculate the bond order as

$$O_2 = \frac{(8-4)}{2} = 2$$

Oxygen's paramagnetism is explained by the presence of two unpaired electrons in the (π_{2py}, π_{2pz})* molecular orbitals.

Exercise 4.5.2

The main component of air is N_2. From the molecular orbital diagram of N_2, predict its bond order and whether it is diamagnetic or paramagnetic.

Answer available at the end of this section.

Example 4.5.3: Ion Predictions with MO Diagrams

Give the molecular orbital configuration for the valence electrons in C_2^{2-}. Will this ion be stable?

Solution

Looking at the appropriate MO diagram, we see that the π orbitals are lower in energy than the σ_p orbital. The valence electron configuration for C_2 is $(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py},\pi_{2pz})^4$. Adding two more electrons to generate the C_2^{2-} anion will give a valence electron configuration of $(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py},\pi_{2pz})^4(\sigma_{2px})^2$. Since this has six more bonding electrons than antibonding, the bond order will be 3, and the ion should be stable.

Exercise 4.5.3

How many unpaired electrons would be present on a Be_2^{2-} ion? Would it be paramagnetic or diamagnetic?

Answer available at the end of this section.

Heteronuclear Diatomic Molecules

Diatomic molecules with two different nuclei are also common. The molecular orbital energy diagrams of these heteronuclear diatomic molecules will have different starting energies on either side of the diagram, corresponding to the atomic orbital energies of each atom. Some of these energies are shown in Table 4.5.1. The difference between the p and s orbital energies can give us insight into the energetic requirements of mixing, described above. O_2, which does not have signficant mixing, has an energy difference of 16.5 eV, whereas N_2, which does have significant mixing, has an energy difference of 12.4 eV. An energy difference of less than ~15 eV will lead to mixing in the heteronuclear diatomic molecular orbital diagram.

Table 4.5.1: Atomic Orbital Energies of Period 2 Elements

Element:	H	Li	Be	B	C	N	O	F
s orbital energy (eV)	-13.61	-5.39	-9.32	-14.05	-19.43	-25.56	-32.38	-40.17
p orbital energy (eV)				-8.30	-10.66	-13.18	-15.85	-18.65

Exercise 4.5.4

Draw a molecular orbital diagram for the CN^- anion.

Solution available at the end of this section.

Orbital Densities of Heteronuclear Diatomic Molecules

The drawings in Figure 4.5.4 (above) show how the orbital shapes change as they mix to become molecular orbitals from atomic orbitals. These orbital shapes are distorted when a molecule has nuclei with (1) different energy levels between each atom and (2) different electronegativities of each nucleus.

Example 4.5.4: Shapes of atomic orbitals

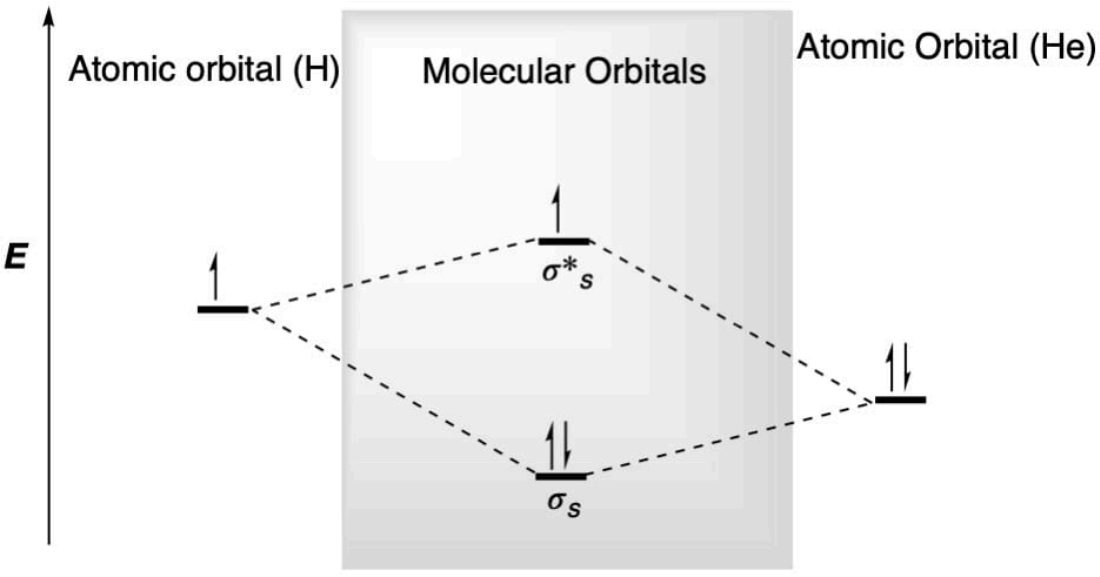
Draw the molecular orbital diagram of the molecule H-He.

(A) What is the bond order of H-He?

(B) Draw the shape of the bonding and antibonding orbitals, taking into account the electronegativities of each atom and the energy levels of the orbitals.

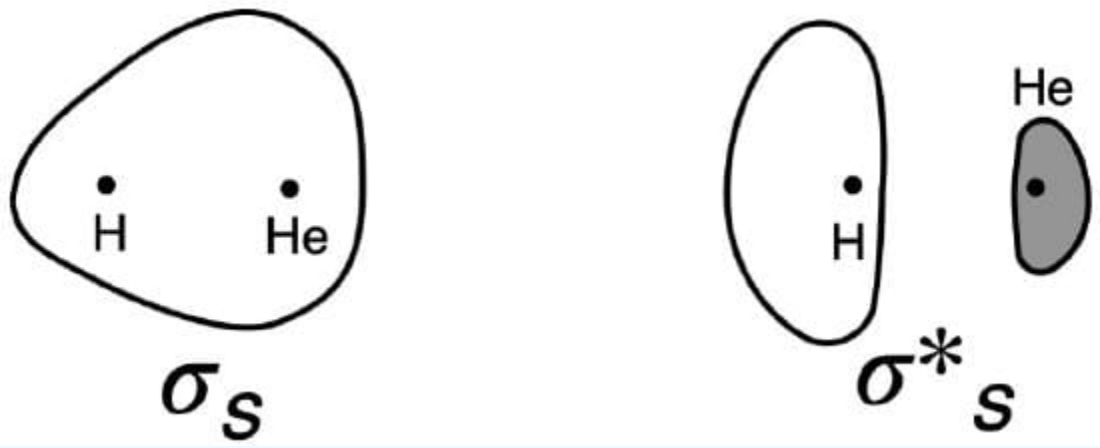
Solution

The helium (He) nucleus has more protons than hydrogen (H), yet both have only a 1s orbital as a valence orbital. Therefore, the starting 1s orbital for He should be lower in energy than the starting 1s orbital for H.



(A) Based on this diagram, the bond order is 1/2. This is because there are two bonding electrons and one antibonding electron.

(B) To draw the bonding and antibonding orbitals, we can start by looking at the bonding and antibonding orbitals shown in Figure 4.5.3. What is different about the heteronuclear orbitals is that He is more electronegative than H, and thus the bonding orbital is closer in energy to He, and the antibonding orbital is closer in energy to H. This affects the shape of the orbitals by biasing the molecular orbitals toward the orbitals they are closer in energy to.



The bonding orbital is closer in energy to He and thus it is biased toward the more electronegative helium. The antibonding orbital is biased toward H, in turn. Importantly, the shading of these orbitals is arbitrary. An answer with different shading would be equally correct, as long as the shading changes across the node in the σ* orbital.

Link to Learning

Creating molecular orbital diagrams for molecules with more than two atoms relies on the same basic ideas as the diatomic examples presented here. However, with more atoms, computers are required to calculate how the atomic orbitals combine. See three-dimensional drawings of the molecular orbitals for C_6H_6.

Answers

Exercise 4.5.1

The orbital is located along the internuclear axis, so it is a σ orbital. There is a node bisecting the internuclear axis, so it is an antibonding orbital.



Exercise 4.5.2

N_2 has a bond order of 3 and is diamagnetic.

Exercise 4.5.3

two, paramagnetic

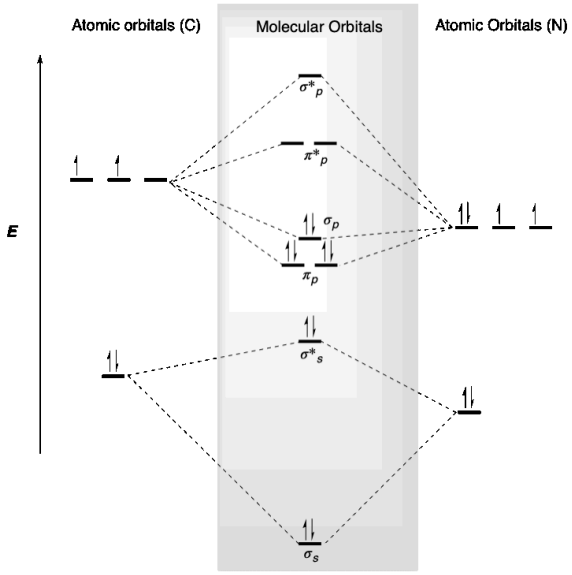
Exercise 4.5.4

1. Electron count: C and N have 4 and 5 valence electrons, respectively, and there is an overall charge of -1. The total number of valence electrons is 10.

2. Starting energies of orbitals: We can check Table 4.5.1 to find the starting energies of the s and p orbitals on C and N, and approximate them in our diagram, below.

3. Mixing or no mixing: The differences across the diagram are the following: s_C and p_N: 6.3 eV; s_N and p_C: 14.9 eV. As one (both, in this case) of these numbers is less than 15 eV, we can assume significant mixing in our orbital diagram, and the σ_p orbital will be raised above the π_p set.

4. All that is left is to draw the diagram, below.



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4.6: Resonance

Objective

After completing this section, you should be able to

- draw resonance forms for molecules and ions.

Key Terms

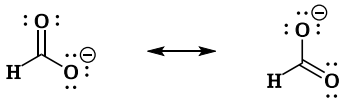
Make certain that you can define, and use in context, the key term below.

- resonance form
- delocalization

Resonance Delocalization

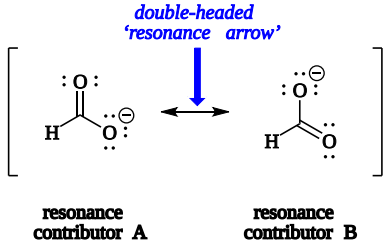
Sometimes, even when formal charges are considered, the bonding in some molecules or ions cannot be described by a single Lewis structure. **Resonance** is a way of describing **delocalized** electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by a single Lewis formula. A molecule or ion with such delocalized electrons is represented by several contributing structures (also called resonance contributors or canonical forms). Resonance contributors involve the 'imaginary movement' of pi-bonded electrons or of lone-pair electrons that are adjacent to pi bonds. Note, sigma bonds cannot be broken during resonance – if you show a sigma bond forming or breaking, you are showing a chemical reaction taking place. Likewise, the positions of atoms in the molecule **cannot change** between resonance contributors.

When looking at the structure of the molecule, formate, we see that there are two equivalent structures possible. Which one is correct? There are two simple answers to this question: 'both' and 'neither one'. Both ways of drawing the molecule are equally acceptable approximations of the bonding picture for the molecule, but neither one, by itself, is an accurate picture of the delocalized pi bonds. The two alternative drawings, however, when considered together, give a much more accurate picture than either one on its own. This is because they imply, together, that the carbon-carbon bonds are not double bonds, not single bonds, but about halfway in between.



Formate Ion Structures are Equivalent in Energy

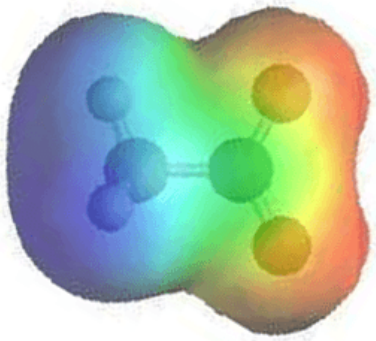
When it is possible to draw more than one valid structure for a compound or ion, we have identified **resonance contributors**: two or more different Lewis structures depicting the same molecule or ion that, when considered together, do a better job of approximating delocalized pi-bonding than any single structure. By convention, resonance contributors are linked by a double-headed arrow, and are sometimes enclosed by brackets:



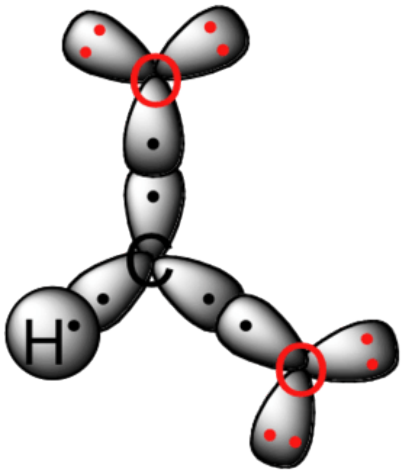
The depiction of formate using the two resonance contributors A and B in the figure above does *not* imply that the molecule at one moment looks like structure A, then at the next moment shifts to look like structure B. Rather, at all moments, the molecule is a combination, or **resonance hybrid** of both A and B. Each individual resonance contributor of the formate ion is drawn with one carbon-oxygen double bond (120 pm) and one carbon-oxygen single bond (135 pm), with a negative formal charge located on the single-bonded oxygen. However, the two carbon-oxygen bonds in formate are actually the same length (127 pm) which implies that neither resonance contributor is correct. Although there is an overall negative formal charge on the formate ion, it is shared equally between the two oxygens. Therefore, the formate ion can be more accurately depicted by a *pair* of resonance contributors. Alternatively, a single structure can be used, with a dashed line depicting the resonance-delocalized pi bond and the negative charge located in between the two oxygens.



The electrostatic potential map of formate shows that there is an equal amount of electron density (shown in red) around each oxygen.

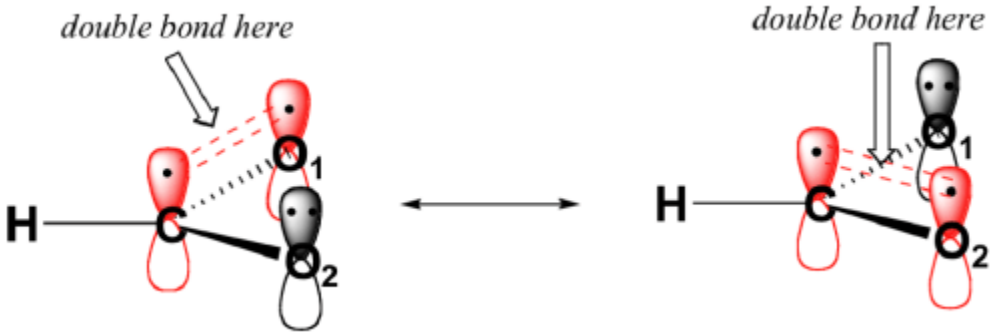


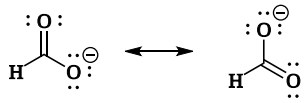
Valence bond theory can be used to develop a picture of the bonding in a carboxylate group. We know that the carbon must be sp^2-hybridized, (the bond angles are close to 120˚, and the molecule is planar), and we will treat both oxygens as being sp^2-hybridized as well. Both carbon-oxygen sigma bonds, then, are formed from the overlap of carbon sp^2 orbitals and oxygen sp^2 orbitals.



the σ-bonding framework of formate

In addition, the carbon and both oxygens each have an un-hybridized $2p_z$ orbital situated perpendicular to the plane of the sigma bonds. These three $2p_z$ orbitals are parallel to each other, and can overlap in a side-by-side fashion to form a delocalized pi bond.

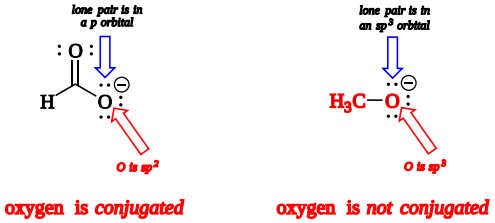




resonance contributor A resonance contributor B

Overall, the situation is one of *three parallel, overlapping $2p_z$ orbitals sharing four delocalized pi electrons*. Because there is one more electron than there are $2p_z$ orbitals, the system has an overall charge of 1–. Resonance contributors are used to approximate overlapping $2p_z$ orbitals and delocalized pi electrons. Molecules with resonance are usually drawn showing only one resonance contributor for the sake of simplicity. However, identifying molecules with resonance is an important skill.

This example shows an important exception to the general rules for determining the hybridization of an atom. The oxygen with the negative charge appears to be sp^3 hybridized because it is surrounded by four electron groups. However, this representation of the oxygen atom is not correct because it is actually part of a resonance hybrid. A pair of lone pair of electrons on the negatively charged oxygen are not localized in an sp^3 orbital, rather, they are delocalized as part of a conjugated pi system. The stability gained though resonance is enough to cause the expected sp^3 to become sp^2. The sp^2 hybridization gives the oxygen a p orbital allowing it to participate in conjugation. As a general rule sp^3 hybridized atoms with lone pair electrons tend to become sp^2 hybridized when adjacent to a conjugated system.



Example: Carbonate (CO_3^{2-})

Like formate, the electronic structure of the carbonate ion cannot be described by a single Lewis electron structure. Unlike O_3, though, the Lewis structures describing CO_3^{2-} has *three* equivalent representations.Edit section

1. Because carbon is the least electronegative element, we place it in the central position:



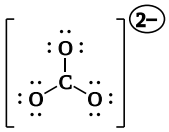
2. Carbon has 4 valence electrons, each oxygen has 6 valence electrons, and there are 2 more for the 2– charge. This gives 4 + (3 × 6) + 2 = 24 valence electrons.

3. Six electrons are used to form three bonding pairs between the oxygen atoms and the carbon:

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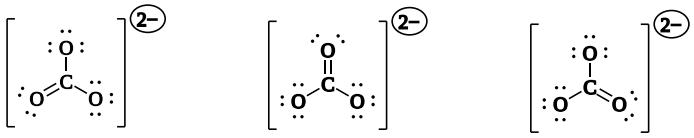


4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the 2– charge:

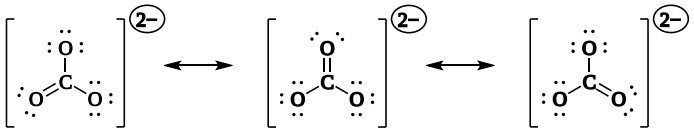


5. There are no electrons left for the central atom.Edit section

6. At this point, the carbon atom has only 6 valence electrons, so we must take one lone pair from an oxygen and use it to form a carbon–oxygen double bond. In this case, however, there are *three* possible choices:



As with formate, none of these structures describes the bonding exactly. Each predicts one carbon–oxygen double bond and two carbon–oxygen single bonds, but experimentally all C–O bond lengths are identical. We can write resonance structures (in this case, three of them) for the carbonate ion:



As the case for formate, the actual structure involves the formation of a molecular orbital from p_z orbitals centered on each atom and sitting above and below the plane of the CO_3^{2-} ion. Edit section

Example 4.6.1

Benzene is a common organic solvent that was previously used in gasoline; it is no longer used for this purpose, however, because it is now known to be a carcinogen. The benzene molecule (C_6H_6) consists of a regular hexagon of carbon atoms, each of which is also bonded to a hydrogen atom. Use resonance structures to describe the bonding in benzene.

Given: molecular formula and molecular geometry

Asked for: resonance structures

Strategy:

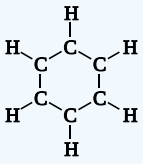
A Draw a structure for benzene illustrating the bonded atoms. Then calculate the number of valence electrons used in this drawing.

B Subtract this number from the total number of valence electrons in benzene and then locate the remaining electrons such that each atom in the structure reaches an octet.

C Draw the resonance structures for benzene.

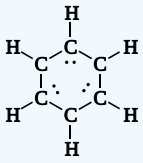
Solution:

A Each hydrogen atom contributes 1 valence electron, and each carbon atom contributes 4 valence electrons, for a total of (6 × 1) + (6 × 4) = 30 valence electrons. If we place a single bonding electron pair between each pair of carbon atoms and between each carbon and a hydrogen atom, we obtain the following:



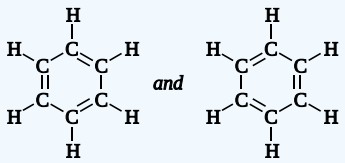
Each carbon atom in this structure has only 6 electrons and has a formal charge of 1+, but we have used only 24 of the 30 valence electrons.

B If the 6 remaining electrons are uniformly distributed pair-wise on alternate carbon atoms, we obtain the following:

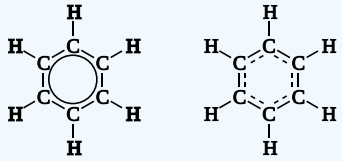


Three carbon atoms now have an octet configuration and a formal charge of 1–, while three carbon atoms have only 6 electrons and a formal charge of 1+. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of electrons and a formal charge of 0, by making three C=C double bonds.

C There are, however, two ways to do this:

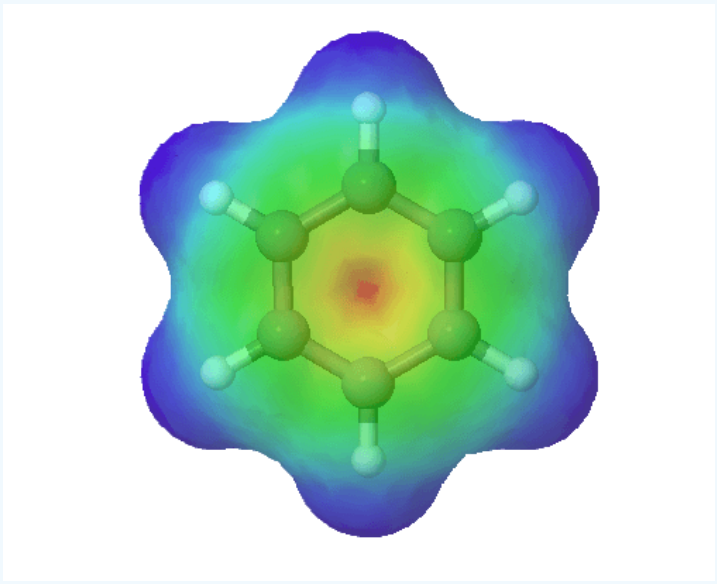


Each structure has alternating double and single bonds, but experimentation shows that each carbon–carbon bond in benzene is identical, with bond lengths (139.9 pm) intermediate between those typically found for a C–C single bond (154 pm) and a C=C double bond (134 pm). We can describe the bonding in benzene using the two resonance structures, but the actual electronic structure is an average of the two. The existence of multiple resonance structures for aromatic hydrocarbons like benzene is often indicated by drawing either a circle or dashed lines inside the hexagon:



benzene

This combination of *p* orbitals for benzene can be visualized as a ring with a node in the plane of the carbon atoms. As can be seen in an electrostatic potential map of benzene, the electrons are distributed symmetrically around the ring.



Exercise 4.6.1

The sodium salt of nitrite is used to relieve muscle spasms. Draw two resonance structures for the nitrite ion (NO_2^-).

Answer available at the end of this section.

Exercises

4.6.3 Resonance

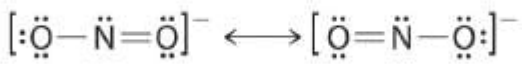
4.6.3 Exercises

Draw the resonance structures for O_3

A molecule or ion with such delocalized electrons is represented by several contributing structures (also called resonance structures or canonical forms). Such is the case for ozone (O_3), an allotrope of oxygen with a V-shaped structure and an O–O–O angle of 117.5°.

Answer available at the end of this section.

Answers



1. We know that ozone has a V-shaped structure, so one O atom is central:

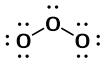
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2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.

Edit section

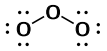
3. Assigning one bonding pair of electrons to each oxygen–oxygen bond gives



with 14 electrons left over.

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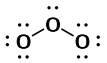
4. If we place three lone pairs of electrons on each terminal oxygen, we obtain



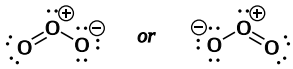
and have 2 electrons left over.

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5. At this point, both terminal oxygen atoms have octets of electrons. We therefore place the last 2 electrons on the central atom:



6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons—but which one? Depending on which one we choose, we obtain either



Which is correct? In fact, neither is correct. Both predict one O–O single bond and one O=O double bond. If the bonds were of different types (one single and one double, for example), they would have different lengths. It turns out, however, that both O–O bond distances are identical, 127.2 pm, which is shorter than a typical O–O single bond (148 pm) and longer than the O=O double bond in O_2 (120.7 pm).Edit section

Equivalent Lewis dot structures, such as those of ozone, are called resonance structures . The position of the *atoms* is the same in the various resonance structures of a compound, but the position of the *electrons* is different. Double-headed arrows link the different resonance structures of a compound:

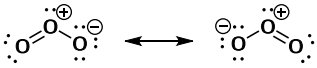
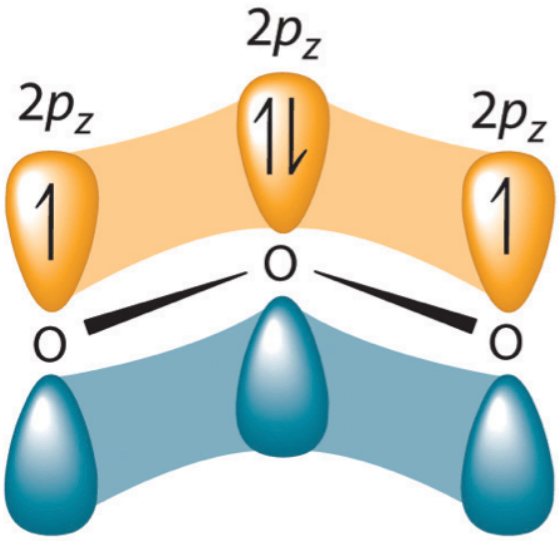


Figure 2.4.1).



The resonance structure of ozone involves a molecular orbital extending all three oxygen atoms.In ozone, a molecular orbital extending over all three oxygen atoms is formed from three atom centered p_z orbitals. Similar molecular orbitals are found in every resonance structure.Edit section

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4.7: Rules for Resonance Forms

Objectives

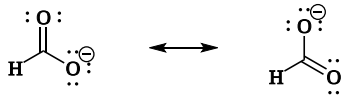
After completing this section, you should be able to

- use the concept of resonance to explain structural features of molecules and ions.
- understand the relationship between resonance and relative stability of molecules and ions.

Rules for Drawing and Working with Resonance Contributors

Recognizing, drawing, and evaluating the relative stability of resonance contributors is essential to understanding organic reaction mechanisms. When learning to draw and interpret resonance structures, there are a few basic guidelines to help. .

1) There is ONLY ONE REAL STRUCTURE for each molecule or ion. This real structure (the **resonance hybrid**) takes its character from the average of all the individual **resonance contributors**. When looking at a resonance contributors, we are seeing the exact same molecule or ion depicted in different ways. Resonance hybrids are really a single, unchanging structure.



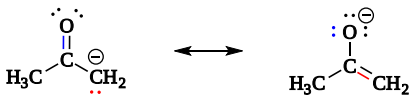
Major resonance contributors of the formate ion



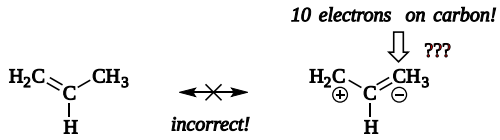
Representations of the formate resonance hybrid

2) The resonance hybrid is more stable than any individual resonance structures. Often, resonance structures represent the movement of a charge between two or more atoms. The charge is spread out amongst these atoms and therefore more stabilized. When looking at the picture above the resonance contributors represent the negative charge as being on one oxygen or the other. The resonance hybrid shows the negative charge being shared equally between two oxygens. In the resonance hybrid, the negative charge is spread out over a larger part of the molecule and is therefore more stable.

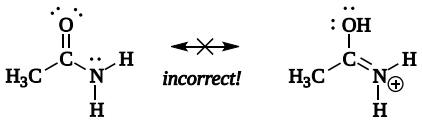
3) Resonance contributors do not have to be equivalent. Because of this, resonance structures do necessarily contribute equally to the resonance hybrid. The two resonance structures shown below are not equivalent because one show the negative charge on an oxygen while the other shows it on a carbon. Later, we will show that the contributor with the negative charge on the oxygen is the more stable of the two. Also, this means that the resonance hybrid will not be an exact mixture of the two structures.



4) All resonance contributors must be correct Lewis structures. Each atom should have a complete valence shell and be shown with correct formal charges. A carbocation (carbon with only 6 valence electrons) is the only allowed exception to the valence shell rules. The structure below is an invalid resonance structure even though it only shows the movement of a pi bond. The resulting structure contains a carbon with ten electrons, which violates the octet rule, making it invalid.



5) All resonance contributors must have the same molecular formula, the same number of electrons, and same net charge. The molecules in the figure below are not resonance structures of the same molecule because then have different molecular formulas (C_2H_5NO Vs. C_2H_6NO). Also, the two structures have different net charges (neutral Vs. positive).

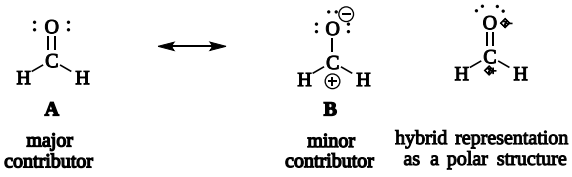


6) Resonance contributors only differ by the positions of pi bond and lone pair electrons. Sigma bonds are never broken or made, because of this atoms must maintain their same position. The molecules in the figure below are not resonance structures of the same molecule even though they have the same molecular formula (C_3H_6O). These molecules are considered structural isomers because their difference involves the breaking of a sigma bond and moving a hydrogen atom.



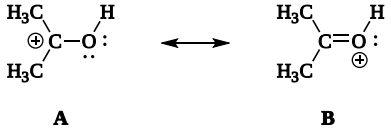
Major and Minor Resonance Contributors

As previously state the true structure of a resonance hybrid is the combination of all the possible resonance structures. If the resonance structures are equal in stability they the contribute equally to the structure of the hybrid. However, if the resonance structures have different stabilities they contribute to the hybrid's structure in proportions related to their relative stabilities. It can be said the the resonance hybrid's structure resembles the most stable resonance structure. Because of this it is important to be able to compare the stabilities of resonance structures. In the example below, structure **B** is much less important in terms of its contribution to the hybrid because it contains the violated octet of a carbocation. The relative stabilities of the two structures are so vastly different that molecules which contain a C=O bond are almost exclusively written in a form like structure **A**. However, as will learn in chapter 19, the positively charged carbon created by structure **B** will explain how the C=O bond will react with electron rich species.

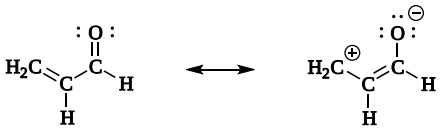


Rules for Estimating Stability of Resonance Structures

1. The resonance structures in which all atoms have complete valence shells is more stable. This means most atoms have a full octet. In the example below structure **A** has a carbon atom with a positive charge and therefore an incomplete octet. Based on this criterion, structure **A** is less stable and is a more minor contributor to the resonance hybrid than structure **B**.

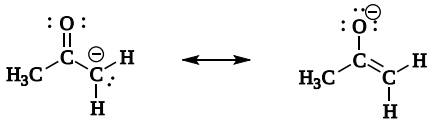


2. The structures with the **least number of formal charges** is more stable. Based on this, structure **B** is less stable because is has two atoms with formal charges while structure **A** has none. Structure **A** would be the major resonance contributor.



A **B**

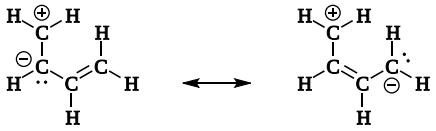
3. The structures with a **negative charge on the more electronegative atom** will be more stable. The difference between the two resonance structures is the placement of a negative charge. Structure **B** is the more stable and the major resonance contributor, because it places the negative charge on the more electronegative oxygen.



A **B**

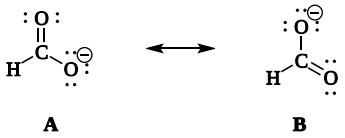
4. The structures with a **positive charges on the least electronegative atom** (most electropositive) is more stable.

5. The structures with the **least separation of formal charges** is more stable. The only difference between the two structures below are the relative positions of the positive and negative charges. In structure **A** the charges are closer together making it more stable.



A **B**

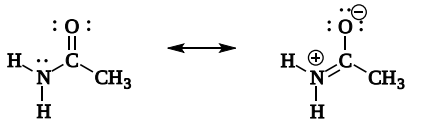
6. **Resonance forms that are equivalent have no difference in stability**. When looking at the two structures below no difference can be made using the rules listed above. This means the two structures are equivalent in stability and would make equal structural contributions to the resonance hybrid.



A **B**

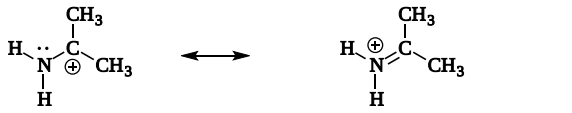
Examples of major and minor contributors

Example 1:



major contributor (neutral structure) minor contributor (charge separation)

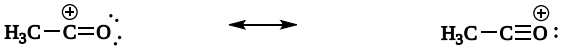
Example 2:



minor contributor
(Incomplete octet on carbon.)

major contributor
(All atoms have octets, even though there is a positive charge on nitrogen.)

Example 3:

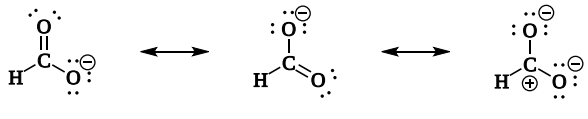


minor contributor
(Incomplete octet on carbon, but more important in terms of reactivity.)

major contributor
(All atoms have octets, even though there is a positive charge on oxygen.)

Carboxylate example

In the case of carboxylates, contributors **A** and **B** below are equivalent in terms of their relative contribution to the hybrid structure. However, there is also a third resonance contributor **C**, in which the carbon bears a positive formal charge (a carbocation) and both oxygens are single-bonded and bear negative charges.



A **B** **C**

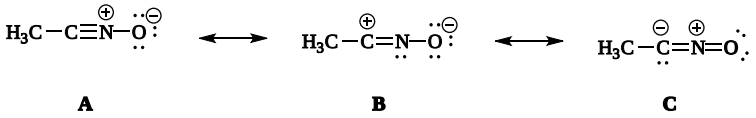
minor contributor
(separation of charge)

Structure **C** makes a less important contribution to the overall bonding picture of the group relative to **A** and **B**. How do we know that structure **C** is the 'minor' contributor? Apply the rules below

- The carbon in contributor **C** does not have an octet. In general, resonance contributors in which a carbon does not fulfill the octet rule are relatively less important. (rule #1)
- In structure **C**, there are only three bonds, compared to four in **A** and **B**. In general, a resonance structure with a lower number of total bonds is relatively less important. (rule #2)
- Structure **C** also has more formal charges than are present in **A** or **B**. In general, resonance contributors in which there is more/greater separation of charge are relatively less important. (rule #3)
- Structures **A** and **B** are equivalent and will be equal contributors to the resonance hybrid. (rule #5).
- The resonance contributor in which a negative formal charge is located on a more electronegative atom, usually oxygen or nitrogen, is more stable than one in which the negative charge is located on a less electronegative atom such as carbon. An example is in the upper left expression in the next figure. (rule #4)

Example with 3 resonance structures

Molecules with more than 2 resonance structures can also be considered using the rules listed above. Of the resonance structures listed below, structure **A** would be the most stable because all the non-hydrogen atoms have a full octet and the negative charge is on the more electronegative atom (oxygen). Structure **C** would be next in stability because all of the non-hydrogen atoms have full octets, though now the negative charge is on carbon rather than oxygen. Structure **B** would be the least stable of the three because it has the carbocation does not have an octet. Of the three, structure **A** would be the major resonance structure and would most resemble the structure of the true resonance hybrid. Structure **B** is considered a minor resonance contributor and would have very little effect on the structure of the resonance hybrid.



A B C

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4.8: Resonance Effects on Hybridization and Bonding

Learning Objectives

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

- Identify delocalized molecular orbitals
- Explain the concept of delocalization and draw minor resonance contributors that affect hybridization
- Identify the hybridization of atoms with delocalized molecular orbitals

Delocalization of Molecular Orbitals

As described in Chapter 3.6, **resonance forms** of a molecule cannot completely describe the bonding in a molecule without taking into account each resonance structure and averaging these as a **resonance hybrid**. This phenomenon is not limited to bond order and charge distribution, and can be applied to molecular orbitals as well. ***Delocalized molecular orbitals*** are orbitals that are extended across multiple atoms rather than being constrained to one or two atoms, and thus molecules with resonance structures will have delocalized molecular orbitals.

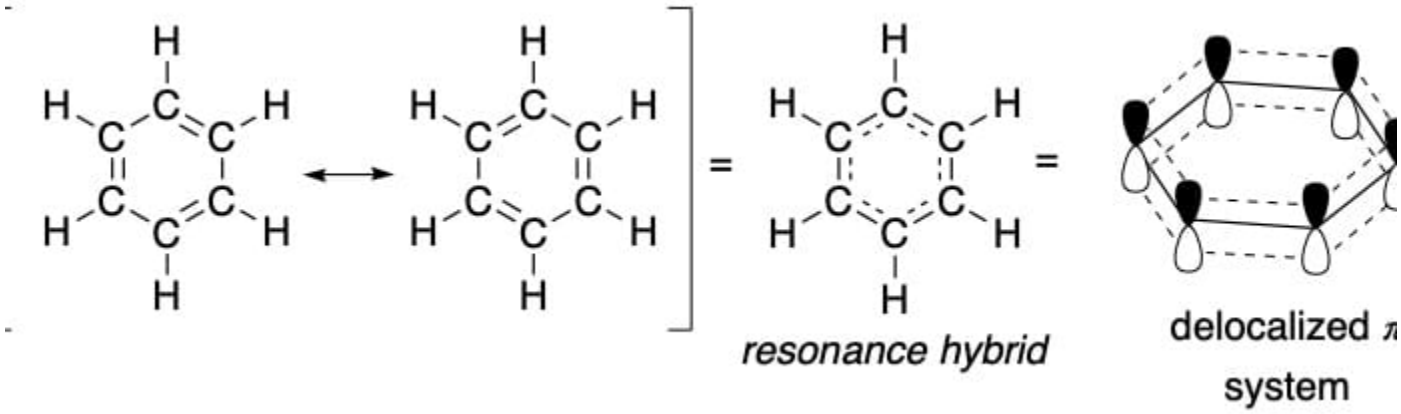


Figure 4.8.1: different visualizations of benzene.

Benzene has two major resonance structures with alternating double bonds (Figure 4.8.1). In the resonance hybrid (and in the actual molecule), each C-C bond is effectively 1.5 bonds, due to resonance. The p orbitals that make up each π bond are conserved in the resonance structures and resonance hybrid, as seen in the delocalized π system.

The hybridization of each carbon in the benzene ring is sp^2, and this hybridization is conserved in the resonance hybrid and delocalized π system that is made up of the unhybridized p orbitals.

Hybridization of Resonance Contributors

Returning to O_3 (ozone) from Chapter 4.6:

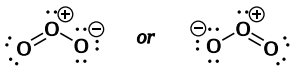


Figure 4.8.2: Two resonance contributors of Ozone

The terminal oxygen atoms on each resonance structure have a different number of regions of electron density. At first glance, the

oxygen atoms would have different hybridizations as a result. However, the resonance hybrid is the true structure of the molecule, with a partial negative charge on each terminal oxygen and a full positive charge on the central oxygen.

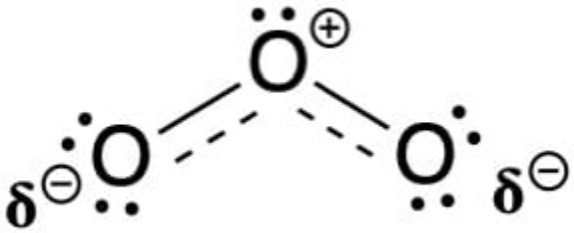


Figure 4.8.3: Ozone resonance Hybrid

The resonance hybrid (Figure 4.8.3) shows how the p orbitals on all three oxygen atoms form a *delocalized* molecular orbital. Thus, each oxygen is sp^2 hybridized, with the p orbitals forming a π system, and 5 lone pairs in sp^2 hybridized orbitals on the oxygen atoms.

This delocalization is favorable for the molecule, because the electrons in the p orbitals are spread out over more atoms. When possible, molecules will adopt hybridization arrangements to allow for delocalization of electrons.

An orbital picture of the resonance hybrid could be drawn as shown in Figure 4.8.4, with the p orbitals and π system shown in grey and the hybridized orbitals shown in blue (minor lobes of hybridized orbitals not shown for clarity). The lone pairs are in hybridized orbitals, and the π system has 4 electrons (not shown) spread out over three atoms. This delocalization of electrons stabilizes the molecule and encourages the sp^2 hybridization.

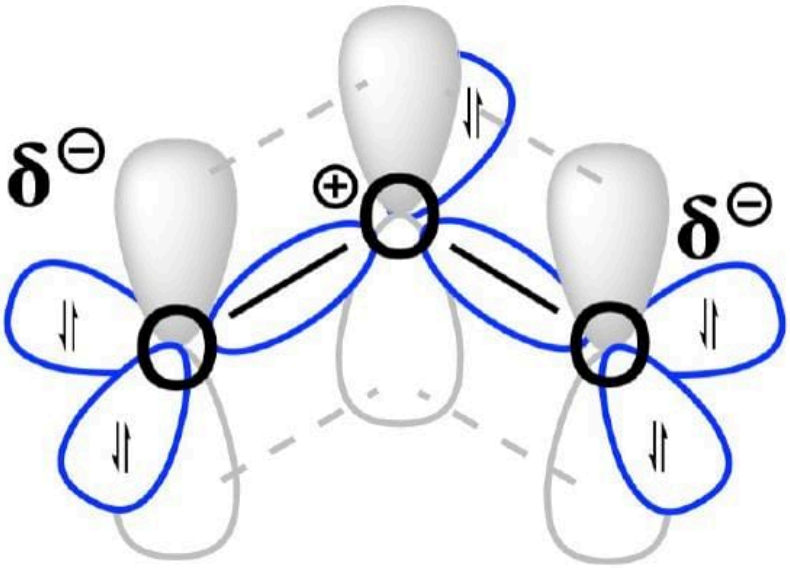


Figure 4.8.4: Delocalized molecular orbitals in Ozone.

Minor Resonance Contributors

While O_3 (above) has two equal resonance contributors, delocalization will occur when possible, even when this involves minor resonance contributors, as shown in Figure 4.8.5.

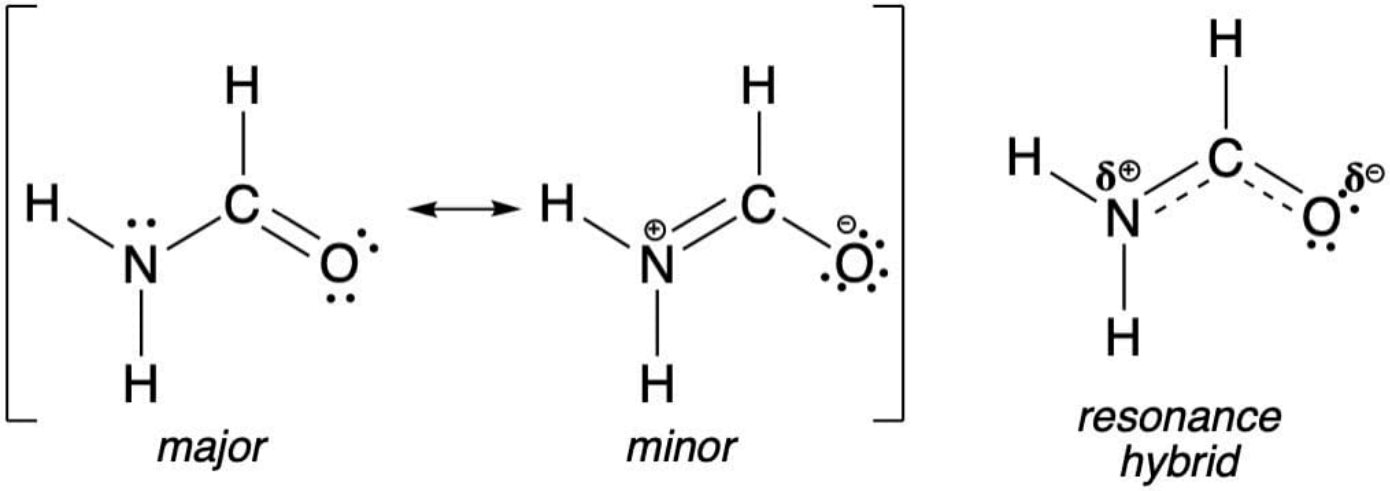


Figure 4.8.5: Major and Minor resonance forms of formamide, and its resonance hybrid.

The resulting hybridization of each atom in formamide will be in accordance with the resonance hybrid, which means that N, C, and O will each have an unhybridized p orbital as part of the delocalized molecular orbital. The hybridizations can be seen in Figure 4.8.6.

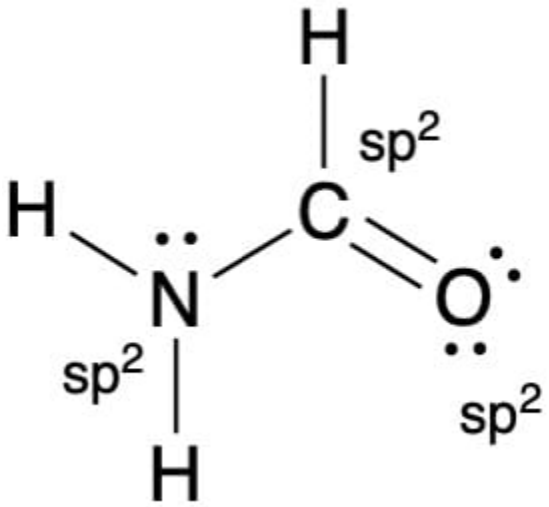


Figure 4.8.6: Hybridization of atoms in formamide due to resonance delocalization.

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4.9: Hybridized Orbital Energy Diagrams

Mixing Hybridized Orbitals and Formation of Antibonding orbitals

As shown in Section 4.3, the energy levels of hybridized atomic orbitals are a weighted average of the mixed atomic orbitals (Figure 4.9.1). When two hybridized atoms approach each other, the orbitals mix to form bonds. However, as with hybridization, mixing of orbitals results in the exact same number of mixed orbitals as there were originally. This means that for every bonding orbital between atoms, there is an antibonding orbital, which is not shown in the diagrams in Chapter 4.3, for the sake of simplicity. Bonding orbitals are lower in energy than the starting atomic orbitals, and the corresponding antibonding orbitals are higher in energy.

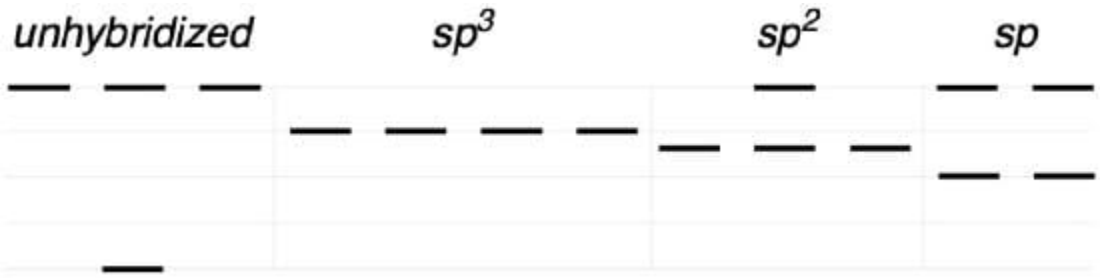


Figure 4.9.1: orbital energies of hybridized orbitals.

Bonding interactions with a large amount of spatial overlap will be the strongest (e.g., σ bonds) and those with less spatial overlap will be weaker (e.g., π bonds). Each interaction between hybridized orbitals will create an in-phase bonding interaction and an out-of-phase antibonding interaction. For more on bonding, antibonding, and phases of orbitals, see Chapter 4.5: Molecular Orbital Theory.

Hybridized orbital energy levels will vary based on the number of s and p orbitals that are hybridized. For example, sp hybridized orbitals have 50% "s-character" and 50% "p-character" and thus their energy will be halfway between the starting s and p orbital energies, and thus lower in energy than an sp^2 orbital on the same element (Figure 4.9.1).

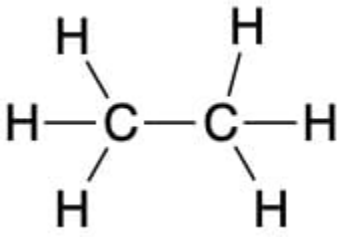
In the same way that we can use hybridized atoms to form bonds through overlapping hybridized orbitals in Chapter 4.3 and 4.4, we can form bonds between the orbitals using energy diagrams to gain insight into the energy levels of different bonds.

Example 4.9.1: Hybridized orbital energy diagram of ethane (C_2H_6)

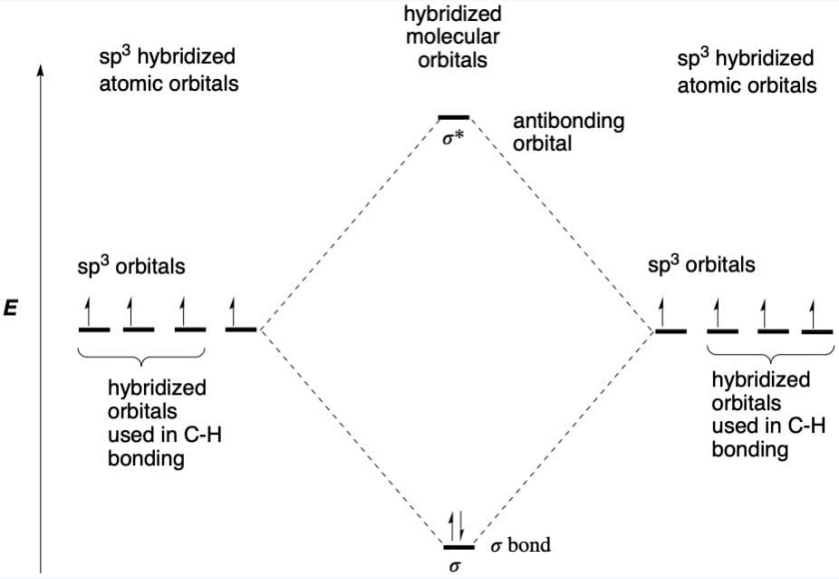
Draw the hybridized orbital energy diagram of the C-C bond in ethane (C_2H_6). What is the lowest energy unoccupied orbital in this diagram?

Solution

1. The Lewis structure of ethane shows a single bond between the two carbons and single bonds with the six Hs.



2. The carbons in ethene are both sp3 hybridized, which gives us four sp^3 orbitals. One of the hybridized orbitals on each carbon is involved in σ bonding (stronger interaction, lower energy bonding orbital). These two orbitals interact to form the bonding interaction, as well as an antibonding interaction. The remaining hybridized orbitals are involved in C-H bonds. There are no lone pairs or π bonds.



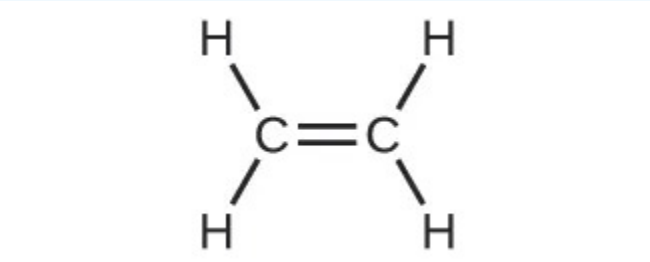
Example 4.9.1 shows how the starting hybridized *atomic* orbitals from Figure 4.9.1 mix to form bonding interactions and antibonding interactions in *molecular* orbitals.

Example 4.9.2: Hybridized orbital energy diagram of ethene (C_2H_4)

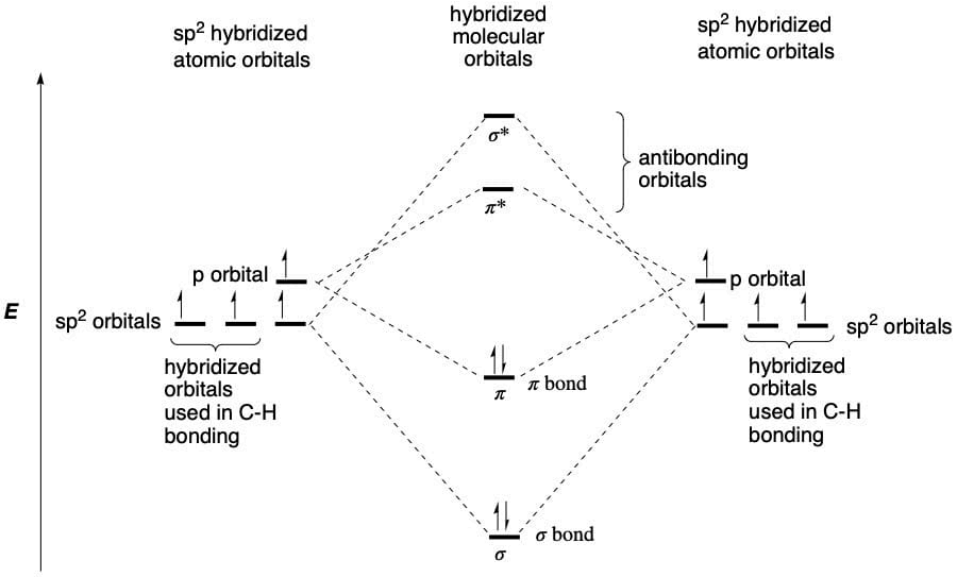
Draw the hybridized orbital energy diagram of the C-C bond in ethene (C_2H_4). What is the lowest energy unoccupied orbital in this diagram?

Solution

1. The Lewis structure of ethene shows a double bond between the two carbons and single bonds with the four Hs.



2. The carbons in ethene are both sp^2 hybridized, which gives us one un-hybridized p orbital on each carbon atom and three sp^2 orbitals. One of the hybridized orbitals on each carbon is involved in σ bonding (stronger interaction, lower energy bonding orbital) and the un-hybridized p orbital on each carbon is involved in π bonding (weaker interaction). These interactions can be shown in the following diagram:



Example 4.9.2 shows how the starting hybridized *atomic* orbitals from Figure 4.9.1 mix to form bonding interactions and antibonding interactions in *molecular* orbitals. These molecular orbitals have different energies based on the overlap between the starting hybridized orbitals. The σ bond is formed between two sp^2 hybridized orbitals, which point towards each other, as shown in Chapter 4.4. This strong overlap in atomic orbitals results in a lower energy and more stable bonding orbital. The two p orbitals have less spatial overlap, and thus the bond is less strong between these atomic orbitals, and the corresponding bonding orbital is higher in energy. The stabilization gained in each bonding interaction is proportional to the destabilization of the antibonding orbitals.

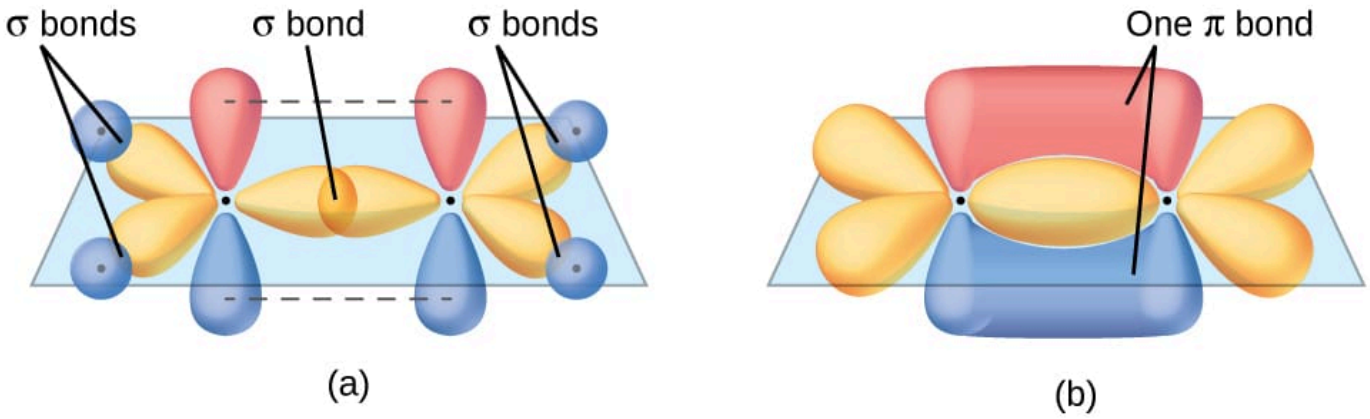


Figure 4.9.2: In the ethene molecule, C_2H_4, there are (a) five σ bonds. One C–C σ bond results from overlap of sp^2 hybrid orbitals on the carbon atom with one sp^2 hybrid orbital on the other carbon atom. Four C–H bonds result from the overlap between the C atoms' sp^2 orbitals with s orbitals on the hydrogen atoms. (b) The π bond is formed by the side-by-side overlap of the two unhybridized *p* orbitals in the two carbon atoms. The two lobes of the π bond are above and below the plane of the σ system. Note: hybridized orbitals are shown as the major lobe to simplify the drawing.

Exercise 4.9.2

Using hybridized orbital energy diagrams for bonding in HCN and $H_2C{=}NH$,

A) What are the hybridizations of each C and N?

B) Which lone pair is highest in energy between these two molecules?

Answer available at the end of this section.

Drawing Bonding and Antibonding Orbitals Starting with Hybridized Orbitals

Figure 4.9.2 (above) shows a cartoon depiction of the bonding orbitals in ethene. These bonding orbitals are formed in the same way bonding orbitals in Molecular Orbital Diagrams are formed, through overlapping atomic orbitals. The corresponding antibonding orbitals can also be drawn in analogy to molecular orbitals (Chapter 4.5).

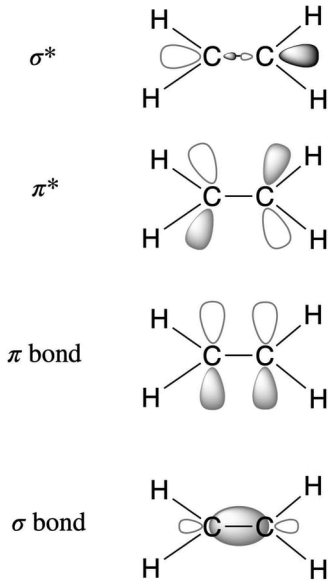


Figure 4.9.3: bonding and antibonding orbitals formed with hybridized orbitals in ethene.

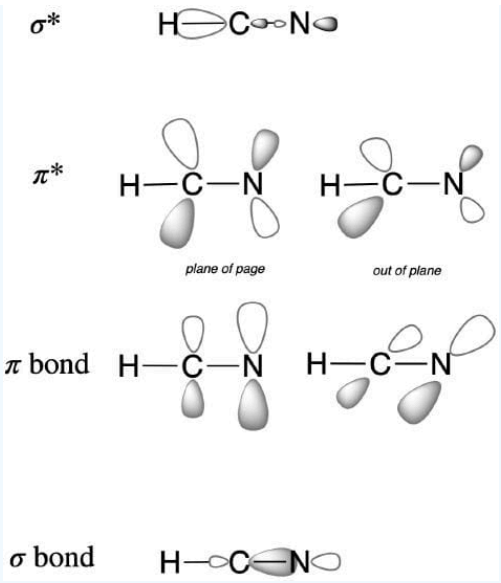
The orbitals shown in Figure 4.9.3 have left and right lobes with the same "orbital density" because the left and right atoms have identical atomic orbitals. These orbitals will distort based on the electronegativities and atomic orbital energies of the starting orbitals - so bonds with two different elements or different hybridizations will have different shapes.

Example 4.9.3: Drawing molecular orbitals with hybridized atoms with different electronegativities.

Draw the molecular orbitals (bonding and antibonding) corresponding to the C-N bond in HCN, using the solution to Exercise 4.9.2.

Solution

The orbitals we need to draw are the σ, σ*, π, and π*. Looking at the solution to Exercise 4.9.2, we can find that σ and π are closer in energy to N (more electronegative) and the σ* and π* are closer in energy to C. Thus, our bonding orbitals should be distorted toward N, and our antibonding orbitals will be distorted toward C.

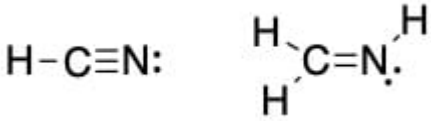


Example 4.9.3 shows how the molecular orbitals formed from hybridized atomic orbitals appear when distorted by atoms with different electronegativities. The p orbitals are combined to form two perpendicular π orbitals (in plane and out of plane) and two perpendicular π* orbitals. The σ and σ* orbitals are formed through the combination of sp hybridized orbitals, and are distorted by the difference in electronegativity between carbon and nitrogen.

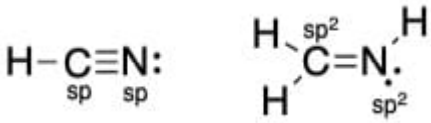
Answers

Exercise 4.9.2

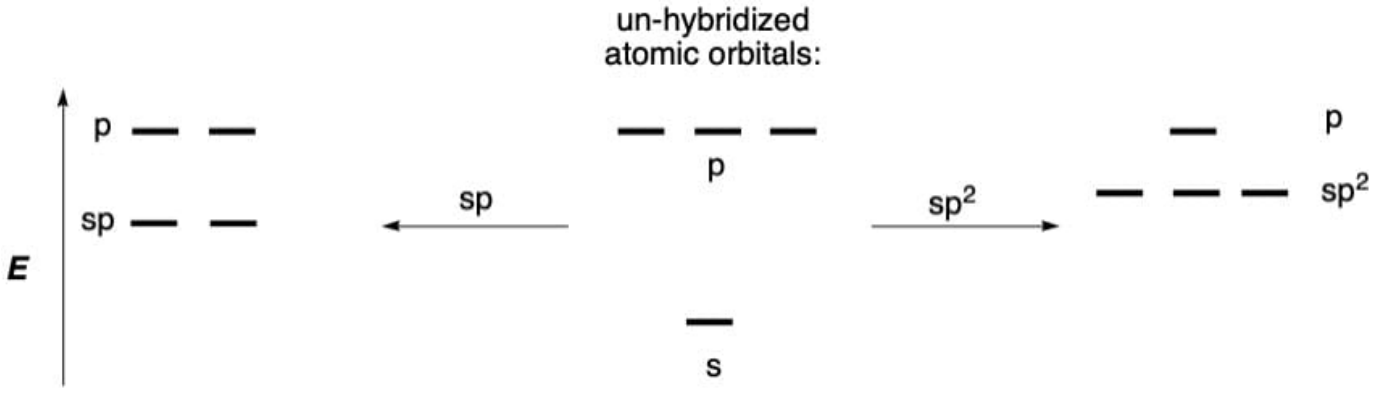
First, we need to draw the Lewis structures of each molecule, as shown below.



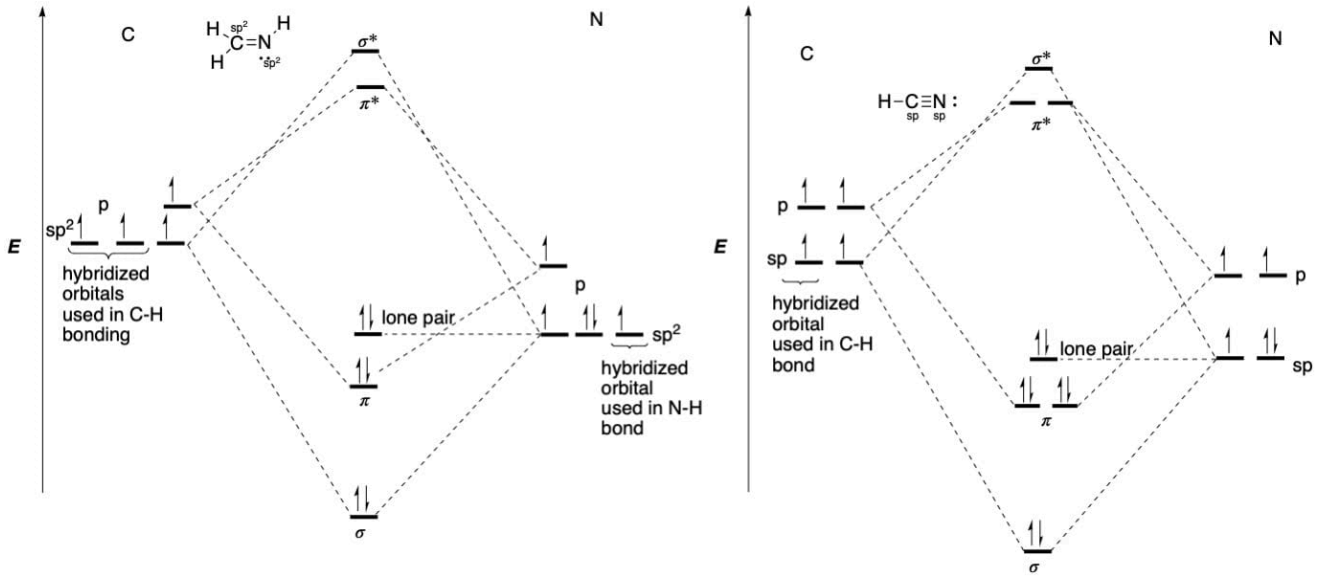
Then, we can assign their hybridizations based on the Lewis structures (Solution to A):



The hybridizations and Lewis structures will allow us to assign starting energies to the hybridized atomic orbitals:



Using these starting energies and the bonding shown in the Lewis structure, we can construct two hybridized orbital energy diagrams.



Now, using the hybridization of the N atoms in each diagram, we can see that an sp hybridized lone pair will be lower in energy than an sp^2 hybridized lone pair. Thus, the higher energy lone pair will be the lone pair in $H_2C{=}NH$.

Note 1: The nitrogen orbitals start lower in energy than the carbon orbitals, because N is more electronegative than C.

Note 2: The nitrogen orbitals are further apart than the carbon orbitals, because the s orbitals are more affected by electronegativity than p orbitals, which leads to a larger s/p orbital difference.

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4.10: Key Terms

antibonding orbital
molecular orbital located outside of the region between two nuclei; electrons in an antibonding orbital destabilize the molecule

bond order
number of pairs of electrons between two atoms; it can be found by the number of bonds in a Lewis structure or by the difference between the number of bonding and antibonding electrons divided by two

bonding orbital
molecular orbital located between two nuclei; electrons in a bonding orbital stabilize a molecule

degenerate orbitals
orbitals that have the same energy

diamagnetism
phenomenon in which a material is not magnetic itself but is repelled by a magnetic field; it occurs when there are only paired electrons present

homonuclear diatomic molecule
molecule consisting of two identical atoms

hybrid orbital
orbital created by combining atomic orbitals on a central atom

hybridization
model that describes the changes in the atomic orbitals of an atom when it forms a covalent compound

linear combination of atomic orbitals
technique for combining atomic orbitals to create molecular orbitals

molecular orbital
region of space in which an electron has a high probability of being found in a molecule

molecular orbital diagram
visual representation of the relative energy levels of molecular orbitals

molecular orbital theory
model that describes the behavior of electrons delocalized throughout a molecule in terms of the combination of atomic wave functions

node
plane separating different lobes of orbitals, where the probability of finding an electron is zero

overlap
coexistence of orbitals from two different atoms sharing the same region of space, leading to the formation of a covalent bond

paramagnetism
phenomenon in which a material is not magnetic itself but is attracted to a magnetic field; it occurs when there are unpaired electrons present

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

s-p mixing
change that causes σ_p orbitals to be less stable than π_p orbitals due to the mixing of s and *p*-based molecular

orbitals of similar energies.

sigma bond (σ bond)
covalent bond formed by overlap of atomic orbitals along the internuclear axis

***sp* hybrid orbital**
one of a set of two orbitals with a linear arrangement that results from combining one *s* and one *p* orbital

***sp*^{2} hybrid orbital**
one of a set of three orbitals with a trigonal planar arrangement that results from combining one *s* and two *p* orbitals

***sp*^{3} hybrid orbital**
one of a set of four orbitals with a tetrahedral arrangement that results from combining one *s* and three *p* orbitals

***sp*^{3}*d* hybrid orbital**
one of a set of five orbitals with a trigonal bipyramidal arrangement that results from combining one *s*, three *p*, and one *d* orbital

***sp*^{3}*d*^{2} hybrid orbital**
one of a set of six orbitals with an octahedral arrangement that results from combining one *s*, three *p*, and two *d* orbitals

valence bond theory
description of bonding that involves atomic orbitals overlapping to form σ or π bonds, within which pairs of electrons are shared

π bonding orbital
molecular orbital formed by side-by-side overlap of atomic orbitals, in which the electron density is found on opposite sides of the internuclear axis

π* bonding orbital
antibonding molecular orbital formed by out of phase side-by-side overlap of atomic orbitals, in which the electron density is found on both sides of the internuclear axis, and there is a node between the nuclei

σ bonding orbital
molecular orbital in which the electron density is found along the axis of the bond

σ* bonding orbital
antibonding molecular orbital formed by out-of-phase overlap of atomic orbital along the axis of the bond, generating a node between the nuclei

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4.11: Key Equations

$$\text{bond order } = \frac{(\text{ number of bonding electron }) - (\text{ number of antibonding electrons })}{2}$$

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4.12: Summary

Valence bond theory describes bonding as a consequence of the overlap of two separate atomic orbitals on different atoms that creates a region with one pair of electrons shared between the two atoms. When the orbitals overlap along an axis containing the nuclei, they form a σ bond. When they overlap in a fashion that creates a node along this axis, they form a π bond. Dipole moments can be used to determine partial separations of charges between atoms.

We can use hybrid orbitals, which are mathematical combinations of some or all of the valence atomic orbitals, to describe the electron density around covalently bonded atoms. These hybrid orbitals either form sigma (σ) bonds directed toward other atoms of the molecule or contain lone pairs of electrons. We can determine the type of hybridization around a central atom from the geometry of the regions of electron density about it. Two such regions imply sp hybridization; three, sp^2 hybridization; four, sp^3 hybridization; five, sp^3d hybridization; and six, sp^3d^2 hybridization. Pi (π) bonds are formed from unhybridized atomic orbitals (p or d orbitals).

Multiple bonds consist of a σ bond located along the axis between two atoms and one or two π bonds. The σ bonds are usually formed by the overlap of hybridized atomic orbitals, while the π bonds are formed by the side-by-side overlap of unhybridized orbitals. Resonance occurs when there are multiple unhybridized orbitals with the appropriate alignment to overlap, so the placement of π bonds can vary.

Molecular orbital (MO) theory describes the behavior of electrons in a molecule in terms of combinations of the atomic wave functions. The resulting molecular orbitals may extend over all the atoms in the molecule. Bonding molecular orbitals are formed by in-phase combinations of atomic wave functions, and electrons in these orbitals stabilize a molecule. Antibonding molecular orbitals result from out-of-phase combinations of atomic wave functions and electrons in these orbitals make a molecule less stable. Molecular orbitals located along an internuclear axis are called σ MOs. They can be formed from s orbitals or from p orbitals oriented in an end-to-end fashion. Molecular orbitals formed from p orbitals oriented in a side-by-side fashion have electron density on opposite sides of the internuclear axis and are called π orbitals.

We can describe the electronic structure of diatomic molecules by applying molecular orbital theory to the valence electrons of the atoms. Electrons fill molecular orbitals following the same rules that apply to filling atomic orbitals; Hund's rule and the Aufbau principle tell us that lower-energy orbitals will fill first, electrons will spread out before they pair up, and each orbital can hold a maximum of two electrons with opposite spins. Materials with unpaired electrons are paramagnetic and attracted to a magnetic field, while those with all-paired electrons are diamagnetic and repelled by a magnetic field. Correctly predicting the magnetic properties of molecules is in advantage of molecular orbital theory over Lewis structures and valence bond theory.

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4.13: Exercises

1.

Explain how σ and π bonds are similar and how they are different.

2.

Use valence bond theory to explain the bonding in F_2, HF, and ClBr. Sketch the overlap of the atomic orbitals involved in the bonds.

3.

Use valence bond theory to explain the bonding in O_2. Sketch the overlap of the atomic orbitals involved in the bonds in O_2.

4.

How many σ and π bonds are present in the molecule HCN?

5.

A friend tells you N_2 has three π bonds due to overlap of the three *p*-orbitals on each N atom. Do you agree?

6.

Draw the Lewis structures for CO_2 and CO, and predict the number of σ and π bonds for each molecule.

(a) CO_2

(b) CO

7.

Why is the concept of hybridization required in valence bond theory?

8.

Give the shape that describes each hybrid orbital set:

(a) sp^2

(b) sp^3d

(c) sp

(d) sp^3d^2

9.

Explain why a carbon atom cannot form five bonds using sp^3d hybrid orbitals.

10.

What is the hybridization of the central atom in each of the following?

(a) BeH_2

(b) SF_6

(c) PO43–PO43–

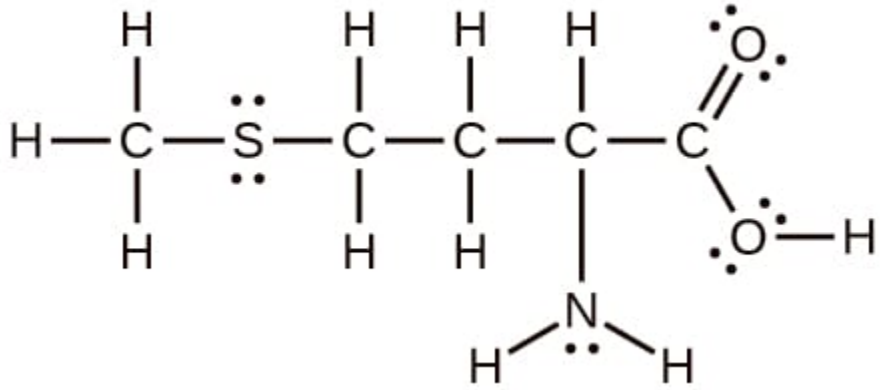
(d) PCl_5

11.

A molecule with the formula AB_3 could have one of four different shapes. Give the shape and the hybridization of the central A atom for each.

12.

Methionine, $CH_3SCH_2CH_2CH(NH_2)CO_2H$, is an amino acid found in proteins. The Lewis structure of this compound is shown below. What is the hybridization type of each carbon, oxygen, the nitrogen, and the sulfur?



13.

Sulfuric acid is manufactured by a series of reactions represented by the following equations:
S8(s)+8O2(g)⟶8SO2(g)S8(s)+8O2(g)⟶8SO2(g)
2SO2(g)+O2(g)⟶2SO3(g)2SO2(g)+O2(g)⟶2SO3(g)
SO3(g)+H2O(l)⟶H2SO4(l)SO3(g)+H2O(l)⟶H2SO4(l)

Draw a Lewis structure, predict the molecular geometry by VSEPR, and determine the hybridization of sulfur for the following:

(a) circular S_8 molecule

(b) SO_2 molecule

(c) SO_3 molecule

(d) H_2SO_4 molecule (the hydrogen atoms are bonded to oxygen atoms)

14.

Two important industrial chemicals, ethene, C_2H_4, and propene, C_3H_6, are produced by the steam (or thermal) cracking process:

2 C 3 H 8 (g) ⟶ C 2 H 4 (g) + C 3 H 6 (g) + CH 4 (g) + H 2 (g) 2 C 3 H 8 (g) ⟶ C 2 H 4 (g) + C 3 H 6 (g) + CH 4 (g) + H 2 (g)

For each of the four carbon compounds, do the following:

(a) Draw a Lewis structure.

(b) Predict the geometry about the carbon atom.

(c) Determine the hybridization of each type of carbon atom.

15.

Analysis of a compound indicates that it contains 77.55% Xe and 22.45% F by mass.

(a) What is the empirical formula for this compound? *(Assume this is also the molecular formula in responding to the remaining parts of this exercise).*

(b) Write a Lewis structure for the compound.

(c) Predict the shape of the molecules of the compound.

(d) What hybridization is consistent with the shape you predicted?

16.

Consider nitrous acid, HNO_2 (HONO).

(a) Write a Lewis structure.

(b) What are the electron pair and molecular geometries of the internal oxygen and nitrogen atoms in the HNO_2 molecule?

(c) What is the hybridization on the internal oxygen and nitrogen atoms in HNO_2?

17.

Strike-anywhere matches contain a layer of $KClO_3$ and a layer of P_4S_3. The heat produced by the friction of striking the match causes these two compounds to react vigorously, which sets fire to the wooden stem of the match. $KClO_3$ contains the ClO3−ClO3− ion. P_4S_3 is an unusual molecule with the skeletal structure.



(a) Write Lewis structures for P_4S_3 and the ClO3–ClO3– ion.

(b) Describe the geometry about the P atoms, the S atom, and the Cl atom in these species.

(c) Assign a hybridization to the P atoms, the S atom, and the Cl atom in these species.

(d) Determine the oxidation states and formal charge of the atoms in P_4S_3 and the ClO3–ClO3– ion.

18.

Identify the hybridization of each carbon atom in the following molecule. (The arrangement of atoms is given; you need to determine how many bonds connect each pair of atoms.)



19.

Write Lewis structures for NF_3 and PF_5. On the basis of hybrid orbitals, explain the fact that NF_3, PF_3, and PF_5 are stable molecules, but NF_5 does not exist.

20.

In addition to NF_3, two other fluoro derivatives of nitrogen are known: N_2F_4 and N_2F_2. What shapes do you predict for these two molecules? What is the hybridization for the nitrogen in each molecule?

21.

The bond energy of a C–C single bond averages 347 kJ mol^{-1}; that of a C≡CC≡C triple bond averages 839 kJ mol^{-1}. Explain why the triple bond is not three times as strong as a single bond.

22.

For the carbonate ion, CO32–,CO32–, draw all of the resonance structures. Identify which orbitals overlap to create each bond.

23.

A useful solvent that will dissolve salts as well as organic compounds is the compound acetonitrile, H_3CCN. It is present in paint strippers.

(a) Write the Lewis structure for acetonitrile, and indicate the direction of the dipole moment in the molecule.

(b) Identify the hybrid orbitals used by the carbon atoms in the molecule to form σ bonds.

(c) Describe the atomic orbitals that form the π bonds in the molecule. Note that it is not necessary to hybridize the nitrogen atom.

24.

For the molecule allene, H2C=C=CH2,H2C=C=CH2, give the hybridization of each carbon atom. Will the hydrogen atoms be in the same plane or perpendicular planes?

25.

Identify the hybridization of the central atom in each of the following molecules and ions that contain multiple bonds:

(a) ClNO (N is the central atom)

(b) CS_2

(c) Cl_2CO (C is the central atom)

(d) Cl_2SO (S is the central atom)

(e) SO_2F_2 (S is the central atom)

(f) XeO_2F_2 (Xe is the central atom)

(g) ClOF2+ClOF2+ (Cl is the central atom)

26.

Describe the molecular geometry and hybridization of the N, P, or S atoms in each of the following compounds.

(a) H_3PO_4, phosphoric acid, used in cola soft drinks

(b) NH_4NO_3, ammonium nitrate, a fertilizer and explosive

(c) S_2Cl_2, disulfur dichloride, used in vulcanizing rubber

(d) $K_4[O_3POPO_3]$, potassium pyrophosphate, an ingredient in some toothpastes

27.

For each of the following molecules, indicate the hybridization requested and whether or not the electrons will be delocalized:

(a) ozone (O_3) central O hybridization

(b) carbon dioxide (CO_2) central C hybridization

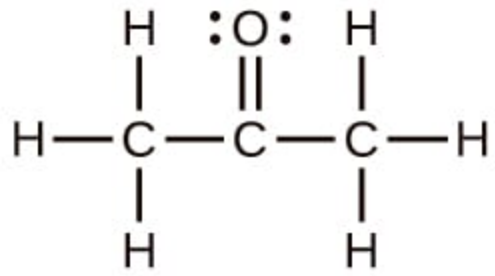
(c) nitrogen dioxide (NO_2) central N hybridization

(d) phosphate ion (PO43−)(PO43−) central P hybridization

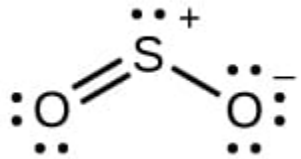
28.

For each of the following structures, determine the hybridization requested and whether the electrons will be delocalized:

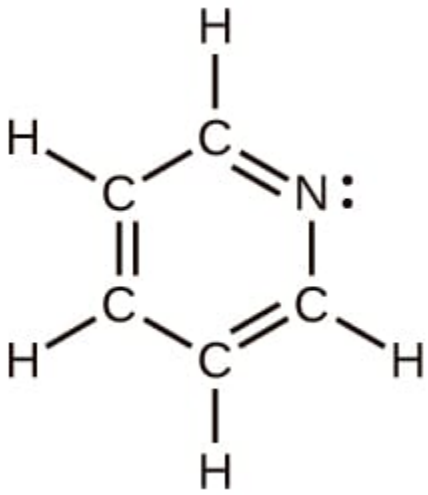
(a) Hybridization of each carbon



(b) Hybridization of sulfur



(c) All atoms



29.

Draw the orbital diagram for carbon in CO_2 showing how many carbon atom electrons are in each orbital.

30.

Sketch the distribution of electron density in the bonding and antibonding molecular orbitals formed from two s orbitals and from two *p* orbitals.

31.

How are the following similar, and how do they differ?

(a) σ molecular orbitals and π molecular orbitals

(b) ψ for an atomic orbital and ψ for a molecular orbital

(c) bonding orbitals and antibonding orbitals

32.

If molecular orbitals are created by combining five atomic orbitals from atom A and five atomic orbitals from atom B combine, how many molecular orbitals will result?

33.

Can a molecule with an odd number of electrons ever be diamagnetic? Explain why or why not.

34.

Can a molecule with an even number of electrons ever be paramagnetic? Explain why or why not.

35.

Why are bonding molecular orbitals lower in energy than the parent atomic orbitals?

36.

Calculate the bond order for an ion with this configuration:

(σ 2 s) 2 (σ 2 s *) 2 (σ 2 p x) 2 (π 2 p y , π 2 p z) 4 (π 2 p y * , π 2 p z *) 3 (σ 2 s) 2 (σ 2 s *) 2 (σ 2 p x) 2 (π 2 p y , π 2 p z) 4 (π 2 p y * , π 2 p z *) 3

37.

Explain why an electron in the bonding molecular orbital in the H_2 molecule has a lower energy than an electron in the 1s atomic orbital of either of the separated hydrogen atoms.

38.

Predict the valence electron molecular orbital configurations for the following, and state whether they will be stable or unstable ions.

(a) Na22+Na22+

(b) Mg22+Mg22+

(c) Al22+Al22+

(d) Si22+Si22+

(e) P22+P22+

(f) S22+S22+

(g) F22+F22+

(h) Ar22+Ar22+

39.

Determine the bond order of each member of the following groups, and determine which member of each group is predicted by the molecular orbital model to have the strongest bond.

(a) H_2, H2+,H2+, H2−H2−

(b) O_2, O22+,O22+, O22−O22−

(c) Li_2, Be2+,Be2+, Be_2

(d) F_2, F2+,F2+, F2−F2−

(e) N_2, N2+,N2+, N2−N2−

40.

For the first ionization energy for an N_2 molecule, what molecular orbital is the electron removed from?

41.

Compare the atomic and molecular orbital diagrams to identify the member of each of the following pairs that has the highest first ionization energy (the most tightly bound electron) in the gas phase:

(a) H and H_2

(b) N and N_2

(c) O and O_2

(d) C and C_2

(e) B and B_2

42.

Which of the period 2 homonuclear diatomic molecules are predicted to be paramagnetic?

43.

A friend tells you that the 2s orbital for fluorine starts off at a much lower energy than the 2s orbital for lithium, so the resulting σ_{2s} molecular orbital in F_2 is more stable than in Li_2. Do you agree?

44.

True or false: Boron contains $2s^2 2p^1$ valence electrons, so only one *p* orbital is needed to form molecular orbitals.

45.

What charge would be needed on F_2 to generate an ion with a bond order of 2?

46.

Predict whether the MO diagram for S_2 would show s-p mixing or not.

47.

Explain why N_2^{2+} is diamagnetic, while O_2^{4+}, which has the same number of valence electrons, is paramagnetic.

48.

Using the MO diagrams, predict the bond order for the stronger bond in each pair:

(a) B_2 or B_2^{2+}

(b) F_2 or F_2^{2+}

(c) O_2 or O_2^{2+}

(d) C_2^{2+} or C_2^{2-}

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5: THERMOCHEMISTRY

5.1: Introduction

5.2: Energy Basics

5.3: Calorimetry

5.4: Enthalpy

5.5: Strengths of Ionic and Covalent Bonds

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5.1: Introduction

Chemical reactions, such as those that occur when you light a match, involve changes in energy as well as matter. Societies at all levels of development could not function without the energy released by chemical reactions. In 2012, about 85% of US energy consumption came from the combustion of petroleum products, coal, wood, and garbage. We use this energy to produce electricity (38%); to transport food, raw materials, manufactured goods, and people (27%); for industrial production (21%); and to heat and power our homes and businesses (10%).[1] While these combustion reactions help us meet our essential energy needs, they are also recognized by the majority of the scientific community as a major contributor to global climate change.



Figure 5.1.1: Sliding a match head along a rough surface initiates a combustion reaction that produces energy in the form of heat and light. (credit: modification of work by Laszlo Ilyes)

Useful forms of energy are also available from a variety of chemical reactions other than combustion. For example, the energy produced by the batteries in a cell phone, car, or flashlight results from chemical reactions. This chapter introduces many of the basic ideas necessary to explore the relationships between chemical changes and energy, with a focus on thermal energy.

The chemical bond is simply another form of energy, and its strength is indicated in exactly the same units as any other process involving energy. That is, in joules (or kilojoules) – or, when taken on a molar basis, in J/mol or kJ/mol. All of the principles involving energy we have examined up to now apply to bond energies exactly as they do to all other forms of energy: that is, energy may change form or be absorbed or released, but it cannot be created or destroyed. The energy of a chemical bond is indicated by the bond enthalpy, taken by convention to be the energy required to break a chemical bond. The same energy is released when a chemical bond is formed. Given that a chemical reaction involves breaking some bonds and making others, the enthalpy change for a chemical reaction can be estimated by analyzing the bonds broken and formed during the reaction. While this procedure gives an estimate of the overall enthalpy, it should be noted that a far more precise method involves using enthalpies of formation; the fact that there can be significant differences between, for example, an O–H bond in water and that in acetic acid accounts for the discrepancy in calculating ΔH using bond enthalpies versus the use of enthalpies of formation.

Footnotes

- 1US Energy Information Administration, *Primary Energy Consumption by Source and Sector, 2012*, http://www.eia.gov/totalenergy/data/...012_energy.pdf. Data derived from US Energy Information Administration, *Monthly Energy Review* (January 2014).

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5.2: Energy Basics

Learning Objectives

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

- Define energy, distinguish types of energy, and describe the nature of energy changes that accompany chemical and physical changes
- Distinguish the related properties of heat, thermal energy, and temperature
- Define and distinguish specific heat and heat capacity, and describe the physical implications of both
- Perform calculations involving heat, specific heat, and temperature change

Chemical changes and their accompanying changes in energy are important parts of our everyday world (Figure 5.2.1). The macronutrients in food (proteins, fats, and carbohydrates) undergo metabolic reactions that provide the energy to keep our bodies functioning. We burn a variety of fuels (gasoline, natural gas, coal) to produce energy for transportation, heating, and the generation of electricity. Industrial chemical reactions use enormous amounts of energy to produce raw materials (such as iron and aluminum). Energy is then used to manufacture those raw materials into useful products, such as cars, skyscrapers, and bridges.



Figure 5.2.1: The energy involved in chemical changes is important to our daily lives: (a) A cheeseburger for lunch provides the energy you need to get through the rest of the day; (b) the combustion of gasoline provides the energy that moves your car (and you) between home, work, and school; and (c) coke, a processed form of coal, provides the energy needed to convert iron ore into iron, which is essential for making many of the products we use daily. (credit a: modification of work by "Pink Sherbet Photography"/Flickr; credit b: modification of work by Jeffery Turner)

Over 90% of the energy we use comes originally from the sun. Every day, the sun provides the earth with almost 10,000 times the amount of energy necessary to meet all of the world's energy needs for that day. Our challenge is to find ways to convert and store incoming solar energy so that it can be used in reactions or chemical processes that are both convenient and nonpolluting. Plants and many bacteria capture solar energy through photosynthesis. We release the energy stored in plants when we burn wood or plant products such as ethanol. We also use this energy to fuel our bodies by eating food that comes directly from plants or from animals that got their energy by eating plants. Burning coal and petroleum also releases stored solar energy: These fuels are fossilized plant and animal matter.

This chapter will introduce the basic ideas of an important area of science concerned with the amount of heat absorbed or released during chemical and physical changes—an area called thermochemistry. The concepts introduced in this chapter are widely used in almost all scientific and technical fields. Food scientists use them to determine the energy content of foods. Biologists study the energetics of living organisms, such as the metabolic combustion of sugar into carbon dioxide and water. The oil, gas, and transportation industries, renewable energy providers, and many others endeavor to find better methods to produce energy for our commercial and personal needs. Engineers strive to improve energy efficiency, find better ways to heat and cool our homes, refrigerate our food and drinks, and meet the energy and cooling needs of computers and electronics, among other applications. Understanding thermochemical principles is essential for chemists, physicists, biologists, geologists, every type of engineer, and just about anyone who studies or does any kind of science.

Energy

Energy can be defined as the capacity to supply heat or do work. One type of work (*w*) is the process of causing matter to move against an opposing force. For example, we do work when we inflate a bicycle tire—we move matter (the air in the pump) against the opposing force of the air already in the tire.

Like matter, energy comes in different types. One scheme classifies energy into two types: potential energy, the energy an object has because of its relative position, composition, or condition, and kinetic energy, the energy that an object possesses because of its motion. Water at the top of a waterfall or dam has potential energy because of its position; when it flows downward through generators, it has kinetic energy that can be used to do work and produce electricity in a hydroelectric plant (Figure 5.2.2). A battery has potential energy because the chemicals within it can produce electricity that can do work.



Figure 5.2.2: (a) Water at a higher elevation, for example, at the top of Victoria Falls, has a higher potential energy than water at a lower elevation. As the water falls, some of its potential energy is converted into kinetic energy. (b) If the water flows through generators at the bottom of a dam, such as the Hoover Dam shown here, its kinetic energy is converted into electrical energy. (credit a: modification of work by Steve Jurvetson; credit b: modification of work by "curimedia"/Wikimedia commons)

Energy can be converted from one form into another, but all of the energy present before a change occurs always exists in some form after the change is completed. This observation is expressed in the law of conservation of energy: during a chemical or physical change, energy can be neither created nor destroyed, although it can be changed in form. (This is also one version of the first law of thermodynamics, as you will learn later.)

When one substance is converted into another, there is always an associated conversion of one form of energy into another. Heat is usually released or absorbed, but sometimes the conversion involves light, electrical energy, or some other form of energy. For example, chemical energy (a type of potential energy) is stored in the molecules that compose gasoline. When gasoline is combusted within the cylinders of a car's engine, the rapidly expanding gaseous products of this chemical reaction generate mechanical energy (a type of kinetic energy) when they move the cylinders' pistons.

According to the law of conservation of matter (seen in an earlier chapter), there is no detectable change in the total amount of matter during a chemical change. When chemical reactions occur, the energy changes are relatively modest and the mass changes are too small to measure, so the laws of conservation of matter and energy hold well. However, in nuclear reactions, the energy changes are much larger (by factors of a million or so), the mass changes are measurable, and matter-energy conversions are significant. This will be examined in more detail in a later chapter on nuclear chemistry.

Thermal Energy, Temperature, and Heat

Thermal energy is kinetic energy associated with the random motion of atoms and molecules. Temperature is a quantitative measure of "hot" or "cold." When the atoms and molecules in an object are moving or vibrating quickly, they have a higher average kinetic energy (KE), and we say that the object is "hot." When the atoms and molecules are moving slowly, they have lower average

KE, and we say that the object is “cold” (Figure 5.2.3). Assuming that no chemical reaction or phase change (such as melting or vaporizing) occurs, increasing the amount of thermal energy in a sample of matter will cause its temperature to increase. And, assuming that no chemical reaction or phase change (such as condensation or freezing) occurs, decreasing the amount of thermal energy in a sample of matter will cause its temperature to decrease.

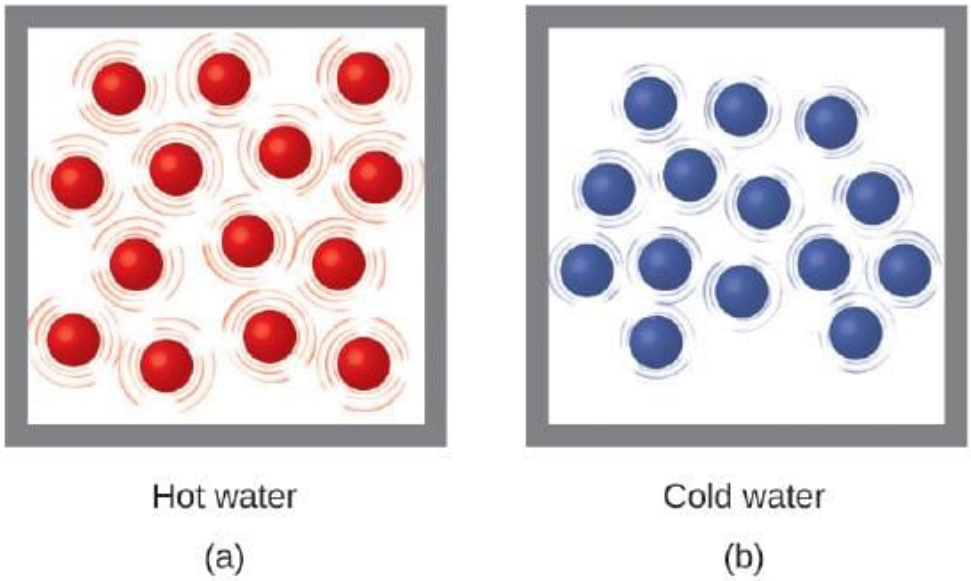


Figure 5.2.3: (a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.

Link to Learning

Click on this interactive simulation to view the effects of temperature on molecular motion.

Most substances expand as their temperature increases and contract as their temperature decreases. This property can be used to measure temperature changes, as shown in Figure 5.2.4. The operation of many thermometers depends on the expansion and contraction of substances in response to temperature changes.

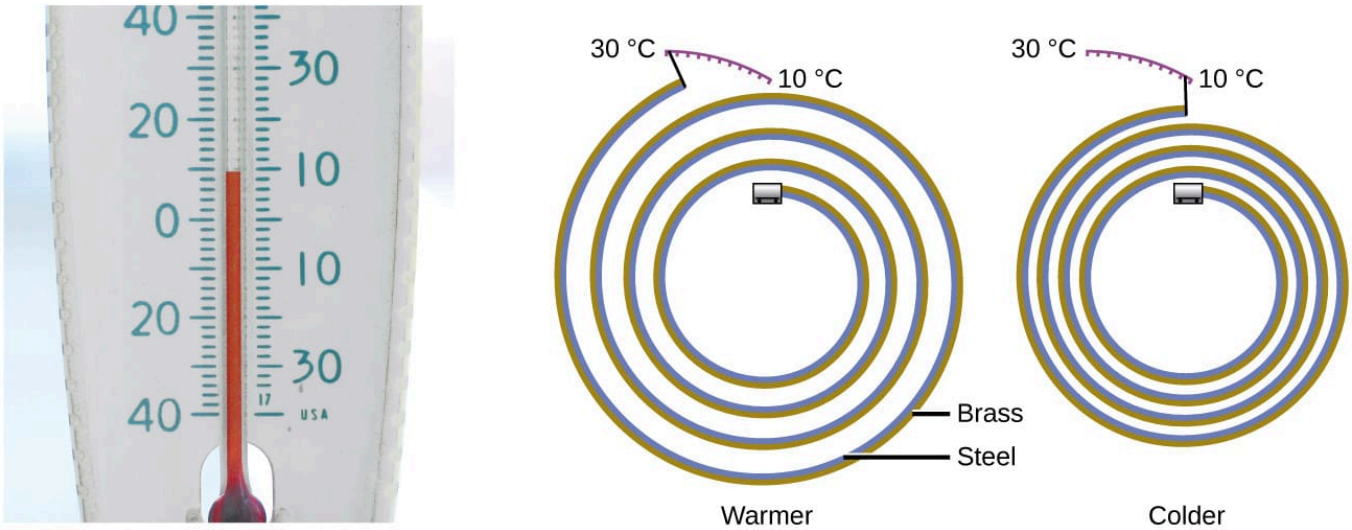


Figure 5.2.4: (a) In an alcohol or mercury thermometer, the liquid (dyed red for visibility) expands when heated and contracts when cooled, much more so than the glass tube that contains the liquid. (b) In a bimetallic thermometer, two different metals (such as brass and steel) form a two-layered strip. When heated or cooled, one of the metals (brass) expands or contracts more than the other metal (steel), causing the strip to coil or uncoil. Both types of thermometers have a calibrated scale that indicates the temperature. (credit a: modification of work by “dwstucke”/Flickr)

Link to Learning

The following demonstration allows one to view the effects of heating and cooling a coiled bimetallic strip.

Heat (q) is the transfer of thermal energy between two bodies at different temperatures. Heat flow (a redundant term, but one commonly used) increases the thermal energy of one body and decreases the thermal energy of the other. Suppose we initially have a high temperature (and high thermal energy) substance (H) and a low temperature (and low thermal energy) substance (L). The atoms and molecules in H have a higher average KE than those in L. If we place substance H in contact with substance L, the thermal energy will flow spontaneously from substance H to substance L. The temperature of substance H will decrease, as will the average KE of its molecules; the temperature of substance L will increase, along with the average KE of its molecules. Heat flow will continue until the two substances are at the same temperature (Figure 5.2.5).

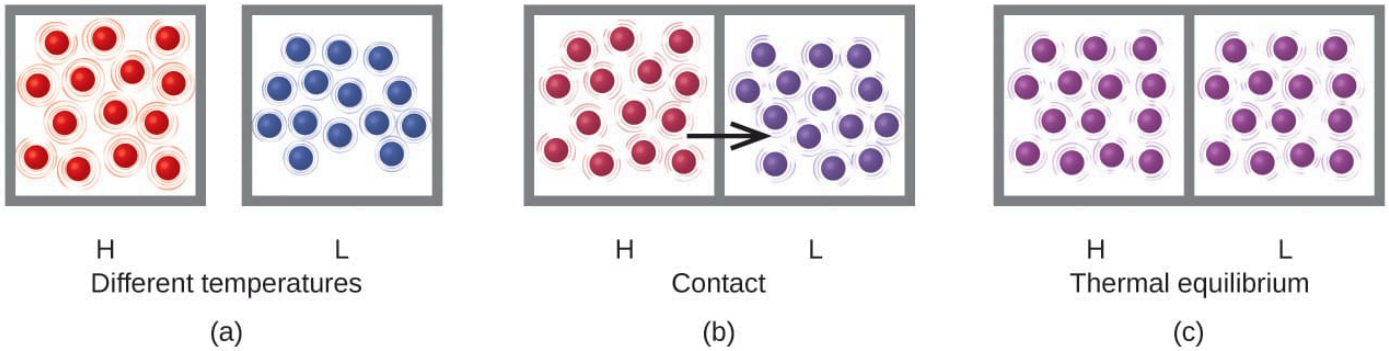


Figure 5.2.5: (a) Substances H and L are initially at different temperatures, and their atoms have different average kinetic energies. (b) When they contact each other, collisions between the molecules result in the transfer of kinetic (thermal) energy from the hotter to the cooler matter. (c) The two objects reach "thermal equilibrium" when both substances are at the same temperature and their molecules have the same average kinetic energy.

Link to Learning

Click on the PhET simulation to explore energy forms and changes. Visit the Energy Systems tab to create combinations of energy sources, transformation methods, and outputs. Click on Energy Symbols to visualize the transfer of energy.

Matter undergoing chemical reactions and physical changes can release or absorb heat. A change that releases heat is called an exothermic process. For example, the combustion reaction that occurs when using an oxyacetylene torch is an exothermic process—this process also releases energy in the form of light as evidenced by the torch's flame (Figure 5.2.6). A reaction or change that absorbs heat is an endothermic process. A cold pack used to treat muscle strains provides an example of an endothermic process. When the substances in the cold pack (water and a salt like ammonium nitrate) are brought together, the resulting process absorbs heat, leading to the sensation of cold.



Figure 5.2.6: (a) An oxyacetylene torch produces heat by the combustion of acetylene in oxygen. The energy released by this exothermic reaction heats and then melts the metal being cut. The sparks are tiny bits of the molten metal flying away. (b) A cold pack uses an endothermic process to create the sensation of cold. (credit a: modification of work by "Skatebiker"/Wikimedia commons)

Historically, energy was measured in units of calories (cal). A calorie is the amount of energy required to raise one gram of water by 1 degree C (1 kelvin). However, this quantity depends on the atmospheric pressure and the starting temperature of the water. The ease of measurement of energy changes in calories has meant that the calorie is still frequently used. The Calorie (with a capital C), or large calorie, commonly used in quantifying food energy content, is a kilocalorie. The SI unit of heat, work, and energy is the joule. A joule (J) is defined as the amount of energy used when a force of 1 newton moves an object 1 meter. It is named in honor of the English physicist James Prescott Joule. One joule is equivalent to 1 kg m^2/s^2, which is also called 1 newton–meter. A kilojoule (kJ) is 1000 joules. To standardize its definition, 1 calorie has been set to equal 4.184 joules.

We now introduce two concepts useful in describing heat flow and temperature change. The heat capacity (*C*) of a body of matter is the quantity of heat (*q*) it absorbs or releases when it experiences a temperature change (ΔT) of 1 degree Celsius (or equivalently, 1 kelvin):

$$C = \frac{q}{\Delta T}$$

Heat capacity is determined by both the type and amount of substance that absorbs or releases heat. It is therefore an extensive property—its value is proportional to the amount of the substance.

For example, consider the heat capacities of two cast iron frying pans. The heat capacity of the large pan is five times greater than that of the small pan because, although both are made of the same material, the mass of the large pan is five times greater than the mass of the small pan. More mass means more atoms are present in the larger pan, so it takes more energy to make all of those atoms vibrate faster. The heat capacity of the small cast iron frying pan is found by observing that it takes 18,150 J of energy to raise the temperature of the pan by 50.0 °C:

$$C_{\text{small pan}} = \frac{18,140J}{50.0°C} = 363J/°C$$

The larger cast iron frying pan, while made of the same substance, requires 90,700 J of energy to raise its temperature by 50.0 °C. The larger pan has a (proportionally) larger heat capacity because the larger amount of material requires a (proportionally) larger amount of energy to yield the same temperature change:

$$C_{\text{large pan}} = \frac{90,700J}{50.0°C} = 1814J/°C$$

The specific heat capacity (*c*) of a substance, commonly called its "specific heat," is the quantity of heat required to raise the temperature of 1 gram of a substance by 1 degree Celsius (or 1 kelvin):

$$c = \frac{q}{m\Delta T}$$

Specific heat capacity depends only on the kind of substance absorbing or releasing heat. It is an intensive property—the type, but not the amount, of the substance is all that matters. For example, the small cast iron frying pan has a mass of 808 g. The specific heat of iron (the material used to make the pan) is therefore:

$$c_{\text{iron}} = \frac{18,140J}{(808g)\,(50.0°C)} = 0.449J/g°C$$

The large frying pan has a mass of 4040 g. Using the data for this pan, we can also calculate the specific heat of iron:

$$c_{\text{iron}} = \frac{90,700J}{(4040g)\,(50.0°C)} = 0.449J/g°C$$

Although the large pan is more massive than the small pan, since both are made of the same material, they both yield the same value for specific heat (for the material of construction, iron). Note that specific heat is measured in units of energy per temperature per mass and is an intensive property, being derived from a ratio of two extensive properties (heat and mass). The molar heat capacity, also an intensive property, is the heat capacity per mole of a particular substance and has units of J/mol °C (Figure 5.2.7).



Figure 5.2.7: Because of its larger mass, a large frying pan has a larger heat capacity than a small frying pan. Because they are made of the same material, both frying pans have the same specific heat. (credit: Mark Blaser)

Water has a relatively high specific heat (about 4.2 J/g °C for the liquid and 2.09 J/g °C for the solid); most metals have much lower specific heats (usually less than 1 J/g °C). The specific heat of a substance varies somewhat with temperature. However, this variation is usually small enough that we will treat specific heat as constant over the range of temperatures that will be considered in this chapter. Specific heats of some common substances are listed in Table 5.2.1.

Table 5.2.1: Specific Heats of Common Substances at 25 °C and 1 bar

Substance	Symbol (*state*)	Specific Heat (J/g °C)
helium	He(*g*)	5.193
water	$H_2O(l)$	4.184
ethanol	$C_2H_6O(l)$	2.376
ice	$H_2O(s)$	2.093 (at –10 °C)
water vapor	$H_2O(g)$	1.864
nitrogen	$N_2(g)$	1.040

Substance	Symbol (*state*)	Specific Heat (J/g °C)
air		1.007
oxygen	$O_2(g)$	0.918
aluminum	Al(s)	0.897
carbon dioxide	$CO_2(g)$	0.853
argon	Ar(*g*)	0.522
iron	Fe(s)	0.449
copper	Cu(s)	0.385
lead	Pb(s)	0.130
gold	Au(s)	0.129
silicon	Si(s)	0.712

If we know the mass of a substance and its specific heat, we can determine the amount of heat, *q*, entering or leaving the substance by measuring the temperature change before and after the heat is gained or lost:

$$\begin{aligned} q &= (\text{ specific heat }) \times (\text{ mass of substance }) \times (\text{ temperature change }) \\ &= c \times m \times \Delta T \\ &= c \times m \times (T_{\text{final}} - T_{\text{initial}}) \end{aligned} \tag{5.2.1}$$

In this equation, *c* is the specific heat of the substance, *m* is its mass, and ΔT (which is read "delta T") is the temperature change, $T_{\text{final}} - T_{\text{initial}}$. If a substance gains thermal energy, its temperature increases, its final temperature is higher than its initial temperature, $T_{\text{final}} - T_{\text{initial}}$ has a positive value, and the value of *q* is positive. If a substance loses thermal energy, its temperature decreases, the final temperature is lower than the initial temperature, $T_{\text{final}} - T_{\text{initial}}$ has a negative value, and the value of *q* is negative.

Example 5.2.1: Measuring Heat

A flask containing $8.0\ 10^2$ g of water is heated, and the temperature of the water increases from 21 °C to 85 °C. How much heat did the water absorb?

Solution

To answer this question, consider these factors:

- the specific heat of the substance being heated (in this case, water)
- the amount of substance being heated (in this case, 8.0×10^2 g)
- the magnitude of the temperature change (in this case, from 21 °C to 85 °C).

The specific heat of water is 4.184 J/g °C, so to heat 1 g of water by 1 °C requires 4.184 J. We note that since 4.184 J is required to heat 1 g of water by 1 °C, we will need *800 times as much* to heat 8.0×10^2 g of water by 1 °C. Finally, we observe that since 4.184 J are required to heat 1 g of water by 1 °C, we will need *64 times as much* to heat it by 64 °C (that is, from 21 °C to 85 °C).

This can be summarized using Equation 5.2.1:

$$\begin{aligned} q = c \times m \times \Delta T &= c \times m \times (T_{\text{final}} - T_{\text{initial}}) \\ &= \left(4.184 J/\frac{g}{\circ}{}^{\circ}C\right) \times \left(8.0 \times 10^2 g\right) \times (85 - 21)^{\circ}C \\ &= (4.184 J/g^{\circ}C) \times \left(8.0 \times 10^2 g\right) \times (64)^{\circ}C \\ &= 210,000 J \left(= 2.1 \times 10^2 kJ\right) \end{aligned} \tag{5.2.2}$$

Because the temperature increased, the water absorbed heat and q is positive.

Exercise 5.2.1

How much heat, in joules, must be added to a 502 g iron skillet to increase its temperature from 25 °C to 250 °C? The specific heat of iron is 0.449 J/g °C.

Answer available at the end of this section.

Note that the relationship between heat, specific heat, mass, and temperature change can be used to determine any of these quantities (not just heat) if the other three are known or can be deduced.

Example 5.2.2: Determining Other Quantities

A piece of unknown metal weighs 348 g. When the metal piece absorbs 6.64 kJ of heat, its temperature increases from 22.4 °C to 43.6 °C. Determine the specific heat of this metal (which might provide a clue to its identity).

Solution

Since mass, heat, and temperature change are known for this metal, we can determine its specific heat using the relationship in Equation 5.2.1:

$$q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$$

Substituting the known values:

$$6640 J = c \times (348 g) \times (43.6 - 22.4)^{\circ}C$$

Solving:

$$c = \frac{6640 J}{(348 g) \times (21.2^{\circ}C)} = 0.900 J/g^{\circ}C$$

Comparing this value with the values in Table 5.2.1, this value matches the specific heat of aluminum, which suggests that the unknown metal may be aluminum.

Exercise 5.2.2

A piece of unknown metal weighs 217 g. When the metal piece absorbs 1.43 kJ of heat, its temperature increases from 24.5 °C to 39.1 °C. Determine the specific heat of this metal, and predict its identity.

Answer available at the end of this section.

Chemistry in Everyday Life: Solar Thermal Energy Power Plants

The sunlight that reaches the earth contains thousands of times more energy than we presently capture. Solar thermal systems provide one possible solution to the problem of converting energy from the sun into energy we can use. Large-scale solar thermal plants have different design specifics, but all concentrate sunlight to heat some substance; the heat "stored" in that substance is then converted into electricity.

The Solana Generating Station in Arizona's Sonora Desert produces 280 megawatts of electrical power. It uses parabolic mirrors that focus sunlight on pipes filled with a heat transfer fluid (HTF) (Figure 5.2.8). The HTF then does two things: It turns water into steam, which spins turbines, which in turn produces electricity, and it melts and heats a mixture of salts, which functions as a thermal energy storage system. After the sun goes down, the molten salt mixture can then release enough of its stored heat to produce steam to run the turbines for 6 hours. Molten salts are used because they possess a number of beneficial properties, including high heat capacities and thermal conductivities.

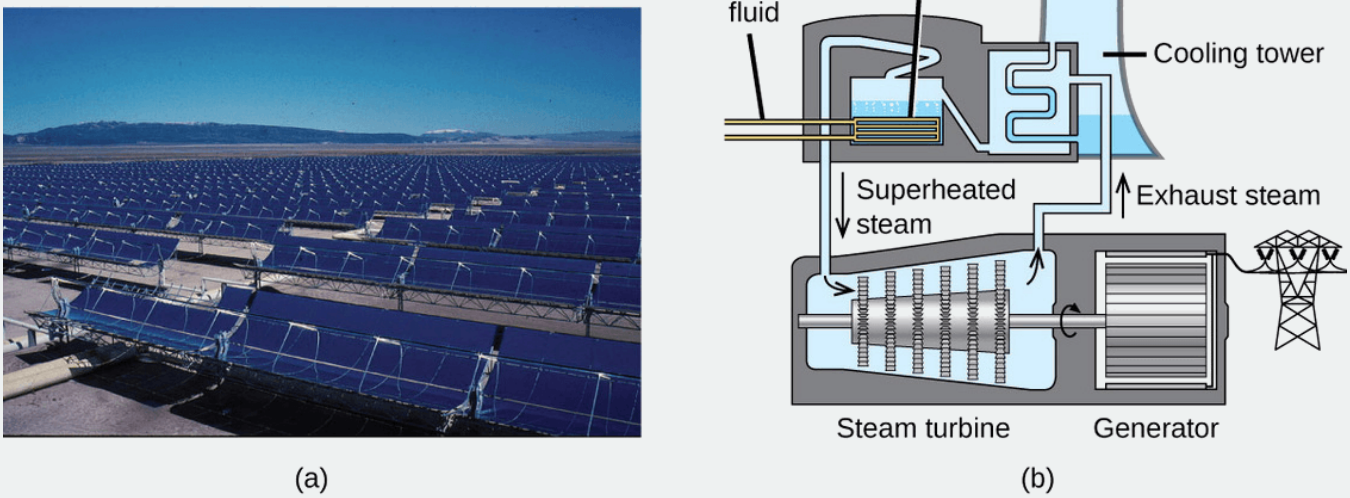


Figure 5.2.8: This solar thermal plant uses parabolic trough mirrors to concentrate sunlight. (credit a: modification of work by Bureau of Land Management)

The 377-megawatt Ivanpah Solar Generating System, located in the Mojave Desert in California, is the largest solar thermal power plant in the world (Figure 5.2.9). Its 170,000 mirrors focus huge amounts of sunlight on three water-filled towers, producing steam at over 538 °C that drives electricity-producing turbines. It produces enough energy to power 140,000 homes. Water is used as the working fluid because of its large heat capacity and heat of vaporization.



(a) (b)

Figure 5.2.9: (a) The Ivanpah solar thermal plant uses 170,000 mirrors to concentrate sunlight on water-filled towers. (b) It covers 4000 acres of public land near the Mojave Desert and the California-Nevada border. (credit a: modification of work by Craig Dietrich; credit b: modification of work by “USFWS Pacific Southwest Region”/Flickr)

Answers

Exercise 5.2.1

5.07×10^4 J

Exercise 5.2.2

c = 0.451 J/g °C; the metal is likely to be iron

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5.3: Calorimetry

Learning Objectives

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

- Explain the technique of calorimetry
- Calculate and interpret heat and related properties using typical calorimetry data

One technique we can use to measure the amount of heat involved in a chemical or physical process is known as calorimetry. Calorimetry is used to measure amounts of heat transferred to or from a substance. To do so, the heat is exchanged with a calibrated object (calorimeter). The temperature change measured by the calorimeter is used to derive the amount of heat transferred by the process under study. The measurement of heat transfer using this approach requires the definition of a system (the substance or substances undergoing the chemical or physical change) and its surroundings (all other matter, including components of the measurement apparatus, that serve to either provide heat to the system or absorb heat from the system).

A calorimeter is a device used to measure the amount of heat involved in a chemical or physical process. For example, when an exothermic reaction occurs in solution in a calorimeter, the heat produced by the reaction is absorbed by the solution, which increases its temperature. When an endothermic reaction occurs, the heat required is absorbed from the thermal energy of the solution, which decreases its temperature (Figure 5.3.1). The temperature change, along with the specific heat and mass of the solution, can then be used to calculate the amount of heat involved in either case.

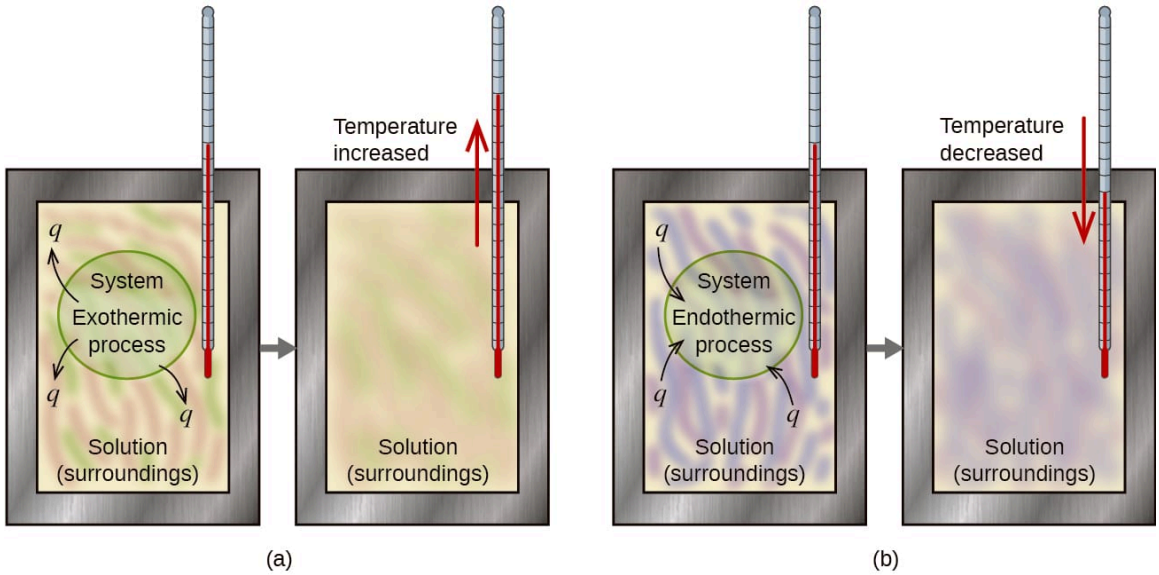


Figure 5.3.1: In a calorimetric determination, either (a) an exothermic process occurs and heat, q, is negative, indicating that thermal energy is transferred from the system to its surroundings, or (b) an endothermic process occurs and heat, q, is positive, indicating that thermal energy is transferred from the surroundings to the system.

Calorimetry measurements are important in understanding the heat transferred in reactions involving everything from microscopic proteins to massive machines. During her time at the National Bureau of Standards, research chemist Reatha Clark King performed calorimetric experiments to understand the precise heats of various flourine compounds. Her work was important to NASA in their quest for better rocket fuels.

Scientists use well-insulated calorimeters that all but prevent the transfer of heat between the calorimeter and its environment, which effectively limits the “surroundings” to the nonsystem components with the calorimeter (and the calorimeter itself). This enables the accurate determination of the heat involved in chemical processes, the energy content of foods, and so on. General chemistry students often use simple calorimeters constructed from polystyrene cups (Figure 5.3.2). These easy-to-use “coffee cup” calorimeters allow more heat exchange with the outside environment, and therefore produce less accurate energy values.

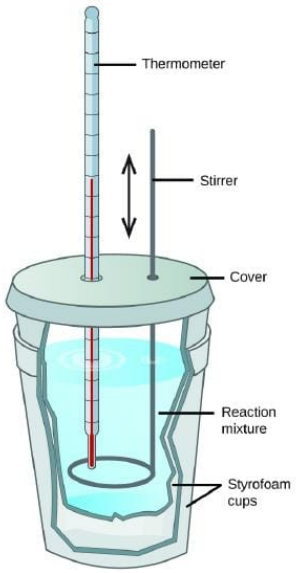


Figure 5.3.2: A simple calorimeter can be constructed from two polystyrene cups. A thermometer and stirrer extend through the cover into the reaction mixture.

Commercial solution calorimeters are also available. Relatively inexpensive calorimeters often consist of two thin-walled cups that are nested in a way that minimizes thermal contact during use, along with an insulated cover, handheld stirrer, and simple thermometer. More expensive calorimeters used for industry and research typically have a well-insulated, fully enclosed reaction vessel, motorized stirring mechanism, and a more accurate temperature sensor (Figure 5.3.3).

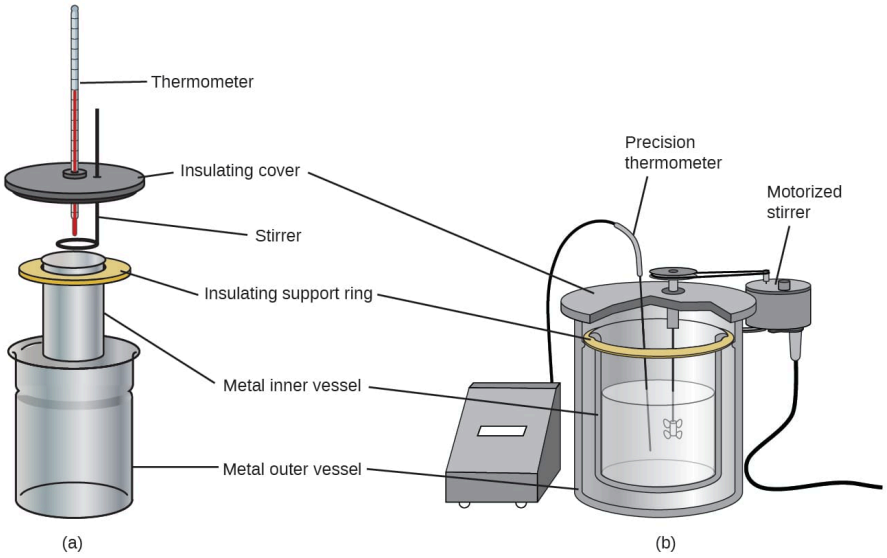


Figure 5.3.3: Commercial solution calorimeters range from (a) simple, inexpensive models for student use to (b) expensive, more accurate models for industry and research.

Before discussing the calorimetry of chemical reactions, consider a simpler example that illustrates the core idea behind calorimetry. Suppose we initially have a high-temperature substance, such as a hot piece of metal (M), and a low-temperature substance, such as cool water (W). If we place the metal in the water, heat will flow from M to W. The temperature of M will decrease, and the temperature of W will increase, until the two substances have the same temperature—that is, when they reach thermal equilibrium (Figure 5.3.4). If this occurs in a calorimeter, ideally all of this heat transfer occurs between the two substances, with no heat gained or lost by either its external environment. Under these ideal circumstances, the net heat change is zero:

$$q_{\text{substance}}\, M + q_{\text{substance}}\, W = 0$$

This relationship can be rearranged to show that the heat gained by substance M is equal to the heat lost by substance W:

$$q_{\text{substance M}} = -q_{\text{substance W}}$$

The magnitude of the heat (change) is therefore the same for both substances, and the negative sign merely shows that $q_{\text{substance M}}$ and $q_{\text{substance W}}$ are opposite in direction of heat flow (gain or loss) but does not indicate the arithmetic sign of either *q* value (that is determined by whether the matter in question gains or loses heat, per definition). In the specific situation described, $q_{\text{substance M}}$ is a negative value and $q_{\text{substance W}}$ is positive, since heat is transferred from M to W.

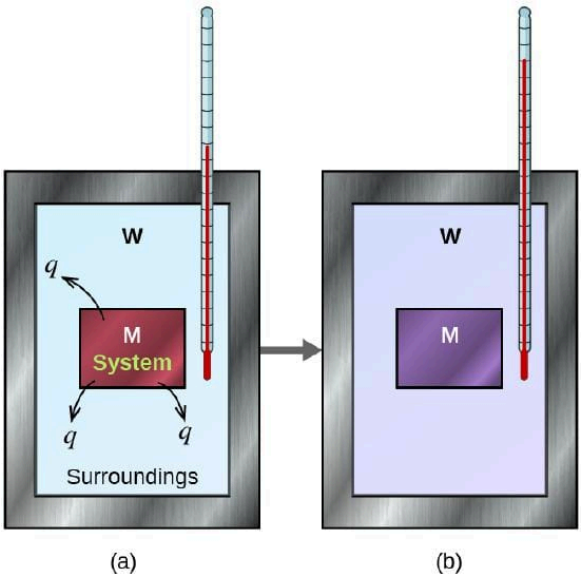


Figure 5.3.4: In a simple calorimetry process, (a) heat, *q*, is transferred from the hot metal, M, to the cool water, W, until (b) both are at the same temperature.

Example 5.3.1: Heat Transfer between Substances at Different Temperatures

A 360.0-g piece of rebar (a steel rod used for reinforcing concrete) is dropped into 425 mL of water at 24.0 °C. The final temperature of the water was measured as 42.7 °C. Calculate the initial temperature of the piece of rebar. Assume the specific heat of steel is approximately the same as that for iron (Table 5.1), and that all heat transfer occurs between the rebar and the water (there is no heat exchange with the surroundings).

Solution

The temperature of the water increases from 24.0 °C to 42.7 °C, so the water absorbs heat. That heat came from the piece of rebar, which initially was at a higher temperature. Assuming that all heat transfer was between the rebar and the water, with no heat "lost" to the outside environment, then *heat given off by rebar = –heat taken in by water*, or:

$$q_{\text{rebar}} = -q_{\text{water}}$$

Since we know how heat is related to other measurable quantities, we have:

$$(c \times m \times \Delta T)_{\text{rebar}} = -(c \times m \times \Delta T)_{\text{water}}$$

Letting f = final and i = initial, in expanded form, this becomes:

$$c_{\text{rebar}} \times m_{\text{rebar}} \times (T_{f,\text{ rebar}} - T_{i,\text{ rebar}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{f,\text{water}} - T_{i,\text{ water}})$$

The density of water is 1.0 g/mL, so 425 mL of water = 425 g. Noting that the final temperature of both the rebar and water is 42.7 °C, substituting known values yields:

$$(0.449 J/g^{\circ}C)\,(360.0g)\,(42.7^{\circ}C - T_{i,\text{ rebar}}) = -(4.184 J/g^{\circ}C)\,(425g)\,(42.7^{\circ}C - 24.0^{\circ}C)$$

$$T_{i,\text{ rebar}} = \frac{(4.184 J/g^{\circ}C)(425g)(42.7^{\circ}C - 24.0^{\circ}C)}{(0.449 J/g^{\circ}C)(360.0g)} + 42.7^{\circ}C$$

Solving this gives $T_{i,\text{ rebar}}$ = 248 °C, so the initial temperature of the rebar was 248 °C.

Exercise 5.3.1A

A 248-g piece of copper is dropped into 390 mL of water at 22.6 °C. The final temperature of the water was measured as 39.9 °C. Calculate the initial temperature of the piece of copper. Assume that all heat transfer occurs between the copper and the water.

Answer available at the end of this section.

Exercise 5.3.1B

A 248-g piece of copper initially at 314 °C is dropped into 390 mL of water initially at 22.6 °C. Assuming that all heat transfer occurs between the copper and the water, calculate the final temperature.

Answer available at the end of this section.

This method can also be used to determine other quantities, such as the specific heat of an unknown metal.

Example 5.3.2: Identifying a Metal by Measuring Specific Heat

A 59.7 g piece of metal that had been submerged in boiling water was quickly transferred into 60.0 mL of water initially at 22.0 °C. The final temperature is 28.5 °C. Use these data to determine the specific heat of the metal. Use this result to identify the metal.

Solution

Assuming perfect heat transfer, *heat given off by metal = –heat taken in by water*, or:

$$q_{\text{metal}} = -q_{\text{water}}$$

In expanded form, this is:

$$c_{\text{metal}} \times m_{\text{metal}} \times (T_{f,\text{ metal}} - T_{i,\text{ metal}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{f,\text{water}} - T_{i,\text{ water}})$$

Noting that since the metal was submerged in boiling water, its initial temperature was 100.0 °C; and that for water, 60.0 mL = 60.0 g; we have:

$$(c_{\text{metal}})(59.7g)(28.5^{\circ}C - 100.0^{\circ}C) = -(4.18 J/g^{\circ}C)(60.0g)(28.5^{\circ}C - 22.0^{\circ}C)$$

Solving this:

$$c_{\text{metal}} = \frac{-(4.184 J/g^{\circ}C)(60.0g)(6.5^{\circ}C)}{(59.7g)(-71.5^{\circ}C)} = 0.38 J/g^{\circ}C$$

Comparing this with values in Table 5.1, our experimental specific heat is closest to the value for copper (0.39 J/g °C), so we identify the metal as copper.

Exercise 5.3.2

A 92.9-g piece of a silver/gray metal is heated to 178.0 °C, and then quickly transferred into 75.0 mL of water initially at 24.0 °C. After 5 minutes, both the metal and the water have reached the same temperature: 29.7 °C. Determine the specific heat and the identity of the metal. (Note: You should find that the specific heat is close to that of two different metals. Explain how you can confidently determine the identity of the metal).

Answer available at the end of this section.

When we use calorimetry to determine the heat involved in a chemical reaction, the same principles we have been discussing apply. The amount of heat absorbed by the calorimeter is often small enough that we can neglect it (though not for highly accurate measurements, as discussed later), and the calorimeter minimizes energy exchange with the outside environment. Because energy is neither created nor destroyed during a chemical reaction, the heat produced or consumed in the reaction (the "system"), \(q_{\text {reaction }}), plus the heat absorbed or lost by the solution (the "surroundings"), q_{solution} , must add up to zero:

$$q_{\text{reaction}} + q_{\text{solution}} = 0$$

This means that the amount of heat produced or consumed in the reaction equals the amount of heat absorbed or lost by the solution:

$$q_{\text{reaction}} = -q_{\text{solution}}$$

This concept lies at the heart of all calorimetry problems and calculations.

Example 5.3.3: 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?

$$\mathrm{HCl\,(aq) + NaOH\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l)}$$

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:

$$q_{\text{reaction}} = -q_{\text{solution}}$$

(It is important to remember that this relationship only holds if the calorimeter does not absorb any heat from the reaction, and there is no heat exchange between the calorimeter and the outside environment.)

Next, we know that the heat absorbed by the solution depends on its specific heat, mass, and temperature change:

$$q_{\text{solution}} = (c \times m \times \Delta T)_{\text{solution}}$$

To proceed with this calculation, we need to make a few more reasonable assumptions or approximations. Since the solution is aqueous, we can proceed as if it were water in terms of its specific heat and mass values. The density of water is approximately 1.0 g/mL, so 100.0 mL has a mass of about 1.0 10^2 g (two significant figures). The specific heat of water is approximately 4.184 J/g °C, so we use that for the specific heat of the solution. Substituting these values gives:

$$q_{\text{solution}} = (4.184 J/g^{\circ}C)\left(1.0 \times 10^2 g\right)(28.9^{\circ}C - 22.0^{\circ}C) = 2.9 \times 10^3 J$$

Finally, since we are trying to find the heat of the reaction, we have:

$$q_{\text{reaction}} = -q_{\text{solution}} = -2.9 \times 10^3 J$$

The negative sign indicates that the reaction is exothermic. It produces 2.9 kJ of heat.

Exercise 5.3.3

When 100 mL of 0.200 M NaCl(*aq*) and 100 mL of 0.200 M $AgNO_3$(*aq*), both at 21.9 °C, are mixed in a coffee cup calorimeter, the temperature increases to 23.5 °C as solid AgCl forms. How much heat is produced by this precipitation reaction? What assumptions did you make to determine your value?

Answer available at the end of this section.

Chemistry in Everyday Life: Thermochemistry of Hand Warmers

When working or playing outdoors on a cold day, you might use a hand warmer to warm your hands (Figure 5.3.5). 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.



Figure 5.3.5: Chemical hand warmers produce heat that warms your hand on a cold day. In this one, you can see the metal disc that initiates the exothermic precipitation reaction. (credit: modification of work by Science Buddies TV/YouTube)

Another common hand warmer produces heat when it is ripped open, exposing iron and water in the hand warmer to oxygen in the air. One simplified version of this exothermic reaction is

$$2\,Fe\,(s) + \tfrac{3}{2}\,O_2\,(g) \longrightarrow Fe_2O_3\,(s)$$

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.

Link to Learning

This link shows the precipitation reaction that occurs when the disk in a chemical hand warmer is flexed.

Example 5.3.4: Heat Flow in an Instant Ice Pack

When solid ammonium nitrate dissolves in water, the solution becomes cold. This is the basis for an "instant ice pack" (Figure 5.3.6). When 3.21 g of solid NH_4NO_3 dissolves in 50.0 g of water at 24.9 °C in a calorimeter, the temperature decreases to 20.3 °C.

Calculate the value of q for this reaction and explain the meaning of its arithmetic sign. State any assumptions that you made.



Figure 5.3.6: An instant cold pack consists of a bag containing solid ammonium nitrate and a second bag of water. When the bag of water is broken, the pack becomes cold because the dissolution of ammonium nitrate is an endothermic process that removes thermal energy from the water. The cold pack then removes thermal energy from your body.

Solution

We assume that the calorimeter prevents heat transfer between the solution and its external environment (including the calorimeter itself), in which case:

$$q_{rxn} = -q_{soln}$$

with "rxn" and "soln" used as shorthand for "reaction" and "solution," respectively.

Assuming also that the specific heat of the solution is the same as that for water, we have:

$$\begin{aligned} q_{rxn} = -q_{soln} &= -(c \times m \times \Delta T)_{soln} \\ &= -\left[(4.184 J/g^{\circ}C) \times (53.2 g) \times (20.3^{\circ}C - 24.9^{\circ}C)\right] \\ &= -\left[(4.184 J/g^{\circ}C) \times (53.2 g) \times (-4.6^{\circ}C)\right] \\ &+ 1.0 \times 10^3 J = +1.0 kJ \end{aligned}$$

The positive sign for q indicates that the dissolution is an endothermic process.

Exercise 5.3.4

When a 3.00-g sample of KCl was added to 3.00 10^2 g of water in a coffee cup calorimeter, the temperature decreased by 1.05 °C. How much heat is involved in the dissolution of the KCl? What assumptions did you make?

Answer available at the end of this section.

If the amount of heat absorbed by a calorimeter is too large to neglect or if we require more accurate results, then we must take into account the heat absorbed both by the solution and by the calorimeter.

The calorimeters described are designed to operate at constant (atmospheric) pressure and are convenient to measure heat flow accompanying processes that occur in solution. A different type of calorimeter that operates at constant volume, colloquially known as a bomb calorimeter, is used to measure the energy produced by reactions that yield large amounts of heat and gaseous products, such as combustion reactions. (The term "bomb" comes from the observation that these reactions can be vigorous enough to resemble explosions that would damage other calorimeters.) This type of calorimeter consists of a robust steel container (the "bomb") that contains the reactants and is itself submerged in water (Figure 5.3.7). The sample is placed in the bomb, which is then filled with oxygen at high pressure. A small electrical spark is used to ignite the sample. The energy produced by the reaction is absorbed by the steel bomb and the surrounding water. The temperature increase is measured and, along with the known heat capacity of the calorimeter, is used to calculate the energy produced by the reaction. Bomb calorimeters require calibration to determine the heat capacity of the calorimeter and ensure accurate results. The calibration is accomplished using a reaction with a known q, such as a measured quantity of benzoic acid ignited by a spark from a nickel fuse wire that is weighed before and after the reaction. The temperature change produced by the known reaction is used to determine the heat capacity of the calorimeter. The calibration is generally performed each time before the calorimeter is used to gather research data.

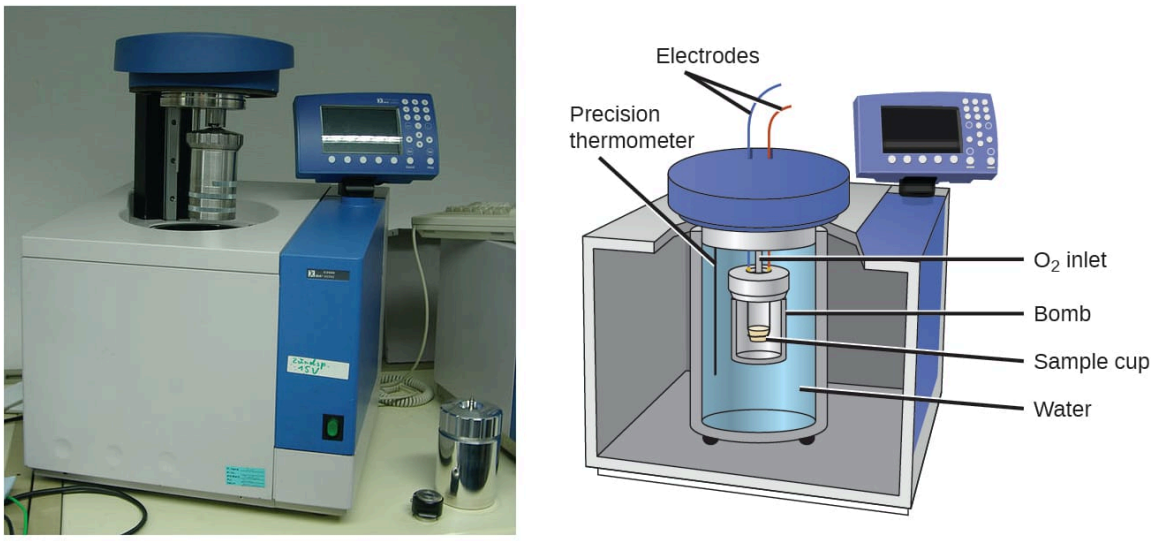


Figure 5.3.7: (a) A bomb calorimeter is used to measure heat produced by reactions involving gaseous reactants or products, such as combustion. (b) The reactants are contained in the gas-tight "bomb," which is submerged in water and surrounded by insulating materials. (credit a: modification of work by "Harbor1"/Wikimedia commons)

Link to Learning

Click on this link to view how a bomb calorimeter is prepared for action. This site shows calorimetric calculations using sample data.

Example 5.3.5: Bomb Calorimetry

When 3.12 g of glucose, $C_6H_{12}O_6$, is burned in a bomb calorimeter, the temperature of the calorimeter increases from 23.8 °C to 35.6 °C. The calorimeter contains 775 g of water, and the bomb itself has a heat capacity of 893 J/°C. How much heat was produced by the combustion of the glucose sample?

Solution

The combustion produces heat that is primarily absorbed by the water and the bomb. (The amounts of heat absorbed by the reaction products and the unreacted excess oxygen are relatively small and dealing with them is beyond the scope of this text. We will neglect them in our calculations.)

The heat produced by the reaction is absorbed by the water and the bomb:

$$\begin{aligned} q_{rxn} &= -\left(q_{\text{water}} + q_{\text{bomb}}\right) \\ &= -\left[(4.184 J/g^{\circ}C) \times (775 g) \times (35.6^{\circ}C - 23.8^{\circ}C) + 893 J/^{\circ}C \times (35.6^{\circ}C - 23.8^{\circ}C)\right] \\ &= -(38,300 J + 10,500 J) \\ &= -48,800 J = -48.8 kJ \end{aligned}$$

This reaction released 48.7 kJ of heat when 3.12 g of glucose was burned.

Exercise 5.3.5

When 0.963 g of benzene, C_6H_6, is burned in a bomb calorimeter, the temperature of the calorimeter increases by 8.39 °C. The bomb has a heat capacity of 784 J/°C and is submerged in 925 mL of water. How much heat was produced by the combustion of the benzene sample?

Answer available at the end of this section.

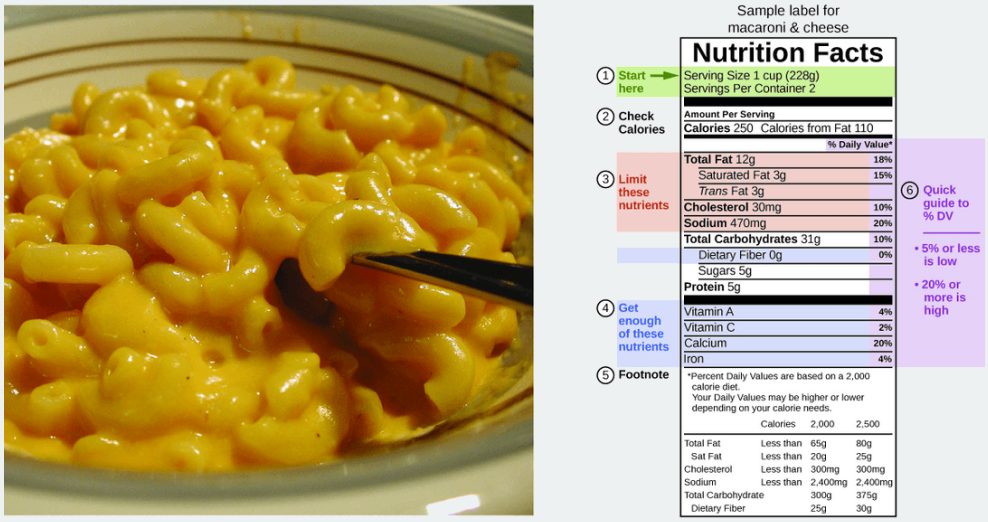
Since the first one was constructed in 1899, 35 calorimeters have been built to measure the heat produced by a living person.[2] These whole-body calorimeters of various designs are large enough to hold an individual human being. More recently, whole-room calorimeters allow for relatively normal activities to be performed, and these calorimeters generate data that more closely reflect the real world. These calorimeters are used to measure the metabolism of individuals under different environmental conditions, different dietary regimes, and with different health conditions, such as diabetes.

For example Carla Prado's team at University of Alberta undertook whole-body calorimetry to understand the energy expenditures of women who had recently given birth. Studies like this help develop better recommendations and regimens for nutrition, exercise, and general wellbeing during this period of significant physiological change. In humans, metabolism is typically measured in Calories per day. A nutritional calorie (Calorie) is the energy unit used to quantify the amount of energy derived from the metabolism of foods; one Calorie is equal to 1000 calories (1 kcal), the amount of energy needed to heat 1 kg of water by 1 °C.

Chemistry in Everyday Life: Measuring Nutritional Calories

In your day-to-day life, you may be more familiar with energy being given in Calories, or nutritional calories, which are used to quantify the amount of energy in foods. One calorie (cal) = exactly 4.184 joules, and one Calorie (note the capitalization) = 1000 cal, or 1 kcal. (This is approximately the amount of energy needed to heat 1 kg of water by 1 °C.)

The macronutrients in food are proteins, carbohydrates, and fats or oils. Proteins provide about 4 Calories per gram, carbohydrates also provide about 4 Calories per gram, and fats and oils provide about 9 Calories/g. Nutritional labels on food packages show the caloric content of one serving of the food, as well as the breakdown into Calories from each of the three macronutrients (Figure 5.3.8).



(a) (b)

Figure 5.3.8: (a) Macaroni and cheese contain energy in the form of the macronutrients in the food. (b) The food's nutritional information is shown on the package label. In the US, the energy content is given in Calories (per serving); the rest of the world usually uses kilojoules. (credit a: modification of work by "Rex Roof"/Flickr)

For the example shown in (b), the total energy per 228-g portion is calculated by:

$$(5g \text{ protein } \times 4 \text{ Calories } /g) + (31g \text{ carb } \times 4 \text{ Calories } /g) + (12g \text{ fat } \times 9 \text{ Calories } /g) = 252 \text{ Calories}$$

So, you can use food labels to count your Calories. But where do the values come from? And how accurate are they? The caloric content of foods can be determined by using bomb calorimetry; that is, by burning the food and measuring the energy it contains. A sample of food is weighed, mixed in a blender, freeze-dried, ground into powder, and formed into a pellet. The pellet is burned inside a bomb calorimeter, and the measured temperature change is converted into energy per gram of food.

Today, the caloric content on food labels is derived using a method called the Atwater system that uses the average caloric content of the different chemical constituents of food, protein, carbohydrate, and fats. The average amounts are those given in the equation and are derived from the various results given by bomb calorimetry of whole foods. The carbohydrate amount is discounted a certain amount for the fiber content, which is indigestible carbohydrate. To determine the energy content of a food, the quantities of carbohydrate, protein, and fat are each multiplied by the average Calories per gram for each and the products summed to obtain the total energy.

Link to Learning

Click on this link to access the US Department of Agriculture (USDA) National Nutrient Database, containing nutritional information on over 8000 foods.

Footnotes

- 2Francis D. Reardon et al. "The Snellen human calorimeter revisited, re-engineered and upgraded: Design and performance characteristics." *Medical and Biological Engineering and Computing* 8 (2006)721–28, http://link.springer.com/article/10....517-006-0086-5.

Answers

Exercise 5.3.1A

The initial temperature of the copper was 335.6 °C.

Exercise 5.3.1B

The final temperature (reached by both copper and water) is 38.7 °C.

Exercise 5.3.2

c_{metal}= 0.13 J/g °C

This specific heat is close to that of either gold or lead. It would be difficult to determine which metal this was based solely on the numerical values. However, the observation that the metal is silver/gray in addition to the value for the specific heat indicates that the metal is lead.

Exercise 5.3.3

1.34 1.3 kJ; assume no heat is absorbed by the calorimeter, no heat is exchanged between the calorimeter and its surroundings, and that the specific heat and mass of the solution are the same as those for water

Exercise 5.3.4

1.33 kJ; assume that the calorimeter prevents heat transfer between the solution and its external environment (including the calorimeter itself) and that the specific heat of the solution is the same as that for water

Exercise 5.3.5

q_{rx} = −39.0 kJ (the reaction produced 39.0 kJ of heat)

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5.4: Enthalpy

Learning Objectives

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

- State the first law of thermodynamics
- Define enthalpy and explain its classification as a state function
- Write and balance thermochemical equations
- Calculate enthalpy changes for various chemical reactions
- Explain Hess's law and use it to compute reaction enthalpies

Thermochemistry is a branch of chemical thermodynamics, the science that deals with the relationships between heat, work, and other forms of energy in the context of chemical and physical processes. As we concentrate on thermochemistry in this chapter, we need to consider some widely used concepts of thermodynamics.

Substances act as reservoirs of energy, meaning that energy can be added to them or removed from them. Energy is stored in a substance when the kinetic energy of its atoms or molecules is raised. The greater kinetic energy may be in the form of increased translations (travel or straight-line motions), vibrations, or rotations of the atoms or molecules. When thermal energy is lost, the intensities of these motions decrease and the kinetic energy falls. The total of all possible kinds of energy present in a substance is called the internal energy (*U*), sometimes symbolized as *E*.

As a system undergoes a change, its internal energy can change, and energy can be transferred from the system to the surroundings, or from the surroundings to the system. Energy is transferred into a system when it absorbs heat (*q*) from the surroundings or when the surroundings do work (*w*) on the system. For example, energy is transferred into room-temperature metal wire if it is immersed in hot water (the wire absorbs heat from the water), or if you rapidly bend the wire back and forth (the wire becomes warmer because of the work done on it). Both processes increase the internal energy of the wire, which is reflected in an increase in the wire's temperature. Conversely, energy is transferred out of a system when heat is lost from the system, or when the system does work on the surroundings.

The relationship between internal energy, heat, and work can be represented by the equation:

$$\Delta U = q + w$$

as shown in Figure $5.4.1$. This is one version of the first law of thermodynamics, and it shows that the internal energy of a system changes through heat flow into or out of the system (positive *q* is heat flow in; negative *q* is heat flow out) or work done on or by the system. The work, *w*, is positive if it is done on the system and negative if it is done by the system.

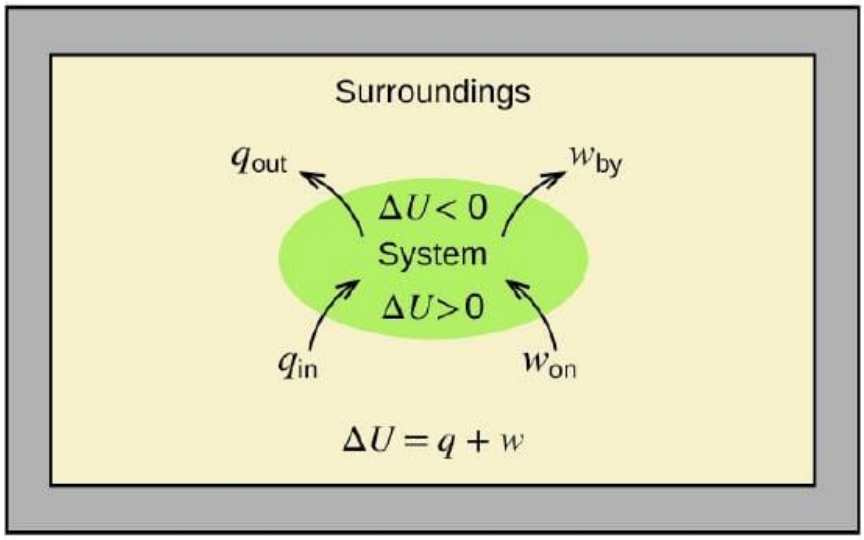


Figure 5.4.1: The internal energy, U, of a system can be changed by heat flow and work. If heat flows into the system, q_{in}, or work is done on the system, w_{on}, its internal energy increases, $\Delta U > 0$. If heat flows out of the system, q_{out}, or work is done by the system, w_{by}, its internal energy decreases, $\Delta U < 0$.

A type of work called expansion work (or pressure-volume work) occurs when a system pushes back the surroundings against a restraining pressure, or when the surroundings compress the system. An example of this occurs during the operation of an internal combustion engine. The reaction of gasoline and oxygen is exothermic. Some of this energy is given off as heat, and some does work pushing the piston in the cylinder. The substances involved in the reaction are the system, and the engine and the rest of the universe are the surroundings. The system loses energy by both heating and doing work on the surroundings, and its internal energy decreases. (The engine is able to keep the car moving because this process is repeated many times per second while the engine is running.) We will consider how to determine the amount of work involved in a chemical or physical change in the chapter on thermodynamics.

Link to Learning

This view of an internal combustion engine illustrates the conversion of energy produced by the exothermic combustion reaction of a fuel such as gasoline into energy of motion.

As discussed, the relationship between internal energy, heat, and work can be represented as $\Delta U = q + w$. Internal energy is an example of a state function (or state variable), whereas heat and work are not state functions. The value of a state function depends only on the state that a system is in, and not on how that state is reached. If a quantity is not a state function, then its value *does* depend on how the state is reached. An example of a state function is altitude or elevation. If you stand on the summit of Mt. Kilimanjaro, you are at an altitude of 5895 m, and it does not matter whether you hiked there or parachuted there. The distance you traveled to the top of Kilimanjaro, however, is not a state function. You could climb to the summit by a direct route or by a more roundabout, circuitous path (Figure 5.4.2). The distances traveled would differ (distance is not a state function) but the elevation reached would be the same (altitude is a state function).

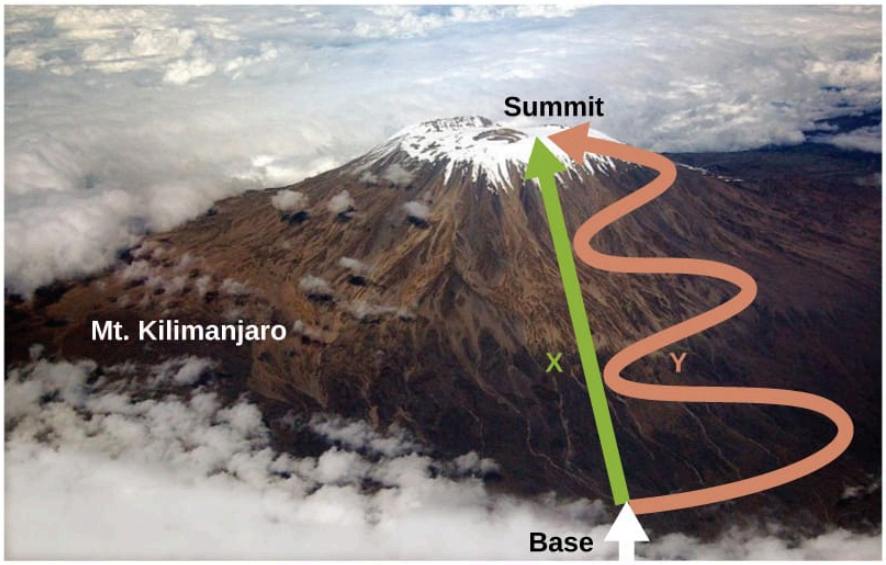


Figure 5.4.2: Paths X and Y represent two different routes to the summit of Mt. Kilimanjaro. Both have the same change in elevation (altitude or elevation on a mountain is a state function; it does not depend on path), but they have very different distances traveled (distance walked is not a state function; it depends on the path). (credit: modification of work by Paul Shaffner)

Chemists ordinarily use a property known as enthalpy (*H*) to describe the thermodynamics of chemical and physical processes. Enthalpy is defined as the sum of a system's internal energy (*U*) and the mathematical product of its pressure (*P*) and volume (*V*):

$$H = U + PV$$

Enthalpy is also a state function. Enthalpy values for specific substances cannot be measured directly; only enthalpy *changes* for chemical or physical processes can be determined. For processes that take place at constant pressure (a common condition for many chemical and physical changes), the enthalpy change (ΔH) is:

$$\Delta H = \Delta U + P\Delta V$$

The mathematical product $P\Delta V$ represents work (w), namely, expansion or pressure-volume work as noted. By their definitions, the arithmetic signs of ΔV and w will **always** be opposite:

$$P\Delta V = -w$$

Substituting this equation and the definition of internal energy into the enthalpy-change equation yields:

$$\begin{aligned}\Delta H &= \Delta U + P\Delta V \\ &= q_p + w - w \\ &= q_p\end{aligned}$$

where q_p is the **heat of reaction** under conditions of constant pressure.

And so, if a chemical or physical process is carried out at constant pressure with the only work done caused by expansion or contraction, then the heat flow (q_p) and enthalpy change (ΔH) for the process are equal.

The heat given off when you operate a Bunsen burner is equal to the enthalpy change of the methane combustion reaction that takes place, since it occurs at the essentially constant pressure of the atmosphere. On the other hand, the heat produced by a reaction measured in a bomb calorimeter is not equal to ΔH because the closed, constant-volume metal container prevents the pressure from remaining constant (it may increase or decrease if the reaction yields increased or decreased amounts of gaseous species). Chemists usually perform experiments under normal atmospheric conditions, at constant external pressure with $q = \Delta H$, which makes enthalpy the most convenient choice for determining heat changes for chemical reactions.

The following conventions apply when using ΔH:

- A negative value of an enthalpy change, $\Delta H < 0$, indicates an exothermic reaction; a positive value, $\Delta H > 0$, indicates an

endothermic reaction. If the direction of a chemical equation is reversed, the arithmetic sign of its ΔH is changed (a process that is endothermic in one direction is exothermic in the opposite direction).

- Chemists use a thermochemical equation to represent the changes in both matter and energy. In a thermochemical equation, the enthalpy change of a reaction is shown as a ΔH value following the equation for the reaction. This ΔH value indicates the amount of heat associated with the reaction involving the number of moles of reactants and products *as shown in the chemical equation*. For example, consider this equation:

$$\mathrm{H_2\,(g)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \longrightarrow \mathrm{H_2O\,(l)} \quad \Delta H = -286kJ$$

This equation indicates that when 1 mole of hydrogen gas and mole of oxygen gas at some temperature and pressure change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released to the surroundings. If the coefficients of the chemical equation are multiplied by some factor, the enthalpy change must be multiplied by that same factor (ΔH is an extensive property):

  - two-fold increase in amounts

$$2\,\mathrm{H_2\,(g)} + \mathrm{O_2\,(g)} \longrightarrow 2\,\mathrm{H_2O\,(l)} \quad \Delta H = 2 \times (-286kJ) = -572kJ$$

  - two-fold decrease in amounts

$$\tfrac{1}{2}\,\mathrm{H_2\,(g)} + \tfrac{1}{4}\,\mathrm{O_2\,(g)} \longrightarrow \tfrac{1}{2}\,\mathrm{H_2O\,(l)} \quad \Delta H = \frac{1}{2} \times (-286kJ) = -143kJ$$

- The enthalpy change of a reaction depends on the physical states of the reactants and products, so these must be shown. For example, when 1 mole of hydrogen gas and mole of oxygen gas change to 1 mole of liquid water at the same temperature and pressure, 286 kJ of heat are released. If gaseous water forms, only 242 kJ of heat are released.

$$\mathrm{H_2\,(g)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)} \longrightarrow \mathrm{H_2O\,(g)} \quad \Delta H = -242kJ$$

Example 5.4.1: Writing Thermochemical Equations

When 0.0500 mol of HCl(*aq*) reacts with 0.0500 mol of NaOH(*aq*) to form 0.0500 mol of NaCl(*aq*), 2.9 kJ of heat are produced. Write a balanced thermochemical equation for the reaction of one mole of HCl.

$$\mathrm{HCl\,(aq)} + \mathrm{NaOH\,(aq)} \longrightarrow \mathrm{NaCl\,(aq)} + \mathrm{H_2O\,(l)}$$

Solution

For the reaction of 0.0500 mol acid (HCl), q = −2.9 kJ. The reactants are provided in stoichiometric amounts (same molar ratio as in the balanced equation), and so the amount of acid may be used to calculate a molar enthalpy change. Since ΔH is an extensive property, it is proportional to the amount of acid neutralized:

$$\Delta H = 1\ \cancel{\text{mol HCl}} \times \frac{-2.9kJ}{0.0500\ \cancel{\text{mol HCl}}} = -58kJ$$

The thermochemical equation is then

$$\mathrm{HCl\,(aq)} + \mathrm{NaOH\,(aq)} \longrightarrow \mathrm{NaCl\,(aq)} + \mathrm{H_2O\,(l)} \quad \Delta H = -58kJ$$

Exercise 5.4.1

When 1.34 g Zn(s) reacts with 60.0 mL of 0.750 M HCl(*aq*), 3.14 kJ of heat are produced. Determine the enthalpy change per mole of zinc reacting for the reaction:

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

Answer available at the end of this section.

Be sure to take both stoichiometry and limiting reactants into account when determining the ΔH for a chemical reaction.

Example 5.4.2: Writing Thermochemical Equations

A gummy bear contains 2.67 g sucrose, $C_{12}H_{22}O_{11}$. When it reacts with 7.19 g potassium chlorate, $KClO_3$, 43.7 kJ of heat are produced. Write a thermochemical equation for the reaction of one mole of sucrose:

$$\mathrm{C_{12}H_{22}O_{11}\,(aq) + 8\,KClO_3\,(aq) \longrightarrow 12\,CO_2\,(g) + 11\,H_2O\,(l) + 8\,KCl\,(aq)}$$

Solution

Unlike the previous example exercise, this one does not involve the reaction of stoichiometric amounts of reactants, and so the *limiting reactant* must be identified (it limits the yield of the reaction and the amount of thermal energy produced or consumed).

The provided amounts of the two reactants are

$$(2.67\,\mathrm{g})\left(\frac{1\,\mathrm{mol}}{342.3\,\mathrm{g}}\right) = 0.00780\,\mathrm{mol\,C_{12}H_{22}O_{11}}$$

$$(7.19\,\mathrm{g})\left(\frac{1\,\mathrm{mol}}{122.5\,\mathrm{g}}\right) = 0.0587\,\mathrm{mol\,KCIO}$$

The provided molar ratio of perchlorate-to-sucrose is then

$$\frac{0.0587\,\mathrm{mol\ KClO_3}}{0.00780\,\mathrm{mol\,C_{12}H_{22}O_{11}}} = 7.52$$

The balanced equation indicates 8 mol $KClO_3$ are required for reaction with 1 mol $C_{12}H_{22}O_{11}$. Since the provided amount of $KClO_3$ is less than the stoichiometric amount, it is the limiting reactant and may be used to compute the enthalpy change:

$$\Delta H = \frac{-43.7\,\mathrm{kJ}}{0.0587\,\mathrm{molKCIO_3}} = \frac{744\,\mathrm{kJ}}{\mathrm{mol\,KCIO_3}}$$

Because the equation, as written, represents the reaction of 8 mol $KClO_3$, the enthalpy change is

$$\left(\frac{744\,\mathrm{kJ}}{1\ \cancel{\mathrm{mol\,KCIO_3}}}\right)\left(8\ \cancel{\mathrm{mol\,KCIO_3}}\right) = 5960\,\mathrm{kJ}$$

The enthalpy change for this reaction is –5960 kJ, and the thermochemical equation is:

$$\mathrm{C_{12}H_{22}O_{11} + 8\,KClO_3 \longrightarrow 12\,CO_2 + 11\,H_2O + 8\,KCl} \quad \Delta H = -5960\,\mathrm{kJ}$$

Exercise 5.4.1

When 1.42 g of iron reacts with 1.80 g of chlorine, 3.22 g of $FeCl_2\,(s)$ and 8.60 kJ of heat is produced. What is the enthalpy change for the reaction when 1 mole of $FeCl_2\,(s)$ is produced?

Answer available at the end of this section.

Enthalpy changes are typically tabulated for reactions in which both the reactants and products are at the same conditions. A standard state is a commonly accepted set of conditions used as a reference point for the determination of properties under other different conditions. For chemists, the IUPAC standard state refers to materials under a pressure of 1 bar and solutions at 1 M, and does not specify a temperature. Many thermochemical tables list values with a standard state of 1 atm. Because the ΔH of a reaction changes very little with such small changes in pressure (1 bar = 0.987 atm), ΔH values (except for the most precisely measured values) are essentially the same under both sets of standard conditions. We will include a superscripted "o" in the enthalpy change symbol to designate standard state. Since the usual (but not technically standard) temperature is 298.15 K, this temperature will be assumed unless some other temperature is specified. Thus, the symbol is used to indicate an enthalpy change for a process occurring under these conditions. (The symbol ΔH is used to indicate an enthalpy change for a reaction occurring under nonstandard conditions.)

The enthalpy changes for many types of chemical and physical processes are available in the reference literature, including those for combustion reactions, phase transitions, and formation reactions. As we discuss these quantities, it is important to pay attention to the *extensive* nature of enthalpy and enthalpy changes. Since the enthalpy change for a given reaction is proportional to the amounts of substances involved, it may be reported on that basis (i.e., as the ΔH for specific amounts of reactants). However, we often find it more useful to divide one extensive property (ΔH) by another (amount of substance), and report a per-amount *intensive* value of ΔH, often "normalized" to a per-mole basis. (Note that this is similar to determining the intensive property specific heat from the extensive property heat capacity, as seen previously.)

Standard Enthalpy of Combustion

Standard enthalpy of combustion is the enthalpy change when 1 mole of a substance burns (combines vigorously with oxygen) under standard state conditions; it is sometimes called "heat of combustion." For example, the enthalpy of combustion of ethanol, –1366.8 kJ/mol, is the amount of heat produced when one mole of ethanol undergoes complete combustion at 25 °C and 1 atmosphere pressure, yielding products also at 25 °C and 1 atm.

$$\mathrm{C_2H_5OH\,(l) + 3\,O_2\,(g) \longrightarrow 2\,CO_2 + 3\,H_2O\,(l)} \quad \Delta H^\circ = -1366.8\,\mathrm{kJ}$$

Enthalpies of combustion for many substances have been measured; a few of these are listed in Table 5.4.1. Many readily available substances with large enthalpies of combustion are used as fuels, including hydrogen, carbon (as coal or charcoal), and hydrocarbons (compounds containing only hydrogen and carbon), such as methane, propane, and the major components of gasoline.

Table 5.4.1: Standard Molar Enthalpies of Combustion

Substance	Combustion Reaction	Enthalpy of Combustion, ΔH_c° (kJ/mol) at 25 °C
carbon	$C(s) + O_2(g) \longrightarrow CO_2(g)$	–393.5
hydrogen	$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$	–285.8
magnesium	$Mg(s) + \frac{1}{2}O_2(g) \longrightarrow MgO(s)$	–601.6
sulfur	$S(s) + O_2(g) \longrightarrow SO_2(g)$	–296.8
carbon monoxide	$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$	–283.0
methane	$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$	–890.8
acetylene	$C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l)$	–1301.1
ethanol	$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$	–1366.8
methanol	$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$	–726.1
isooctane	$C_8H_{18}(l) + \frac{25}{2}O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(l)$	–5461

Example 5.4.3: Using Enthalpy of Combustion

As Figure 5.4.3: suggests, the combustion of gasoline is a highly exothermic process. Let us determine the approximate amount of heat produced by burning 1.00 L of gasoline, assuming the enthalpy of combustion of gasoline is the same as that of isooctane, a common component of gasoline. The density of isooctane is 0.692 g/mL.



Figure 5.4.3: The combustion of gasoline is very exothermic. (credit: modification of work by "AlexEagle"/Flickr)

Solution

Starting with a known amount (1.00 L of isooctane), we can perform conversions between units until we arrive at the desired amount of heat or energy. The enthalpy of combustion of isooctane provides one of the necessary conversions. Table 5.4.1 gives this value as –5460 kJ per 1 mole of isooctane (C_8H_{18}).

Using these data,

$$1.00\ \cancel{\text{L C}_8\text{H}_{18}} \times \left(\frac{1000\ \cancel{\text{mL C}_8\text{H}_{18}}}{1\ \cancel{\text{L C}_8\text{H}_{18}}}\right) \times \left(\frac{0.692\ \cancel{\text{g C}_8\text{H}_{18}}}{1\ \cancel{\text{mL C}_8\text{H}_{18}}}\right) \times \left(\frac{1\ \cancel{\text{mol C}_8\text{H}_{18}}}{114\ \cancel{\text{g C}_8\text{H}_{18}}}\right) \times \frac{-5460\,\text{kJ}}{1\ \cancel{\text{mol C}_8\text{H}_{18}}} = -3.31 \times 10^4\,\text{kJ}$$

The combustion of 1.00 L of isooctane produces 33,100 kJ of heat. (This amount of energy is enough to melt 99.2 kg, or about 218 lbs, of ice.)

Note: If you do this calculation one step at a time, you would find:

$$1.00\,\text{L C}_8\text{H}_{18} \longrightarrow 1.00 \times 10^3\,\text{mL C}_8\text{H}_{18}$$
$$1.00 \times 10^3\,\text{mL C}_8\text{H}_{18} \longrightarrow 692\,\text{g C}_8\text{H}_{18}$$
$$692\,\text{g C}_8\text{H}_{18} \longrightarrow 6.07\,\text{mol C}_8\text{H}_{18}$$
$$6.07\,\text{mol C}_8\text{H}_{18} \longrightarrow -3.31 \times 10^4 kJ$$

Exercise 5.4.3

How much heat is produced by the combustion of 125 g of acetylene?

Answer available at the end of this section.

Chemistry in Everyday Life: Emerging Algae-Based Energy Technologies (Biofuels)

As reserves of fossil fuels diminish and become more costly to extract, the search is ongoing for replacement fuel sources for the future. Among the most promising biofuels are those derived from algae (Figure 5.22). The species of algae used are nontoxic, biodegradable, and among the world's fastest growing organisms. About 50% of algal weight is oil, which can be

readily converted into fuel such as biodiesel. Algae can yield 26,000 gallons of biofuel per hectare—much more energy per acre than other crops. Some strains of algae can flourish in brackish water that is not usable for growing other crops. Algae can produce biodiesel, biogasoline, ethanol, butanol, methane, and even jet fuel.

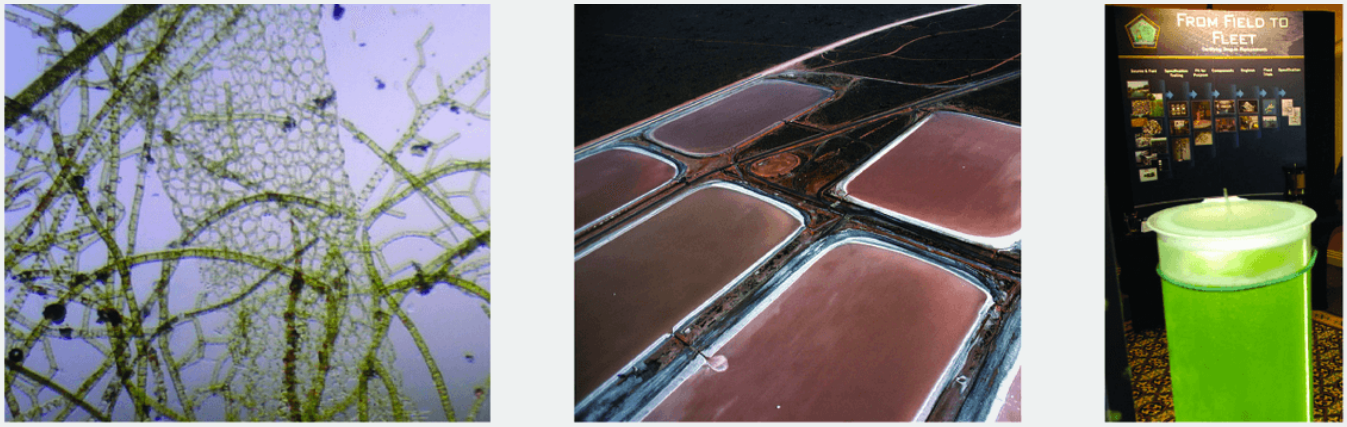


Figure 5.22 (a) Tiny algal organisms can be (b) grown in large quantities and eventually (c) turned into a useful fuel such as biodiesel. (credit a: modification of work by Micah Sittig; credit b: modification of work by Robert Kerton; credit c: modification of work by John F. Williams)

According to the US Department of Energy, only 39,000 square kilometers (about 0.4% of the land mass of the US or less than of the area used to grow corn) can produce enough algal fuel to replace all the petroleum-based fuel used in the US. The cost of algal fuels is becoming more competitive—for instance, the US Air Force is producing jet fuel from algae at a total cost of under $5 per gallon.[3] The process used to produce algal fuel is as follows: grow the algae (which use sunlight as their energy source and CO_2 as a raw material); harvest the algae; extract the fuel compounds (or precursor compounds); process as necessary (e.g., perform a transesterification reaction to make biodiesel); purify; and distribute (Figure 5.4.4).

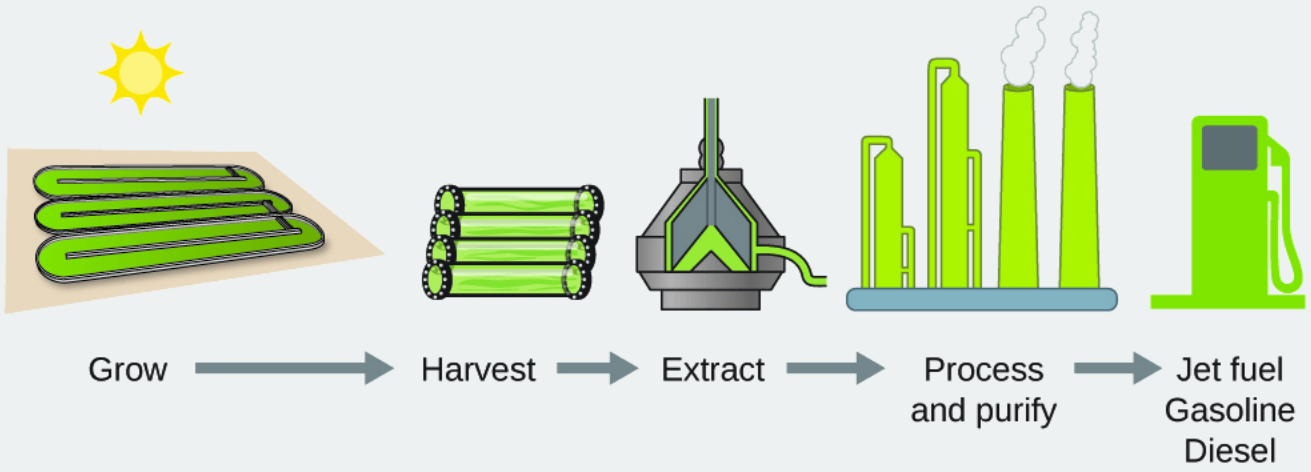


Figure 5.4.4: Algae convert sunlight and carbon dioxide into oil that is harvested, extracted, purified, and transformed into a variety of renewable fuels.

Link to Learning

Click here to learn more about the process of creating algae biofuel.

Standard Enthalpy of Formation

A standard enthalpy of formation is an enthalpy change for a reaction in which exactly 1 mole of a pure substance is formed from free elements in their most stable states under standard state conditions. These values are especially useful for computing or predicting enthalpy changes for chemical reactions that are impractical or dangerous to carry out, or for processes for which it is difficult to make measurements. If we have values for the appropriate standard enthalpies of formation, we can determine the enthalpy change for any reaction, which we will practice in the next section on Hess's law.

The standard enthalpy of formation of $CO_2(g)$ is –393.5 kJ/mol. This is the enthalpy change for the exothermic reaction:

$$\mathrm{C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H_f^\circ = \Delta H^\circ = -393.5\,kJ}$$

starting with the reactants at a pressure of 1 atm and 25 °C (with the carbon present as graphite, the most stable form of carbon under these conditions) and ending with one mole of CO_2, also at 1 atm and 25 °C. For nitrogen dioxide, $NO_2(g)$, is 33.2 kJ/mol. This is the enthalpy change for the reaction:

$$\mathrm{\tfrac{1}{2}\,N_2(g) + O_2(g) \longrightarrow NO_2(g) \quad \Delta H_f^\circ = \Delta H^\circ = +33.2\,kJ}$$

A reaction equation with mole of $\mathrm{N_2}$ and 1 mole of $\mathrm{O_2}$ is correct in this case because the standard enthalpy of formation always refers to 1 mole of product, $\mathrm{NO_2(g)}$.

You will find a table of standard enthalpies of formation of many common substances in Appendix 11.7. These values indicate that formation reactions range from highly exothermic (such as –2984 kJ/mol for the formation of $\mathrm{P_4O_{10}}$) to strongly endothermic (such as +226.7 kJ/mol for the formation of acetylene, $\mathrm{C_2H_2}$). By definition, the standard enthalpy of formation of an element in its most stable form is equal to zero under standard conditions, which is 1 atm for gases and 1 M for solutions.

Example 5.4.4: Evaluating an Enthalpy of Formation

Ozone, $\mathrm{O_3(g)}$, forms from oxygen, $\mathrm{O_2(g)}$, by an endothermic process. Ultraviolet radiation is the source of the energy that drives this reaction in the upper atmosphere. Assuming that both the reactants and products of the reaction are in their standard states, determine the standard enthalpy of formation, of ozone from the following information:

$$\mathrm{3\,O_2(g) \longrightarrow 2\,O_3(g) \quad \Delta H^\circ = +286\,kJ}$$

Solution

ΔH_f° is the enthalpy change for the formation of one mole of a substance in its standard state from the elements in their standard states. Thus, for $\mathrm{O_3(g)}$ is the enthalpy change for the reaction:

$$\mathrm{\tfrac{3}{2}\,O_2(g) \longrightarrow O_3(g)}$$

For the formation of 2 mol of $\mathrm{O_3(g)}$, $\Delta H^\circ = +286$ kJ. This ratio, can be used as a conversion factor to find the heat produced when 1 mole of $O_3(g)$ is formed, which is the enthalpy of formation for $\mathrm{O_3(g)}$:

$$\mathrm{\Delta H^\circ \text{ for 1 mole of } O_3(g) = 1\,\cancel{mol\,O_3} \times \frac{286\,kJ}{2\,mol\,O_3} = 143\,kJ}$$

Therefore,

$$\mathrm{\Delta H_f^\circ\,[O_3(g)] = +143\,kJ/mol.}$$

Exercise 5.4.4

Hydrogen gas, $\mathrm{H_2}$, reacts explosively with gaseous chlorine, $\mathrm{Cl_2}$, to form hydrogen chloride, $\mathrm{HCl(g)}$. What is the enthalpy change for the reaction of 1 mole of $\mathrm{H_2(g)}$ with 1 mole of $\mathrm{Cl_2(g)}$ if both the reactants and products are at standard state conditions? The standard enthalpy of formation of $\mathrm{HCl(g)}$ is –92.3 kJ/mol.

Answer available at the end of this section.

Example 5.4.5: Writing Reaction Equations for

Write the heat of formation reaction equations for:

a. $C_2H_5OH\,(l)$
b. $Ca_3(PO_4)_2\,(s)$

Solution

Remembering that reaction equations are for forming 1 mole of the compound from its constituent elements under standard conditions, we have:

a. $$2\,C\,(s, \text{graphite}) + 3\,H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow C_2H_5OH\,(l)$$
b. $$3\,Ca\,(s) + \tfrac{1}{2}\,P_4\,(s) + 4\,O_2\,(g) \longrightarrow Ca_3(PO_4)_2\,(s)$$

Note: The standard state of carbon is graphite, and phosphorus exists as P_4.

Exercise 5.4.5

Write the heat of formation reaction equations for:

a. $C_2H_5OC_2H_5\,(l)$
b. $Na_2CO_3\,(s)$

Answer available at the end of this section.

Hess's Law

There are two ways to determine the amount of heat involved in a chemical change: measure it experimentally, or calculate it from other experimentally determined enthalpy changes. Some reactions are difficult, if not impossible, to investigate and make accurate measurements for experimentally. And even when a reaction is not hard to perform or measure, it is convenient to be able to determine the heat involved in a reaction without having to perform an experiment.

This type of calculation usually involves the use of Hess's law, which states: *If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps*. Hess's law is valid because enthalpy is a state function: Enthalpy changes depend only on where a chemical process starts and ends, but not on the path it takes from start to finish. For example, 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 direct process is written:

$$C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g) \quad \Delta H^\circ = -394kJ$$

In the two-step process, first carbon monoxide is formed:

$$C\,(s) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow CO\,(g) \quad \Delta H^\circ = -111kJ$$

Then, carbon monoxide reacts further to form carbon dioxide:

$$CO\,(g) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow CO_2\,(g) \quad \Delta H^\circ = -283kJ$$

The equation describing the overall reaction is the sum of these two chemical changes:

$$\begin{array}{ll} \text{step 1} & \mathrm{C\,(s) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow CO\,(g)} \\ \text{step 2} & \mathrm{CO\,(g) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow CO_2\,(g)} \\ \text{sum} & \mathrm{C\,(s) + \cancel{CO(g)} + O_2\,(g) \longrightarrow \cancel{CO(g)} + CO_2\,(g)} \end{array}$$

Because the $\mathrm{CO\,(g)}$ produced in Step 1 is consumed in Step 2, the net change is:

$$\mathrm{C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g)}$$

According to Hess's law, the enthalpy change of the reaction will equal the sum of the enthalpy changes of the steps.

$$\begin{array}{lll} \text{step 1} & \mathrm{C\,(s) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow \cancel{CO(g)}} & \Delta H^\circ = -111\,\mathrm{kJ} \\ \text{step 2} & \mathrm{\cancel{CO(g)} + \tfrac{1}{2}\,O_2\,(g) \longrightarrow CO_2\,(g)} & \Delta H^\circ = -283\,\mathrm{kJ} \\ \text{sum} & \mathrm{C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g)} & \Delta H^\circ = -394\,\mathrm{kJ} \end{array}$$

The result is shown in Figure 5.4.5. We see that Δ*H* of the overall reaction is the same whether it occurs in one step or two. This finding (overall Δ*H* for the reaction = sum of Δ*H* values for reaction "steps" in the overall reaction) is true in general for chemical and physical processes.

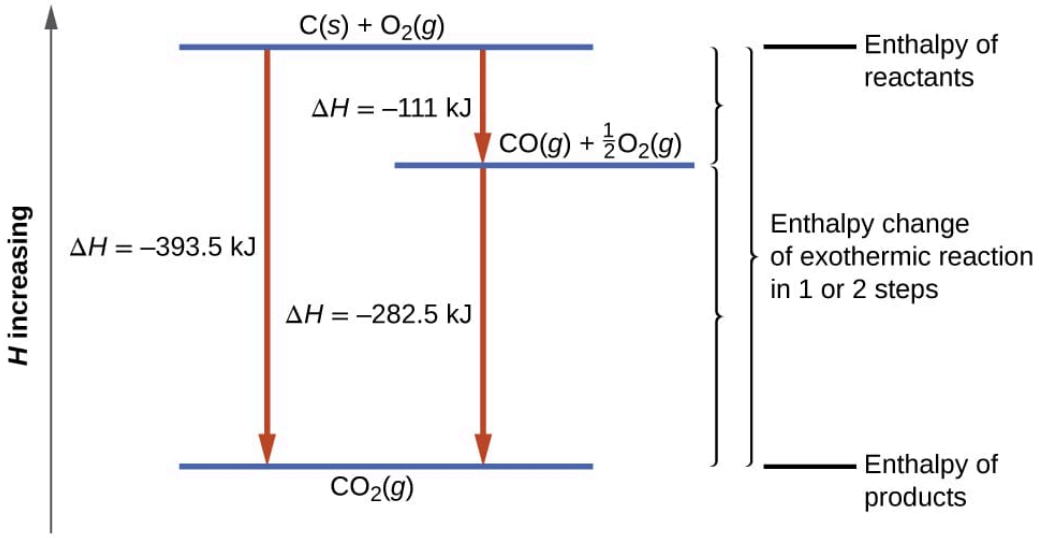


Figure 5.4.5: The formation of $\mathrm{CO_2\,(g)}$ from its elements can be thought of as occurring in two steps, which sum to the overall reaction, as described by Hess's law. The horizontal blue lines represent enthalpies. For an exothermic process, the products are at lower enthalpy than are the reactants.

Before we further practice using Hess's law, let us recall two important features of ΔH.

1. ΔH is directly proportional to the quantities of reactants or products. For example, the enthalpy change for the reaction forming 1 mole of $NO_2(g)$ is +33.2 kJ:

   $$\mathrm{\tfrac{1}{2}\,N_2\,(g) + O_2\,(g) \longrightarrow NO_2\,(g)} \quad \Delta H = +33.2\,\mathrm{kJ}$$

   When 2 moles of $\mathrm{NO_2}$ (twice as much) are formed, the Δ*H* will be twice as large:

   $$\mathrm{N_2\,(g) + 2\,O_2\,(g) \longrightarrow 2\,NO_2\,(g)} \quad \Delta H = +66.4\,\mathrm{kJ}$$

   In general, if we multiply or divide an equation by a number, then the enthalpy change should also be multiplied or divided by the same number.

2. ΔH for a reaction in one direction is equal in magnitude and opposite in sign to $\Delta H$for the reaction in the reverse direction. For example, given that:

$$\mathrm{H_2\,(g) + Cl_2\,(g) \longrightarrow 2\,HCl\,(g)} \quad \Delta H = -184.6\,\mathrm{kJ}$$

Then, for the "reverse" reaction, the enthalpy change is also "reversed":

Example 5.4.6: Stepwise Calculation of Heat of Formation Using Hess's Law

Determine the enthalpy of formation, of $\mathrm{FeCl_3\,(s)}$ from the enthalpy changes of the following two-step process that occurs under standard state conditions:

$$\mathrm{Fe\,(s) + Cl_2\,(g) \longrightarrow FeCl_2\,(s)} \quad \Delta H^\circ = -341.8\,\mathrm{kJ}$$

$$\mathrm{FeCl_2\,(s) + \tfrac{1}{2}\,Cl_2\,(g) \longrightarrow FeCl_3\,(s)} \quad \Delta H^\circ = -57.7\,\mathrm{kJ}$$

Solution

We are trying to find the standard enthalpy of formation of $\mathrm{FeCl_3\,(s)}$, which is equal to ΔH° for the reaction:

$$\mathrm{Fe\,(s) + \tfrac{3}{2}\,Cl_2\,(g) \longrightarrow FeCl_3\,(s)} \quad \Delta H_f^\circ = ?$$

Looking at the reactions, we see that the reaction for which we want to find ΔH° is the sum of the two reactions with known ΔH values, so we must sum their ΔH values:

step 1	$\mathrm{Fe\,(s) + Cl_2\,(g) \longrightarrow \cancel{FeCl2(s)}}$	$\Delta H^\circ = -341.8\,\mathrm{kJ}$
step 2	$\mathrm{\cancel{FeCl2(s)} + \tfrac{1}{2}\,Cl_2\,(g) \longrightarrow FeCl_3\,(s)}$	$\Delta H^\circ = -57.7\,\mathrm{kJ}$
sum	$\mathrm{Fe\,(s) + \tfrac{3}{2}\,Cl_2\,(g) \longrightarrow FeCl_3\,(s)}$	$\Delta H^\circ = -399.5\,\mathrm{kJ}$

The enthalpy of formation, ΔH_f° of $\mathrm{FeCl_3\,(s)}$ is –399.5 kJ/mol.

Exercise 5.4.6

Calculate ΔH for the process:

$$\mathrm{N_2\,(g) + 2\,O_2\,(g) \longrightarrow 2\,NO_2\,(g)}$$

from the following information:

$$\mathrm{N_2\,(g) + O_2\,(g) \longrightarrow 2\,NO\,(g)} \quad \Delta H = 180.5\,\mathrm{kJ}$$

$$\mathrm{NO\,(g) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow NO_2\,(g)} \quad \Delta H = -57.06\,\mathrm{kJ}$$

Answer available at the end of this section.

Here is a less straightforward example that illustrates the thought process involved in solving many Hess's law problems. It shows how we can find many standard enthalpies of formation (and other values of ΔH) if they are difficult to determine experimentally.

Example 5.4.7: A More Challenging Problem Using Hess's Law

Chlorine monofluoride can react with fluorine to form chlorine trifluoride:

i. $$\mathrm{ClF\,(g) + F_2\,(g) \longrightarrow ClF_3\,(g)} \quad \Delta H^\circ = ?$$

Use the reactions here to determine the ΔH^o for reaction (i):

ii. $$\mathrm{2\,OF_2\,(g) \longrightarrow O_2\,(g) + 2\,F_2\,(g)} \quad \Delta H^\circ_{(ii)} = -49.4\,\mathrm{kJ}$$

iii. $$\mathrm{2\,ClF\,(g) + O_2\,(g) \longrightarrow Cl_2O\,(g) + OF_2\,(g)} \quad \Delta H^\circ_{(iii)} = +214.0\,\mathrm{kJ}$$

iv. $$\mathrm{ClF_3\,(g) + O_2\,(g) \longrightarrow \tfrac{1}{2}\,Cl_2O\,(g) + \tfrac{3}{2}\,OF_2\,(g)} \quad \Delta H^\circ_{(in)} = +236.2\,\mathrm{kJ}$$

Solution

Our goal is to manipulate and combine reactions (ii), (iii), and (iv) such that they add up to reaction (i). Going from left to right in (i), we first see that ClF(g) is needed as a reactant. This can be obtained by multiplying reaction (iii) by $\frac{1}{2}$ which means that the ΔH^o change is also multiplied by $\frac{1}{2}$:

$$\mathrm{ClF\,(g) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow \tfrac{1}{2}\,Cl_2O\,(g) + \tfrac{1}{2}\,OF_2\,(g)} \quad \Delta H^\circ = \frac{1}{2}(214.0) = +107.0\,\mathrm{kJ}$$

Next, we see that F_2 is also needed as a reactant. To get this, reverse and halve reaction *(ii)*, which means that the ΔH^o changes sign and is halved:

$$\mathrm{\tfrac{1}{2}\,O_2\,(g) + F_2\,(g) \longrightarrow OF_2\,(g)} \quad \Delta H^\circ = +24.7\,\mathrm{kJ}$$

To get $\mathrm{ClF_3}$ as a product, reverse (iv), changing the sign of ΔH^o:

$$\mathrm{\tfrac{1}{2}\,Cl_2O\,(g) + \tfrac{3}{2}\,OF_2\,(g) \longrightarrow ClF_3\,(g) + O_2\,(g)} \quad \Delta H^\circ = -236.2kJ$$

Now check to make sure that these reactions add up to the reaction we want:

step 1	$\mathrm{ClF\,(g) + \cancel{1/2O2(g)} \longrightarrow \cancel{1/2Cl2O(g)} + \cancel{1/2OF2(g)}}$	$\Delta H^\circ = +107.0\,\mathrm{kJ}$
step 2	$\mathrm{\cancel{1/2O2(g)} + F_2\,(g) \longrightarrow \cancel{OF2(g)}}$	$\Delta H^\circ = +24.7\,\mathrm{kJ}$
step 3	$\mathrm{\cancel{1/2Cl2O(g)} + \cancel{3/2OF2(g)} \longrightarrow ClF_3\,(g) + \cancel{O2(g)}}$	$\Delta H^\circ = -236.2\,\mathrm{kJ}$
sum	$\mathrm{ClF\,(g) + F_2\,(g) \longrightarrow ClF_3\,(g)}$	$\Delta H^\circ = -104.5\,\mathrm{kJ}$

Reactants $\frac{1}{2}\,O_2$ and $\frac{1}{2}\,O_2$ cancel out the product O_2; the $\frac{1}{2}\,Cl_2O$ product cancels $\frac{1}{2}\,Cl_2O$ reactant and $\frac{3}{2}\,Cl_2O$ reactant is cancelled by products $\frac{1}{2}\,OF_2$ and OF_2. This leaves only reactants $\mathrm{ClF\,(g)}$ and $\mathrm{F_2\,(g)}$ and product $\mathrm{ClF_3\,(g)}$, which are what we want. Since summing these three modified reactions yields the reaction of interest, summing the three modified ΔH^o values will give the desired ΔH^o:

$$\Delta H^\circ = (+107.0kJ) + (24.7kJ) + (-236.2kJ) = -104.5\,\mathrm{kJ}$$

Exercise 5.4.7

Aluminum chloride can be formed from its elements:

i. $$\mathrm{2\,Al\,(s) + 3\,Cl_2\,(g) \longrightarrow 2\,AlCl_3\,(s)} \quad \Delta H^\circ = ?$$

Use the reactions here to determine the ΔH^o for reaction *(i)*:

ii. $$\mathrm{HCl\,(g) \longrightarrow HCl\,(aq)} \quad \Delta H^\circ_{(ii)} = -74.8\,\mathrm{kJ}$$

iii. $$\mathrm{H_2\,(g) + Cl_2\,(g) \longrightarrow 2\,HCl\,(g)} \quad \Delta H^\circ_{(iii)} = -185\,\mathrm{kJ}$$

iv. $$\mathrm{AlCl_3\,(aq) \longrightarrow AlCl_3\,(s)} \quad \Delta H^\circ_{(iv)} = +323\,\mathrm{kJ}$$

v. $$\mathrm{2\,Al\,(s) + 6\,HCl\,(aq) \longrightarrow 2\,AlCl_3\,(aq) + 3\,H_2\,(g)} \quad \Delta H^\circ_{(v)} = -1049\,\mathrm{kJ}$$

Answer available at the end of this section.

We also can use Hess's law to determine the enthalpy change of any reaction if the corresponding enthalpies of formation of the reactants and products are available. The stepwise reactions we consider are:

i. decompositions of the reactants into their component elements (for which the enthalpy changes are proportional to the negative of the enthalpies of formation of the reactants), followed by
ii. re-combinations of the elements to give the products (with the enthalpy changes proportional to the enthalpies of formation of the products).

The standard enthalpy change of the overall reaction is therefore equal to: (ii) the sum of the standard enthalpies of formation of all the products plus (i) the sum of the negatives of the standard enthalpies of formation of the reactants. This is usually rearranged slightly to be written as follows, with ∑ representing "the sum of" and *n* standing for the stoichiometric coefficients:

$$\Delta H^\circ_{\text{reaction}} = \sum n \times \Delta H^\circ_f(\text{ products }) - \sum n \times \Delta H^\circ_f(\text{ reactants })$$

The following example shows in detail why this equation is valid, and how to use it to calculate the enthalpy change for a reaction of interest.

Example 5.4.8: Using Hess's Law

What is the standard enthalpy change for the reaction:

$$3\,NO_2\,(g) + H_2O\,(l) \longrightarrow 2\,HNO_3\,(aq) + NO\,(g) \quad \Delta H^\circ = ?$$

Solution: Using the Equation

Use the special form of Hess's law given previously, and values from Appendix 11.7:

$$\begin{aligned}
\Delta H^\circ_{\text{reaction}} &= \sum n \times \Delta H^\circ_f(\text{ products }) - \sum n \times \Delta H^\circ_f(\text{ reactants }) \\
&= \left[2\ \cancel{\text{mol HNO}_3\,(aq)} \times \frac{-207.4\,\text{kJ}}{1\ \cancel{\text{mol HNO}_3\,(aq)}} + 1\ \cancel{\text{mol NO}\,(g)} \times \frac{+90.2\,\text{kJ}}{1\ \cancel{\text{mol NO}\,(g)}}\right] \\
&\quad - \left[3\ \cancel{\text{mol NO}_2\,(g)} \times \frac{+33.2\,\text{kJ}}{1\ \cancel{\text{mole NO}_2\,(g)}} + 1\ \cancel{\text{mol H}_2\text{O}\,(l)} \times \frac{-285.8\,\text{kJ}}{1\ \cancel{\text{mol H}_2\text{O}\,(l)}}\right] \\
&= [2 \times (-206.64) + 90.25] - [3 \times 33.2 + -(-285.83)] \\
&= -323.03 + 186.23 \\
&= -136.80\,\text{kJ}
\end{aligned}$$

Solution: Supporting Why the General Equation is Valid

Alternatively, we can write this reaction as the sum of the decompositions of $3\,NO_2\,(g)$ and $H2O(l)$ into their constituent elements, and the formation of $2\,HNO_3\,(aq)$ and $1\,NO\,(g)$ from their constituent elements. Writing out these reactions, and noting their relationships to the ΔH° values for these compounds (from Appendix 11.7), we have:

$$\begin{aligned}
3\,NO_2\,(g) &\longrightarrow \tfrac{3}{2}\,N_2\,(g) + 3\,O_2\,(g) && \Delta H^\circ_1 = -99.6\,\text{kJ} \\
H_2O\,(l) &\longrightarrow H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) && \Delta H^\circ_2 = +285.8\,\text{kJ}\,\left[-1 \times \Delta H^\circ_f\,(H_2O)\right] \\
H_2\,(g) + N_2\,(g) + 3\,O_2\,(g) &\longrightarrow 2\,HNO_3\,(aq) && \Delta H^\circ_3 = -414.8\,\text{kJ}\,\left[2 \times \Delta H^\circ_f\,(HNO_3)\right] \\
\tfrac{1}{2}\,N_2\,(g) + \tfrac{1}{2}\,O_2\,(g) &\longrightarrow NO\,(g) && \Delta H^\circ_4 = +90.2\,\text{kJ}\,\left[1 \times \Delta H^\circ_f(NO)\right]
\end{aligned}$$

Summing these reaction equations gives the reaction we are interested in:

$$3\,NO_2\,(g) + H_2O\,(l) \longrightarrow 2\,HNO_3\,(aq) + NO\,(g)$$

Summing their enthalpy changes gives the value we want to determine:

$$\begin{aligned}
\Delta H^\circ_{rxn} &= \Delta H^\circ_1 + \Delta H^\circ_2 + \Delta H^\circ_3 + \Delta H^\circ_4 \\
&= (-99.6\,\text{kJ}) + (+285.8\,\text{kJ}) + (-414.8\,\text{kJ}) + (+90.2\,\text{kJ}) \\
&= -138.4\,\text{kJ}
\end{aligned}$$

So the standard enthalpy change for this reaction is ΔH° = –138.4 kJ.

Note that this result was obtained by:

a. multiplying the of each product by its stoichiometric coefficient and summing those values,
b. multiplying the of each reactant by its stoichiometric coefficient and summing those values, and then
c. subtracting the result found in (2) from the result found in (1).

This is also the procedure in using the general equation, as shown.

Exercise 5.4.8

Calculate the heat of combustion of 1 mole of ethanol, $C_2H_5OH\,(l)$, when $H_2O\,(l)$ and $CO_2\,(g)$ are formed. Use the following enthalpies of formation: $C_2H_5OH\,(l)$, –278 kJ/mol; $H_2O\,(l)$, –286 kJ/mol; and $CO_2\,(g)$, –394 kJ/mol.

Answer available at the end of this section.

Footnotes

- 3For more on algal fuel, see http://www.theguardian.com/environme...n-fuel-problem.

Answers

Exercise 5.4.1
ΔH = –153 kJ

Exercise 5.4.1
ΔH = –338 kJ

Exercise 5.4.3
6.25 10^3 kJ

Exercise 5.4.4
For the reaction

$$H_2\,(g) + Cl_2\,(g) \longrightarrow 2\,HCl\,(g) \quad \Delta H^\circ = -184.6\,kJ$$

Exercise 5.4.5

a. $4\,C\,(s, \text{graphite}) + 5\,H_2\,(g) + \frac{1}{2}\,O_2\,(g) \longrightarrow C_2H_5OC_2H_5\,(l)$

b. $2\,Na\,(s) + C\,(s, \text{graphite}) + \frac{3}{2}\,O_2\,(g) \longrightarrow Na_2CO_3\,(s)$

Exercise 5.4.6
66.4 kJ

Exercise 5.4.7
–1407 kJ

Exercise 5.4.8
–1368 kJ/mol

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5.5: Strengths of Ionic and Covalent Bonds

Learning Objectives

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

- Describe the energetics of covalent and ionic bond formation and breakage
- Use the Born-Haber cycle to compute lattice energies for ionic compounds
- Use average covalent bond energies to estimate enthalpies of reaction

A bond's strength describes how strongly each atom is joined to another atom, and therefore how much energy is required to break the bond between the two atoms. In this section, you will learn about the bond strength of covalent bonds, and then compare that to the strength of ionic bonds, which is related to the lattice energy of a compound.

Bond Strength: Covalent Bonds

Stable molecules exist because covalent bonds hold the atoms together. We measure the strength of a covalent bond by the energy required to break it, that is, the energy necessary to separate the bonded atoms. Separating any pair of bonded atoms requires energy. The stronger a bond, the greater the energy required to break it.

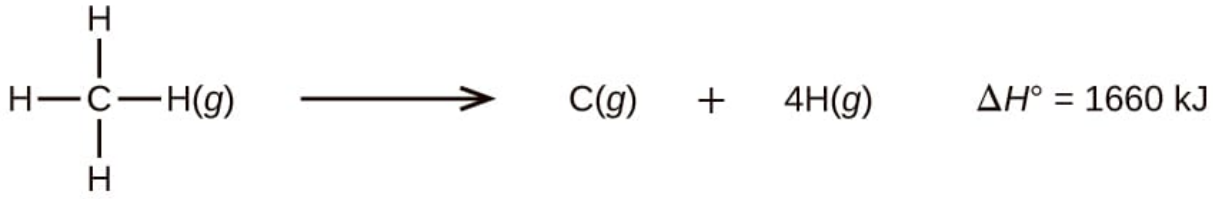
The energy required to break a specific covalent bond in one mole of gaseous molecules is called the **bond energy** or the **bond dissociation energy**. The bond energy for a diatomic molecule, $\mathrm{D_{X-Y}}$, is defined as the **standard enthalpy change** for the endothermic reaction:

$$\mathrm{H_2}(g) \longrightarrow 2\mathrm{H}(g) \quad \text{bond energy } = 436 \text{ kJ}$$

For example, the bond energy of the pure covalent $\mathrm{H{-}H}$ bond, $\mathrm{D_{H-H}}$, is 436 kJ per mole of $\mathrm{H{-}H}$ bonds broken:

$$\mathrm{H_2\,(g)} \longrightarrow \mathrm{2\,H\,(g)} \qquad D_{\mathrm{H-H}} = \Delta H^\circ = 436\,\mathrm{kJ}$$

Molecules with three or more atoms have two or more bonds. The sum of all bond energies in such a molecule is equal to the standard enthalpy change for the endothermic reaction that breaks all the bonds in the molecule. For example, the sum of the four $\mathrm{C{-}H}$ bond energies in $\mathrm{CH_4}$, 1660 kJ, is equal to the standard enthalpy change of the reaction:



The average $\mathrm{C{-}H}$ bond energy, $\mathrm{D_{C-H}}$, is 1660/4 = 415 kJ/mol because there are four moles of $\mathrm{C{-}H}$ bonds broken per mole of the reaction. Although the four $\mathrm{C{-}H}$ bonds are equivalent in the original molecule, they do not each require the same energy to break; once the first bond is broken (which requires 439 kJ/mol), the remaining bonds are easier to break. The 415 kJ/mol value is the average, not the exact value required to break any one bond.

The strength of a bond between two atoms increases as the number of electron pairs in the bond increases. Generally, as the bond strength increases, the bond length decreases. Thus, we find that triple bonds are stronger and shorter than double bonds between the same two atoms; likewise, double bonds are stronger and shorter than single bonds between the same two atoms. Average bond energies for some common bonds appear in Table $5.5.1$, and a comparison of bond lengths and bond strengths for some common bonds appears in Table $5.5.2$. When one atom bonds to various atoms in a group, the bond strength typically decreases as we move down the group. For example, $\mathrm{C{-}F}$ is 439 kJ/mol, $\mathrm{C{-}Cl}$ is 330 kJ/mol, and $\mathrm{C{-}Br}$ is 275 kJ/mol.

Table 5.5.1: Bond Energies (kJ/mol)

Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy
H–H	436	C–S	260	F–Cl	255
H–C	415	C–Cl	330	F–Br	235
H–N	390	C–Br	275	Si–Si	230
H–O	464	C–I	240	Si–P	215
H–F	569	N–N	160	Si–S	225
H–Si	395	N=N	418	Si–Cl	359
H–P	320	N≡N	946	Si–Br	290
H–S	340	N–O	200	Si–I	215
H–Cl	432	N–F	270	P–P	215
H–Br	370	N–P	210	P–S	230
H–I	295	N–Cl	200	P–Cl	330
C–C	345	N–Br	245	P–Br	270
C=C	611	O–O	140	P–I	215
C≡C	837	O=O	498	S–S	215
C–N	290	O–F	160	S–Cl	250
C=N	615	O–Si	370	S–Br	215
C≡N	891	O–P	350	Cl–Cl	243
C–O	350	O–Cl	205	Cl–Br	220
C=O	741	O–I	200	Cl–I	210
C≡O	1080	F–F	160	Br–Br	190
C–F	439	F–Si	540	Br–I	180
C–Si	360	F–P	489	I–I	150
C–P	265	F–S	285		

Table 5.5.2: Average Bond Lengths and Bond Energies for Some Common Bonds

Bond	Bond Length (Å)	Bond Energy (kJ/mol)
C–C	1.54	345
C=C	1.34	611
C≡C	1.20	837
C–N	1.43	290
C=N	1.38	615
C≡N	1.16	891
C–O	1.43	350
C=O	1.23	741
C≡O	1.13	1080

We can use bond energies to calculate approximate enthalpy changes for reactions where enthalpies of formation are not available. Calculations of this type will also tell us whether a reaction is exothermic or endothermic. An exothermic reaction (ΔH

negative, heat produced) results when the bonds in the products are stronger than the bonds in the reactants. An endothermic reaction (Δ*H* positive, heat absorbed) results when the bonds in the products are weaker than those in the reactants.

The enthalpy change, Δ*H*, for a chemical reaction is approximately equal to the sum of the energy required to break all bonds in the reactants (energy "in", positive sign) plus the energy released when all bonds are formed in the products (energy "out," negative sign). This can be expressed mathematically in the following way:

$$\Delta H = \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}}$$

In this expression, the symbol $\sum$ means "the sum of" and D represents the bond energy in kilojoules per mole, which is always a positive number. The bond energy is obtained from a table (like Table 5.5.2) and will depend on whether the particular bond is a single, double, or triple bond. Thus, in calculating enthalpies in this manner, it is important that we consider the bonding in all reactants and products. Because D values are typically averages for one type of bond in many different molecules, this calculation provides a rough estimate, not an exact value, for the enthalpy of reaction.

Consider the following reaction:

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

or

$$\mathrm{H{-}H\,(g) + Cl{-}Cl\,(g) \longrightarrow 2\,H{-}Cl\,(g)}$$

To form two moles of HCl, one mole of H−H bonds and one mole of Cl−Cl bonds must be broken. The energy required to break these bonds is the sum of the bond energy of the H−H bond (436 kJ/mol) and the Cl−Cl bond (243 kJ/mol). During the reaction, two moles of H−Cl bonds are formed (bond energy = 432 kJ/mol), releasing 2×432 kJ; or 864 kJ. Because the bonds in the products are stronger than those in the reactants, the reaction releases more energy than it consumes:

$$\begin{aligned}\Delta H &= \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}} \\ &= [D_{\mathrm{H{-}H}} + D_{\mathrm{Cl{-}Cl}}] - 2D_{\mathrm{H{-}Cl}} \\ &= [436 + 243] - 2(432) \\ &= -185\ \text{kJ}\end{aligned}$$

This excess energy is released as heat, so the reaction is exothermic. Appendix 11.7 gives a value for the standard molar enthalpy of formation of HCl(g), ΔH_f° of –92.307 kJ/mol. Twice that value is –184.6 kJ, which agrees well with the answer obtained earlier for the formation of two moles of HCl.

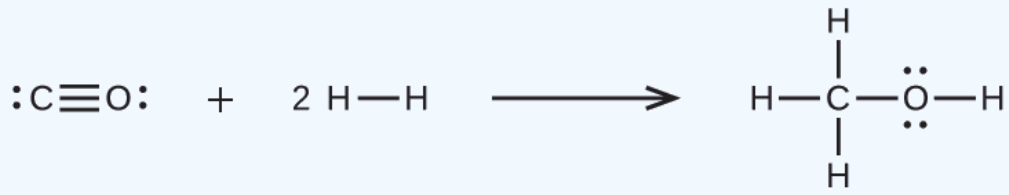
Example 5.5.1: Using Bond Energies to Calculate Approximate Enthalpy Changes

Methanol, CH_3OH, may be an excellent alternative fuel. The high-temperature reaction of steam and carbon produces a mixture of the gases carbon monoxide, CO, and hydrogen, H_2, from which methanol can be produced. Using the bond energies in Table 5.5.2, calculate the approximate enthalpy change, Δ*H*, for the reaction here:

$$\mathrm{CO\,(g) + 2\,H_2\,(g) \longrightarrow CH_3OH\,(g)}$$

Solution

First, we need to write the Lewis structures of the reactants and the products:



From this, we see that Δ*H* for this reaction involves the energy required to break a C–O triple bond and two H–H single bonds, as well as the energy produced by the formation of three C–H single bonds, a C–O single bond, and an O–H single bond. We can express this as follows:

$$\begin{aligned}\Delta H &= \Sigma D_{\text{bonds broken}} - \Sigma D_{\text{bonds formed}} \\ &= [D_{C\equiv O} + 2\,(D_{H-H})] - [3\,(D_{C-H}) + D_{C-O} + D_{O-H}]\end{aligned}$$

Using the bond energy values in Table 5.5.2, we obtain:

$$\begin{aligned}\Delta H &= [1080 + 2(436)] - [3(415) + 350 + 464] \\ &= -107kJ\end{aligned}$$

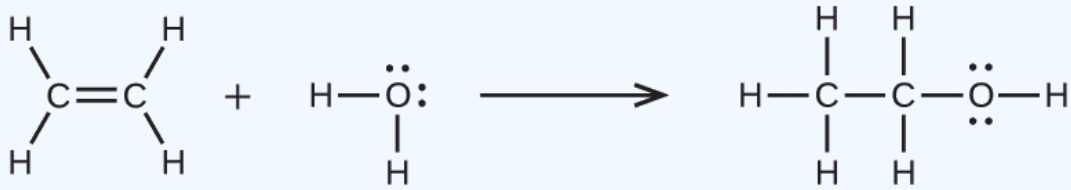
We can compare this value to the value calculated based on data from Appendix 11.7:

$$\begin{aligned}\Delta H &= \left[\Delta H_f^\circ CH_3OH(g)\right] - \left[\Delta H_f^\circ CO(g) + 2 \times \Delta H_f^\circ H_2\right] \\ &= [-201.0] - [-110.52 + 2 \times 0] \\ &= -90.5kJ\end{aligned}$$

Note that there is a fairly significant gap between the values calculated using the two different methods. This occurs because D values are the *average* of different bond strengths; therefore, they often give only rough agreement with other data.

Exercise 5.5.1

Ethyl alcohol, CH_3CH_2OH, was one of the first organic chemicals deliberately synthesized by humans. It has many uses in industry, and it is the alcohol contained in alcoholic beverages. It can be obtained by the fermentation of sugar or synthesized by the hydration of ethylene in the following reaction:



Using the bond energies in Table 5.5.2, calculate an approximate enthalpy change, Δ*H*, for this reaction.

Answer available at the end of this section.

Ionic Bond Strength and Lattice Energy

An ionic compound is stable because of the electrostatic attraction between its positive and negative ions. The lattice energy of a compound is a measure of the strength of this attraction. The **lattice energy** ($\Delta H_{lattice}$) of an ionic compound is defined as the energy required to separate one mole of the solid into its component gaseous ions. For the ionic solid MX, the lattice energy is the enthalpy change of the process:

$$MX(s) \longrightarrow M^{n+}(g) + X^{n-}(g) \quad \Delta H_{\text{lattice}}$$

Note that we are using the convention where the ionic solid is separated into ions, so our lattice energies will be *endothermic* (positive values). Some texts use the equivalent but opposite convention, defining lattice energy as the energy released when separate ions combine to form a lattice and giving negative (exothermic) values. Thus, if you are looking up lattice energies in another reference, be certain to check which definition is being used. In both cases, a larger magnitude for lattice energy indicates a more stable ionic compound. For sodium chloride, $\Delta H_{\text{lattice}}$ = 769 kJ. Thus, it requires 769 kJ to separate one mole of solid NaCl into gaseous Na^+ and Cl^- ions. When one mole each of gaseous Na^+ and Cl^- ions form solid NaCl, 769 kJ of heat is released.

The lattice energy $\Delta H_{\text{lattice}}$ of an ionic crystal can be expressed by the following equation (derived from Coulomb's law, governing the forces between electric charges):

$$\Delta H_{\text{lattice}} = \frac{C(Z^+)(Z^-)}{R_0}$$

in which C is a constant that depends on the type of crystal structure; Z^+ and Z^- are the charges on the ions; and R_o is the interionic distance (the sum of the radii of the positive and negative ions). Thus, the lattice energy of an ionic crystal increases rapidly as the charges of the ions increase and the sizes of the ions decrease. When all other parameters are kept constant, doubling the charge of both the cation and anion quadruples the lattice energy. For example, the lattice energy of LiF (Z^+ and Z^- = 1) is 1023 kJ/mol, whereas that of MgO (Z^+ and Z^- = 2) is 3900 kJ/mol (R_o is nearly the same—about 200 pm for both compounds).

Different interatomic distances produce different lattice energies. For example, we can compare the lattice energy of MgF_2 (2957 kJ/mol) to that of MgI_2 (2327 kJ/mol) to observe the effect on lattice energy of the smaller ionic size of F^- as compared to I^-.

Example 5.5.2: Lattice Energy Comparisons

The precious gem ruby is aluminum oxide, Al_2O_3, containing traces of Cr^{3+}. The compound Al_2Se_3 is used in the fabrication of some semiconductor devices. Which has the larger lattice energy, Al_2O_3 or Al_2Se_3?

Solution

In these two ionic compounds, the charges Z^+ and Z^- are the same, so the difference in lattice energy will depend upon R_o. The O^{2-} ion is smaller than the Se^{2-} ion. Thus, Al_2O_3 would have a shorter interionic distance than Al_2Se_3, and Al_2O_3 would have the larger lattice energy.

Exercise 5.5.1

Zinc oxide, ZnO, is a very effective sunscreen. How would the lattice energy of ZnO compare to that of NaCl?

Answer available at the end of this section.

The Born-Haber Cycle

It is not possible to measure lattice energies directly. However, the lattice energy can be calculated using the equation given in the previous section or by using a thermochemical cycle. The **Born-Haber cycle** is an application of Hess's law that breaks down the formation of an ionic solid into a series of individual steps:

- ΔH_f° the standard enthalpy of formation of the compound
- IE, the ionization energy of the metal
- EA, the electron affinity of the nonmetal
- ΔH_s° the enthalpy of sublimation of the metal
- D, the bond dissociation energy of the nonmetal
- $\Delta H_{lattice}$, the lattice energy of the compound

Figure 5.5.1: diagrams the Born-Haber cycle for the formation of solid cesium fluoride.

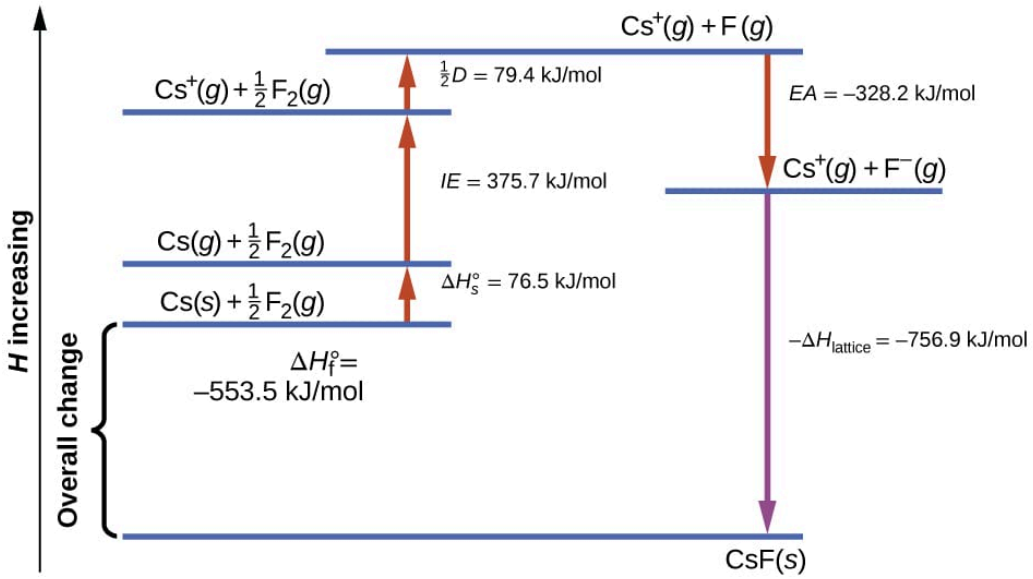


Figure 5.5.1: The Born-Haber cycle shows the relative energies of each step involved in the formation of an ionic solid from the necessary elements in their reference states.

We begin with the elements in their most common states, $\mathrm{Cs\,(s)}$ and $\mathrm{F_2\,(g)}$. The represents the conversion of solid cesium into a gas, and then the ionization energy converts the gaseous cesium atoms into cations. In the next step, we account for the energy required to break the F–F bond to produce fluorine atoms. Converting one mole of fluorine atoms into fluoride ions is an exothermic process, so this step gives off energy (the electron affinity) and is shown as decreasing along the *y*-axis. We now have one mole of Cs cations and one mole of F anions. These ions combine to produce solid cesium fluoride. The enthalpy change in this step is the negative of the lattice energy, so it is also an exothermic quantity. The total energy involved in this conversion is equal to the experimentally determined enthalpy of formation, ΔH_f° of the compound from its elements. In this case, the overall change is exothermic.

Hess's law can also be used to show the relationship between the enthalpies of the individual steps and the enthalpy of formation. Table 5.5.3 shows this for fluoride, CsF.

Table 5.5.3

Enthalpy of sublimation of $\mathrm{Cs\,(s)}$	$\mathrm{Cs\,(s)} \longrightarrow \mathrm{Cs\,(g)}$	$\Delta H = \Delta H_s^\circ = 76.5\ \mathrm{kJ/mol}$
One-half of the bond energy of $\mathrm{F_2}$	$\frac{1}{2}\,\mathrm{F_2\,(g)} \longrightarrow \mathrm{F\,(g)}$	$\Delta H = \frac{1}{2}D = 79.4\ \mathrm{kJ/mol}$
Ionization energy of $\mathrm{Cs\,(g)}$	$\mathrm{Cs\,(g)} \longrightarrow \mathrm{Cs^+\,(g)} + \mathrm{e^-}$	$\Delta H = IE = 375.7\ \mathrm{kJ/mol}$
Electron affinity of F	$\mathrm{F\,(g)} + \mathrm{e^-} \longrightarrow \mathrm{F^-\,(g)}$	$\Delta H = EA = -328.2\ \mathrm{kJ/mol}$
Negative of the lattice energy of $\mathrm{CsF\,(s)}$	$\mathrm{Cs^+\,(g)} + \mathrm{F^-\,(g)} \longrightarrow \mathrm{CsF\,(s)}$	$\Delta H = -\Delta H_{\mathrm{lattice}} = ?$
Enthalpy of formation of $\mathrm{CsF\,(s)}$, add steps 1–5	$\Delta H = \Delta H_f^\circ = \Delta H_s^\circ + \frac{1}{2}D + IE + (EA) + (-\Delta H_{\mathrm{lattice}})$ $\mathrm{Cs\,(s)} + \frac{1}{2}\,\mathrm{F_2\,(g)} \longrightarrow \mathrm{CsF\,(s)}$	$\Delta H = -553.5\ \mathrm{kJ/mol}$

Thus, the lattice energy can be calculated from other values. For cesium fluoride, using this data, the lattice energy is:

$$\Delta H_{\mathrm{lattice}} = 76.5 + 79.4 + 375.7 + (-328.2) - (-553.5) = 756.9\,\mathrm{kJ/mol}$$

The Born-Haber cycle may also be used to calculate any one of the other quantities in the equation for lattice energy, provided that the remainder is known. For example, if the relevant enthalpy of sublimation ΔH_s°, ionization energy (IE), bond dissociation enthalpy (D), lattice energy $\Delta H_{\mathrm{lattice}}$, and standard enthalpy of formation are known, the Born-Haber cycle can be used to determine the electron affinity of an atom.

Lattice energies calculated for ionic compounds are typically much higher than bond dissociation energies measured for covalent bonds. Whereas lattice energies typically fall in the range of 600–4000 kJ/mol (some even higher), covalent bond dissociation energies are typically between 150–400 kJ/mol for single bonds. Keep in mind, however, that these are not directly comparable values. For ionic compounds, lattice energies are associated with many interactions, as cations and anions pack together in an extended lattice. For covalent bonds, the bond dissociation energy is associated with the interaction of just two atoms.

Answers

Exercise 5.5.1

–35 kJ

Exercise 5.5.1

ZnO would have the larger lattice energy because the Z values of both the cation and the anion in ZnO are greater, and the interionic distance of ZnO is smaller than that of NaCl.

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5.6: Key Terms

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 energy
: (also, bond dissociation energy) energy required to break a covalent bond in a gaseous substance

Born-Haber cycle
: thermochemical cycle relating the various energetic steps involved in the formation of an ionic solid from the relevant elements

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

chemical thermodynamics
: area of science that deals with the relationships between heat, work, and all forms of energy associated with chemical and physical processes

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 (ΔH)
: heat released or absorbed by a system under constant pressure during a chemical or physical process

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

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

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)

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

hydrocarbon
compound composed only of hydrogen and carbon; the major component of fossil fuels

internal energy (*U*)
total of all possible kinds of energy present in a substance or substances

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

kinetic energy
energy of a moving body, in joules, equal to $\frac{1}{2}mv^2$ (where *m* = mass and *v* = velocity)

lattice energy ($\Delta H_{lattice}$)
energy required to separate one mole of an ionic solid into its component gaseous ions

nutritional calorie (Calorie)
unit used for quantifying energy provided by digestion of foods, defined as 1000 cal or 1 kcal

potential energy
energy of a particle or system of particles derived from relative position, composition, or condition

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)

standard enthalpy of combustion ($\Delta H°_c$)
heat released when one mole of a compound undergoes complete combustion under standard conditions

standard enthalpy of formation ($\Delta H°$,)
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 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

state function
property depending only on the state of a system, and not the path taken to reach that state

surroundings
all matter other than the system being studied

system
portion of matter undergoing a chemical or physical change being studied

temperature
intensive property of matter that is a quantitative measure of “hotness” and “coldness”

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

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

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5.7: Key Equations

$q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$

$\Delta U = q + w$

$\Delta H^{\circ}_{\text{reaction}} = \sum n \times \Delta H^{\circ}_{\text{f}}(\text{ products }) - \sum n \times \Delta H^{\circ}_{\text{f}}(\text{ reactants })$

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5.8: Summary

Energy is the capacity to supply heat or do work (applying a force to move matter). Kinetic energy (KE) is the energy of motion; potential energy is energy due to relative position, composition, or condition. When energy is converted from one form into another, energy is neither created nor destroyed (law of conservation of energy or first law of thermodynamics).

The thermal energy of matter is due to the kinetic energies of its constituent atoms or molecules. Temperature is an intensive property of matter reflecting hotness or coldness that increases as the average kinetic energy increases. Heat is the transfer of thermal energy between objects at different temperatures. Chemical and physical processes can absorb heat (endothermic) or release heat (exothermic). The SI unit of energy, heat, and work is the joule (J).

Specific heat and heat capacity are measures of the energy needed to change the temperature of a substance or object. The amount of heat absorbed or released by a substance depends directly on the type of substance, its mass, and the temperature change it undergoes.

Calorimetry is used to measure the amount of thermal energy transferred in a chemical or physical process. This requires careful measurement of the temperature change that occurs during the process and the masses of the system and surroundings. These measured quantities are then used to compute the amount of heat produced or consumed in the process using known mathematical relations.

Calorimeters are designed to minimize energy exchange between their contents and the external environment. They range from simple coffee cup calorimeters used by introductory chemistry students to sophisticated bomb calorimeters used to determine the energy content of food.

If a chemical change is carried out at constant pressure and the only work done is caused by expansion or contraction, q for the change is called the enthalpy change with the symbol ΔH, or ΔH° for reactions occurring under standard state conditions at 298 K. The value of ΔH for a reaction in one direction is equal in magnitude, but opposite in sign, to ΔH for the reaction in the opposite direction, and ΔH is directly proportional to the quantity of reactants and products. The standard enthalpy of formation, $\Delta H_\mathrm{f}^\circ$,the enthalpy change accompanying the formation of 1 mole of a substance from the elements in their most stable states at 1 bar and 298.15 K. If the enthalpies of formation are available for the reactants and products of a reaction, the enthalpy change can be calculated using Hess's law: If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes of the various steps.

The strength of a covalent bond is measured by its bond dissociation energy, that is, the amount of energy required to break that particular bond in a mole of molecules. Multiple bonds are stronger than single bonds between the same atoms. The enthalpy of a reaction can be estimated based on the energy input required to break bonds and the energy released when new bonds are formed. For ionic bonds, the lattice energy is the energy required to separate one mole of a compound into its gas phase ions. Lattice energy increases for ions with higher charges and shorter distances between ions. Lattice energies are often calculated using the Born-Haber cycle, a thermochemical cycle including all of the energetic steps involved in converting elements into an ionic compound.

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5.9: Exercises

1.

A burning match and a bonfire may have the same temperature, yet you would not sit around a burning match on a fall evening to stay warm. Why not?

2.

Prepare a table identifying several energy transitions that take place during the typical operation of an automobile.

3.

Explain the difference between heat capacity and specific heat of a substance.

4.

Calculate the heat capacity, in joules and in calories per degree, of the following:

(a) 28.4 g of water

(b) 1.00 oz of lead

5.

Calculate the heat capacity, in joules and in calories per degree, of the following:

(a) 45.8 g of nitrogen gas

(b) 1.00 pound of aluminum metal

6.

How much heat, in joules and in calories, must be added to a 75.0-g iron block with a specific heat of 0.449 J/g °C to increase its temperature from 25 °C to its melting temperature of 1535 °C?

7.

How much heat, in joules and in calories, is required to heat a 28.4-g (1-oz) ice cube from −23.0 °C to −1.0 °C?

8.

How much would the temperature of 275 g of water increase if 36.5 kJ of heat were added?

9.

If 14.5 kJ of heat were added to 485 g of liquid water, how much would its temperature increase?

10.

A piece of unknown substance weighs 44.7 g and requires 2110 J to increase its temperature from 23.2 °C to 89.6 °C.

(a) What is the specific heat of the substance?

(b) If it is one of the substances found in Table 9.1, what is its likely identity?

11.

A piece of unknown solid substance weighs 437.2 g, and requires 8460 J to increase its temperature from 19.3 °C to 68.9 °C.

(a) What is the specific heat of the substance?

(b) If it is one of the substances found in Table 9.1, what is its likely identity?

12.

An aluminum kettle weighs 1.05 kg.

(a) What is the heat capacity of the kettle?

(b) How much heat is required to increase the temperature of this kettle from 23.0 °C to 99.0 °C?

(c) How much heat is required to heat this kettle from 23.0 °C to 99.0 °C if it contains 1.25 L of water (density of 0.997 g/mL and a specific heat of 4.184 J/g °C)?

13.

Most people find waterbeds uncomfortable unless the water temperature is maintained at about 85 °F. Unless it is heated, a waterbed that contains 892 L of water cools from 85 °F to 72 °F in 24 hours. Estimate the amount of electrical energy required over 24 hours, in kWh, to keep the bed from cooling. Note that 1 kilowatt-hour (kWh) = 3.6×10^6 J, and assume that the density of water is 1.0 g/mL (independent of temperature). What other assumptions did you make? How did they affect your calculated result (i.e., were they likely to yield “positive” or “negative” errors)?

14.

A 500-mL bottle of water at room temperature and a 2-L bottle of water at the same temperature were placed in a refrigerator. After 30 minutes, the 500-mL bottle of water had cooled to the temperature of the refrigerator. An hour later, the 2-L of water had cooled to the same temperature. When asked which sample of water lost the most heat, one student replied that both bottles lost the same amount of heat because they started at the same temperature and finished at the same temperature. A second student thought that the 2-L bottle of water lost more heat because there was more water. A third student believed that the 500-mL bottle of water lost more heat because it cooled more quickly. A fourth student thought that it was not possible to tell because we do not know the initial temperature and the final temperature of the water. Indicate which of these answers is correct and describe the error in each of the other answers.

15.

Would the amount of heat measured for the reaction in Example 9.5 be greater, lesser, or remain the same if we used a calorimeter that was a poorer insulator than a coffee cup calorimeter? Explain your answer.

16.

Would the amount of heat absorbed by the dissolution in Example 9.6 appear greater, lesser, or remain the same if the experimenter used a calorimeter that was a poorer insulator than a coffee cup calorimeter? Explain your answer.

17.

Would the amount of heat absorbed by the dissolution in Example 9.6 appear greater, lesser, or remain the same if the heat capacity of the calorimeter were taken into account? Explain your answer.

18.

How many milliliters of water at 23 °C with a density of 1.00 g/mL must be mixed with 180 mL (about 6 oz) of coffee at 95 °C so that the resulting combination will have a temperature of 60 °C? Assume that coffee and water have the same density and the same specific heat.

19.

How much will the temperature of a cup (180 g) of coffee at 95 °C be reduced when a 45 g silver spoon (specific heat 0.24 J/g °C) at 25 °C is placed in the coffee and the two are allowed to reach the same temperature? Assume that the coffee has the same density and specific heat as water.

20.

A 45-g aluminum spoon (specific heat 0.88 J/g °C) at 24 °C is placed in 180 mL (180 g) of coffee at 85 °C and the temperature of the two become equal.

(a) What is the final temperature when the two become equal? Assume that coffee has the same specific heat as water.

(b) The first time a student solved this problem she got an answer of 88 °C. Explain why this is clearly an incorrect answer.

21.

The temperature of the cooling water as it leaves the hot engine of an automobile is 240 °F. After it passes through the radiator it has a temperature of 175 °F. Calculate the amount of heat transferred from the engine to the surroundings by one gallon of water with a specific heat of 4.184 J/g °C.

22.

A 70.0-g piece of metal at 80.0 °C is placed in 100 g of water at 22.0 °C contained in a calorimeter like that shown in Figure 9.12. The metal and water come to the same temperature at 24.6 °C. How much heat did the metal give up to the water? What is the specific heat of the metal?

23.

If a reaction produces 1.506 kJ of heat, which is trapped in 30.0 g of water initially at 26.5 °C in a calorimeter like that in Figure 9.12, what is the resulting temperature of the water?

24.

A 0.500-g sample of KCl is added to 50.0 g of water in a calorimeter (Figure 9.12). If the temperature decreases by 1.05 °C, what is the approximate amount of heat involved in the dissolution of the KCl, assuming the specific heat of the resulting solution is 4.18 J/g °C? Is the reaction exothermic or endothermic?

25.

Dissolving 3.0 g of $CaCl_2(s)$ in 150.0 g of water in a calorimeter (Figure 9.12) at 22.4 °C causes the temperature to rise to 25.8 °C. What is the approximate amount of heat involved in the dissolution, assuming the specific heat of the resulting solution is 4.18 J/g °C? Is the reaction exothermic or endothermic?

26.

When 50.0 g of 0.200 M NaCl(*aq*) at 24.1 °C is added to 100.0 g of 0.100 M $AgNO_3(aq)$ at 24.1 °C in a calorimeter, the temperature increases to 25.2 °C as AgCl(s) forms. Assuming the specific heat of the solution and products is 4.20 J/g °C, calculate the approximate amount of heat in joules produced.

27.

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:

$$Ba(OH)_2{\cdot}8H_2O(s) + 2NH_4SCN(aq) \diamond Ba(SCN)_2(aq) + 2NH_3(aq) + 10H_2O(l)$$

28.

The reaction of 50 mL of acid and 50 mL of base described in Example 9.5 increased the temperature of the solution by 6.9 °C. How much would the temperature have increased if 100 mL of acid and 100 mL of base had been used in the same calorimeter starting at the same temperature of 22.0 °C? Explain your answer.

29.

If the 3.21 g of NH_4NO_3 in Example 9.6 were dissolved in 100.0 g of water under the same conditions, how much would the temperature change? Explain your answer.

30.

When 1.0 g of fructose, $C_6H_{12}O_6(s)$, a sugar commonly found in fruits, is burned in oxygen in a bomb calorimeter, the temperature of the calorimeter increases by 1.58 °C. If the heat capacity of the calorimeter and its contents is 9.90 kJ/°C, what is q for this combustion?

31.

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?

32.

One method of generating electricity is by burning coal to heat water, which produces steam that drives an electric generator. To determine the rate at which coal is to be fed into the burner in this type of plant, the heat of combustion per ton of coal must be determined using a bomb calorimeter. When 1.00 g of coal is burned in a bomb calorimeter (Figure 9.17), the temperature increases by 1.48 °C. If the heat capacity of the calorimeter is 21.6 kJ/°C, determine the heat produced by combustion of a ton of coal (2.000×10^3 pounds).

33.

The amount of fat recommended for someone with a daily diet of 2000 Calories is 65 g. What percent of the calories in this diet would be supplied by this amount of fat if the average number of Calories for fat is
9.1 Calories/g?

34.

A teaspoon of the carbohydrate sucrose (common sugar) contains 16 Calories (16 kcal). What is the mass of one teaspoon of sucrose if the average number of Calories for carbohydrates is 4.1 Calories/g?

35.

What is the maximum mass of carbohydrate in a 6-oz serving of diet soda that contains less than 1 Calorie per can if the average number of Calories for carbohydrates is 4.1 Calories/g?

36.

A pint of premium ice cream can contain 1100 Calories. What mass of fat, in grams and pounds, must be produced in the body to store an extra 1.1×10^3 Calories if the average number of Calories for fat is
9.1 Calories/g?

37.

A serving of a breakfast cereal contains 3 g of protein, 18 g of carbohydrates, and 6 g of fat. What is the Calorie content of a serving of this cereal if the average number of Calories for fat is 9.1 Calories/g, for carbohydrates is 4.1 Calories/g, and for protein is 4.1 Calories/g?

38.

Which is the least expensive source of energy in kilojoules per dollar: a box of breakfast cereal that weighs 32 ounces and costs $4.23, or a liter of isooctane (density, 0.6919 g/mL) that costs $0.45? Compare the nutritional value of the cereal with the heat produced by combustion of the isooctane under standard conditions. A 1.0-ounce serving of the cereal provides 130 Calories.

39.

Explain how the heat measured in Example 9.5 differs from the enthalpy change for the exothermic reaction described by the following equation:
$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq)$ ⟐NaCl(aq)+H2O(l)HCl(aq)+NaOH(aq)⟐NaCl(aq)+H2O(l)

40.

Using the data in the check your learning section of Example 9.5, calculate Δ*H* in kJ/mol of $AgNO_3$(*aq*) for the reaction: $\mathrm{NaCl}(aq) + \mathrm{AgNO_3}(aq) \longrightarrow \mathrm{AgCl}(s) +$ [redacted]NaNO3(aq)NaCl(aq)+AgNO3(aq)⟐AgCl(s)+NaNO3(aq)

41.

Calculate the enthalpy of solution (Δ*H* for the dissolution) per mole of NH_4NO_3 under the conditions described in Example 9.6.

42.

Calculate Δ*H* for the reaction described by the equation. (*Hint*: Use the value for the approximate amount of heat absorbed by the reaction that you calculated in a previous exercise.)

$\mathrm{Ba(OH)_2 \cdot 8H_2O}(s) + 2\mathrm{NH_4SCN}(aq) \longrightarrow \mathrm{Ba(SCN)_2}(aq) + 2\mathrm{NH_3}(aq) + 10\mathrm{H_2O}(l)$

43.

Calculate the enthalpy of solution (Δ*H* for the dissolution) per mole of $CaCl_2$ (refer to Exercise 9.25).

44.

Although the gas used in an oxyacetylene torch (Figure 9.7) is essentially pure acetylene, the heat produced by combustion of one mole of acetylene in such a torch is likely not equal to the enthalpy of combustion of acetylene listed in Table 9.2. Considering the conditions for which the tabulated data are reported, suggest an explanation.

45.

How much heat is produced by burning 4.00 moles of acetylene under standard state conditions?

46.

How much heat is produced by combustion of 125 g of methanol under standard state conditions?

47.

How many moles of isooctane must be burned to produce 100 kJ of heat under standard state conditions?

48.

What mass of carbon monoxide must be burned to produce 175 kJ of heat under standard state conditions?

49.

When 2.50 g of methane burns in oxygen, 125 kJ of heat is produced. What is the enthalpy of combustion per mole of methane under these conditions?

50.

How much heat is produced when 100 mL of 0.250 M HCl (density, 1.00 g/mL) and 200 mL of 0.150 M NaOH (density, 1.00 g/mL) are mixed?
$\mathrm{HCl}\,(aq) + \mathrm{NaOH}\,(aq)$ ⟐NaCl(aq)+H2O(l)ΔH°=−58kJHCl(aq)+NaOH(aq)⟐NaCl(aq)+H2O(l)ΔH°=−58kJ

If both solutions are at the same temperature and the specific heat of the products is 4.19 J/g °C, how much will the temperature increase? What assumption did you make in your calculation?

51.

A sample of 0.562 g of carbon is burned in oxygen in a bomb calorimeter, producing carbon dioxide. Assume both the reactants and products are under standard state conditions, and that the heat released is directly proportional to the enthalpy of combustion of graphite. The temperature of the calorimeter increases from 26.74 °C to 27.93 °C. What is the heat capacity of the calorimeter and its contents?

52.

Before the introduction of chlorofluorocarbons, sulfur dioxide (enthalpy of vaporization, 6.00 kcal/mol) was used in household refrigerators. What mass of SO_2 must be evaporated to remove as much heat as evaporation of 1.00 kg of CCl_2F_2 (enthalpy of vaporization is 17.4 kJ/mol)?

The vaporization reactions for $\mathrm{SO_2}$ and $\mathrm{CCl_2\ F_2}$ are $\mathrm{SO_2}(l) \longrightarrow \mathrm{SO_2}(g)$ and $\mathrm{CCl_2\ F_2}(l) \longrightarrow \mathrm{CCl_2\ F_2}(g)$, respectively.

53.

Homes may be heated by pumping hot water through radiators. What mass of water will provide the same amount of heat when cooled from 95.0 to 35.0 °C, as the heat provided when 100 g of steam is cooled from 110 °C to 100 °C.

54.

Which of the enthalpies of combustion in Table 9.2 the table are also standard enthalpies of formation?

55.

Does the standard enthalpy of formation of $\mathrm{H_2O}(g)$ differ from ΔH° for the reaction

$2\mathrm{H_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\mathrm{H_2O}(g)$?

56.

Joseph Priestly prepared oxygen in 1774 by heating red mercury(II) oxide with sunlight focused through a lens. How much heat is required to decompose exactly 1 mole of red HgO(s) to Hg(*l*) and O_2(*g*) under standard conditions?

57.

How many kilojoules of heat will be released when exactly 1 mole of manganese, Mn, is burned to form Mn_3O_4(s) at standard state conditions?

58.

How many kilojoules of heat will be released when exactly 1 mole of iron, Fe, is burned to form Fe_2O_3(s) at standard state conditions?

59.

The following sequence of reactions occurs in the commercial production of aqueous nitric acid:

$4\mathrm{NH_3}(g) + 5\mathrm{O_2}(g) \longrightarrow 4\mathrm{NO}(g) + 6\mathrm{H_2O}(l) \quad \Delta H = -907\ \mathrm{kJ}$
$2\mathrm{NO}(g) + \mathrm{O_2}(g) \longrightarrow 2\mathrm{NO_2}(g) \quad \Delta H = -113\ \mathrm{kJ}$
$3\mathrm{NO_2} + \mathrm{H_2O}(l) \longrightarrow 2\mathrm{HNO_3}(aq) + \mathrm{NO}(g) \quad \Delta H = -139\ \mathrm{kJ}$

Determine the total energy change for the production of one mole of aqueous nitric acid by this process.

60.

Both graphite and diamond burn.
$\mathrm{C}\,(s,\ \mathrm{diamond}) + \mathrm{O_2}(g)$ ⟐CO2(g)C(s,diamond)+O2(g)⟐CO2(g)

For the conversion of graphite to diamond:
$\mathrm{C}\,(s,\ \text{graphite})$ ⟐C(s,diamond)ΔH°=1.90kJC(s,graphite)⟐C(s,diamond)ΔH°=1.90kJ

Which produces more heat, the combustion of graphite or the combustion of diamond?

61.

From the molar heats of formation in Appendix G, determine how much heat is required to evaporate one mole of water:

$\mathrm{H_2O}(l) \longrightarrow \mathrm{H_2O}(g)$

62.

Which produces more heat?

$\mathrm{Os}(s) + 2\mathrm{O_2}(g) \longrightarrow \mathrm{OsO_4}(s)$

or

$\mathrm{Os}(s) + 2\mathrm{O_2}(g) \longrightarrow \mathrm{OsO_4}(g)$

for the phase change $\mathrm{OsO_4}(s) \longrightarrow \mathrm{OsO_4}(g) \quad \Delta H = 56.4\ \mathrm{kJ}$

63.
Calculate ΔH° for the process

$\mathrm{Sb}(s) + \frac{5}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{SbCl_5}(s)$

from the following information:

$\mathrm{Sb}(s) + \frac{3}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{SbCl_3}(s) \quad \Delta H^\circ = -314\ \mathrm{kJ}$
$\mathrm{SbCl_3}(s) + \mathrm{Cl_2}(g) \longrightarrow \mathrm{SbCl_5}(s) \quad \Delta H^\circ = -80\ \mathrm{kJ}$

64.

Calculate ΔH° for the process $\mathrm{Zn}(s) + \mathrm{S}(s) + 2\mathrm{O_2}(g) \longrightarrow \mathrm{ZnSO_4}(s)$ from the following information:

$\mathrm{Zn}(s) + \mathrm{S}(s) \longrightarrow \mathrm{ZnS}(s) \quad \Delta H^\circ = -206.0\ \mathrm{kJ}$
$\mathrm{ZnS}(s) + 2\mathrm{O_2}(g) \longrightarrow \mathrm{ZnSO_4}(s) \quad \Delta H^\circ = -776.8\ \mathrm{kJ}$

65.

Calculate ΔH for the process $\mathrm{Hg_2Cl_2}(s) \longrightarrow 2\mathrm{Hg}(l) + \mathrm{Cl_2}(g)$ from the following information:

$\mathrm{Hg}(l) + \mathrm{Cl_2}(g) \longrightarrow \mathrm{HgCl_2}(s) \quad \Delta H = -224\ \mathrm{kJ}$
$\mathrm{Hg}(l) + \mathrm{HgCl_2}(s) \longrightarrow \mathrm{Hg_2Cl_2}(s) \quad \Delta H = -41.2\ \mathrm{kJ}$

66.

Calculate ΔH° for the process $\mathrm{Co_3O_4}(s) \longrightarrow 3\mathrm{Co}(s) + 2\mathrm{O_2}(g)$ from the following information:

$\mathrm{Co}(s) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{CoO}(s) \quad \Delta H^\circ = -237.9\ \mathrm{kJ}$
$3\mathrm{CoO}(s) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{Co_3O_4}(s) \quad \Delta H^\circ = -177.5\ \mathrm{kJ}$

67.

Calculate the standard molar enthalpy of formation of $\mathrm{NO}(g)$ from the following data:

$\mathrm{N_2}(g) + 2\mathrm{O_2}(g) \longrightarrow 2\mathrm{NO_2}(g) \quad \Delta H^\circ = 66.4\ \mathrm{kJ}$
$2\mathrm{NO}(g) + \mathrm{O_2}(g) \longrightarrow 2\mathrm{NO_2}(g) \quad \Delta H^\circ = -114.1\ \mathrm{kJ}$

68.

Using the data in Appendix G, calculate the standard enthalpy change for each of the following reactions:

(a) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$

(b) $Si(s) + 2Cl_2(g) \longrightarrow SiCl_4(g)$

(c) $Fe_2O_3(s) + 3H_2(g) \longrightarrow 2Fe(s) + 3H_2O(l)$

(d) $2LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(g)$

69.

Using the data in Appendix 11.7, calculate the standard enthalpy change for each of the following reactions:

(a) $Si(s) + 2\ F_2(g) \longrightarrow SiF_4(g)$

(b) $2C(s) + 2H_2(g) + O_2(g) \rightarrow CH_3CO_2H(l)$

(c) $CH_4(g) + N_2(g) \longrightarrow HCN(g) + NH_3(g);$

(d) $CS_2(g) + 3Cl_2(g) \longrightarrow CCl_4(g) + S_2Cl_2(g)$

70.

The following reactions can be used to prepare samples of metals. Determine the enthalpy change under standard state conditions for each.

(a) $2Ag_2O(s) \longrightarrow 4Ag(s) + O_2(g)$

(b) $SnO(s) + CO(g) \longrightarrow Sn(s) + CO_2(g)$

(c) $Cr_2O_3(s) + 3H_2(g) \longrightarrow 2Cr(s) + 3H_2O(l)$

(d) $2Al(s) + Fe_2O_3(s) \longrightarrow Al_2O_3(s) + 2Fe(s)$

71.

The decomposition of hydrogen peroxide, H_2O_2, has been used to provide thrust in the control jets of various space vehicles. Using the data in Appendix 11.7, determine how much heat is produced by the decomposition of exactly 1 mole of H_2O_2 under standard conditions.
$2H_2O_2(l) \longrightarrow 2H_2O\,(g) + O_2(g)$

72.

Calculate the enthalpy of combustion of propane, $C_3H_8(g)$, for the formation of $H_2O(g)$ and $CO_2(g)$. The enthalpy of formation of propane is –104 kJ/mol.

73.

Calculate the enthalpy of combustion of butane, $C_4H_{10}(g)$ for the formation of $H_2O(g)$ and $CO_2(g)$. The enthalpy of formation of butane is –126 kJ/mol.

74.

Both propane and butane are used as gaseous fuels. Which compound produces more heat per gram when burned?

75.

The white pigment TiO_2 is prepared by the reaction of titanium tetrachloride, $TiCl_4$, with water vapor in the gas phase: $TiCl_4(g) + 2H_2O\,(g) \longrightarrow TiO_2(s) + 4HCl\,(g)\,.$

How much heat is evolved in the production of exactly 1 mole of TiO_2(s) under standard state conditions?

76.

Water gas, a mixture of H_2 and CO, is an important industrial fuel produced by the reaction of steam with red hot coke, essentially pure carbon: $\mathrm{C}\,(s)$ +H2O(g)⟐CO(g)+H2(g).C(s)+H2O(g)⟐CO(g)+H2(g).

(a) Assuming that coke has the same enthalpy of formation as graphite, calculate ΔH°ΔH° for this reaction.

(b) Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and additional hydrogen at high temperature and pressure in the presence of a suitable catalyst: $2\mathrm{H}_2(g) + \mathrm{CO}(g) \longrightarrow \mathrm{CH}_3\mathrm{OH}(g).$

Under the conditions of the reaction, methanol forms as a gas. Calculate $\Delta H°$ for this reaction and for the condensation of gaseous methanol to liquid methanol.

(c) Calculate the heat of combustion of 1 mole of liquid methanol to $H_2O(g)$ and $CO_2(g)$.

77.

In the early days of automobiles, illumination at night was provided by burning acetylene, C_2H_2. Though no longer used as auto headlamps, acetylene is still used as a source of light by some cave explorers. The acetylene is (was) prepared in the lamp by the reaction of water with calcium carbide, CaC_2:
$\mathrm{CaC}_2(s) + 2\mathrm{H}_2\mathrm{O}\,(l) \longrightarrow \mathrm{Ca(OH)}_2(s) + \mathrm{C}_2\mathrm{H}_2(g).$
Calculate the standard enthalpy of the reaction. The ΔHf°ΔHf° of CaC_2 is –15.14 kcal/mol.

78.

From the data in Table 9.2, determine which of the following fuels produces the greatest amount of heat per gram when burned under standard conditions: $CO(g)$, $CH_4(g)$, or $C_2H_2(g)$.

79.

The enthalpy of combustion of hard coal averages –35 kJ/g, that of gasoline, 1.28×10^5 kJ/gal. How many kilograms of hard coal provide the same amount of heat as is available from 1.0 gallon of gasoline? Assume that the density of gasoline is 0.692 g/mL (the same as the density of isooctane).

80.

Ethanol, C_2H_5OH, is used as a fuel for motor vehicles, particularly in Brazil.

(a) Write the balanced equation for the combustion of ethanol to $CO_2(g)$ and $H_2O(g)$, and, using the data in Appendix 11.7, calculate the enthalpy of combustion of 1 mole of ethanol.

(b) The density of ethanol is 0.7893 g/mL. Calculate the enthalpy of combustion of exactly 1 L of ethanol.

(c) Assuming that an automobile's mileage is directly proportional to the heat of combustion of the fuel, calculate how much farther an automobile could be expected to travel on 1 L of gasoline than on 1 L of ethanol. Assume that gasoline has the heat of combustion and the density of n-octane, C_8H_{18} $(\Delta H_\mathrm{f}^\circ = -208.4\ \mathrm{kJ/mol};\ \text{density} = 0.7025\ \mathrm{g/mL})$.

81.

Among the substances that react with oxygen and that have been considered as potential rocket fuels are diborane $[\mathrm{B}_2\mathrm{H}_6$, produces $\mathrm{B}_2\mathrm{O}_3(\ \mathrm{s})$ and $\mathrm{H}_2\mathrm{O}(g)]$, methane [CH_4, produces $\mathrm{CO}_2(g)$ and $\mathrm{H}_2\mathrm{O}(g)$], and hydrazine $[\mathrm{N}_2\mathrm{H}_4$, produces $\mathrm{N}_2(g)$ and $\mathrm{H}_2\mathrm{O}(g)$]. On the basis of the heat released by 1.00 g of each substance in its reaction with oxygen, which of these compounds offers the best possibility as a rocket fuel? The $\Delta H_\mathrm{f}^\circ$ of $\mathrm{B}_2\mathrm{H}_6(g), \mathrm{CH}_4(g)$, and $\mathrm{N}_2\mathrm{H}_4(l)$ may be found in Appendix G

82.

How much heat is produced when 1.25 g of chromium metal reacts with oxygen gas under standard conditions?

83.

Ethylene, C_2H_4, a byproduct from the fractional distillation of petroleum, is fourth among the 50 chemical compounds produced commercially in the largest quantities. About 80% of synthetic ethanol is manufactured from ethylene by its reaction with water in the presence of a suitable catalyst.

$$\mathrm{C_2H_4}(g) + \mathrm{H_2O}(g) \longrightarrow \mathrm{C_2H_5OH}(l)$$

Using the data in the table in Appendix G, calculate ΔH° for the reaction.

84.

The oxidation of the sugar glucose, $C_6H_{12}O_6$, is described by the following equation:

$$\mathrm{C_6H_{12}O_6}(s) + 6\mathrm{O_2}(g) \longrightarrow 6\mathrm{CO_2}(g) + 6\mathrm{H_2O}(l) \quad \Delta H = -2816 \text{ kJ}$$

The metabolism of glucose gives the same products, although the glucose reacts with oxygen in a series of steps in the body.

(a) How much heat in kilojoules can be produced by the metabolism of 1.0 g of glucose?

(b) How many Calories can be produced by the metabolism of 1.0 g of glucose?

85.

Propane, C_3H_8, is a hydrocarbon that is commonly used as a fuel.

(a) Write a balanced equation for the complete combustion of propane gas.

(b) Calculate the volume of air at 25 °C and 1.00 atmosphere that is needed to completely combust 25.0 grams of propane. Assume that air is 21.0 percent O_2 by volume. (Hint: We will see how to do this calculation in a later chapter on gases—for now use the information that 1.00 L of air at 25 °C and 1.00 atm contains 0.275 g of O_2.)

(c) The heat of combustion of propane is $-2,219.2 \text{ kJ/mol}$. Calculate the heat of formation, $\Delta H_\mathrm{f}^\circ$ of propane given that $\Delta H_\mathrm{f}^\circ$ of $\mathrm{H_2O}(l) = -285.8 \text{ kJ/mol}$ and $\Delta H_\mathrm{f}^\circ$ of $\mathrm{CO_2}(g) = -393.5 \text{ kJ/mol}$.

(d) Assuming that all of the heat released in burning 25.0 grams of propane is transferred to 4.00 kilograms of water, calculate the increase in temperature of the water.

86.

During a recent winter month in Sheboygan, Wisconsin, it was necessary to obtain 3500 kWh of heat provided by a natural gas furnace with 89% efficiency to keep a small house warm (the efficiency of a gas furnace is the percent of the heat produced by combustion that is transferred into the house).

(a) Assume that natural gas is pure methane and determine the volume of natural gas in cubic feet that was required to heat the house. The average temperature of the natural gas was 56 °F; at this temperature and a pressure of 1 atm, natural gas has a density of 0.681 g/L.

(b) How many gallons of LPG (liquefied petroleum gas) would be required to replace the natural gas used? Assume the LPG is liquid propane [C_3H_8: density, 0.5318 g/mL; enthalpy of combustion, 2219 kJ/mol for the formation of $CO_2(g)$ and $H_2O(l)$] and the furnace used to burn the LPG has the same efficiency as the gas furnace.

(c) What mass of carbon dioxide is produced by combustion of the methane used to heat the house?

(d) What mass of water is produced by combustion of the methane used to heat the house?

(e) What volume of air is required to provide the oxygen for the combustion of the methane used to heat the house? Air contains 23% oxygen by mass. The average density of air during the month was 1.22 g/L.

(f) How many kilowatt–hours (1 kWh = 3.6×10^6 J) of electricity would be required to provide the heat necessary to heat the house? Note electricity is 100% efficient in producing heat inside a house.

(g) Although electricity is 100% efficient in producing heat inside a house, production and distribution of electricity is not 100% efficient. The efficiency of production and distribution of electricity produced in a coal-fired power plant is about 40%. A certain type of coal provides 2.26 kWh per pound upon combustion. What mass of this coal in kilograms will be required to produce the electrical energy necessary to heat the house if the efficiency of generation and distribution is 40%?

87.

Which bond in each of the following pairs of bonds is the strongest?

(a) C–C or $\mathrm{C=C}$

(b) C–N or $\mathrm{C\equiv N}$

(c)$\mathrm{C\equiv O}$ or $\mathrm{C=O}$

(d) H–F or H–Cl

(e) C–H or O–H

(f) C–N or C–O

88.

Using the bond energies in Table 9.3, determine the approximate enthalpy change for each of the following reactions:

(a) $\mathrm{H_2}(g) + \mathrm{Br_2}(g) \longrightarrow 2\mathrm{HBr}(g)$
(b) $\mathrm{CH_4}(g) + \mathrm{I_2}(g) \longrightarrow \mathrm{CH_3I}(g) + \mathrm{HI}(g)$
(c) $\mathrm{C_2H_4}(g) + 3\mathrm{O_2}(g) \longrightarrow 2\mathrm{CO_2}(g) + 2\mathrm{H_2O}(g)$

89.

Using the bond energies in Table 9.3, determine the approximate enthalpy change for each of the following reactions:

(a) $\mathrm{Cl_2}(g) + 3\ \mathrm{F_2}(g) \longrightarrow 2\mathrm{ClF_3}(g)$
(b) $\mathrm{H_2C=CH_2}(g) + \mathrm{H_2}(g) \longrightarrow \mathrm{H_3CCH_3}(g)$
(c) $2\mathrm{C_2H_6}(g) + 7\mathrm{O_2}(g) \longrightarrow 4\mathrm{CO_2}(g) + 6\mathrm{H_2O}(g)$

90.

Draw a curve that describes the energy of a system with H and Cl atoms at varying distances. Then, find the minimum energy of this curve two ways.

(a) Use the bond energy found in Table 9.3 and Table 9.4 to calculate the energy for one single HCl bond (Hint: How many bonds are in a mole?)

(b) Use the enthalpy of reaction and the bond energies for H_2 and Cl_2 to solve for the energy of one mole of HCl bonds.

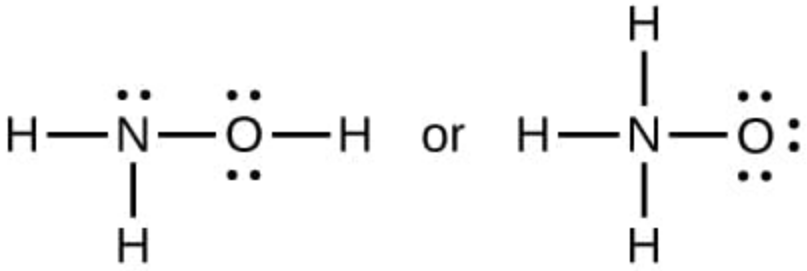
$$\mathrm{H_2}(g) + \mathrm{Cl_2}(g) \rightleftharpoons 2\mathrm{HCl}(g) \qquad \Delta H^\circ_{\mathrm{rxn}} = -184.7\ \mathrm{kJ/mol}$$

91.

Explain why bonds occur at specific average bond distances instead of the atoms approaching each other infinitely close.

92.

When a molecule can form two different structures, the structure with the stronger bonds is usually the more stable form. Use bond energies to predict the correct structure of the hydroxylamine molecule:



93.

How does the bond energy of HCl(*g*) differ from the standard enthalpy of formation of HCl(*g*)?

94.

Using the standard enthalpy of formation data in Appendix 11.7, show how the standard enthalpy of formation of HCl(*g*) can be used to determine the bond energy.

95.

Using the standard enthalpy of formation data in Appendix 11.7, calculate the bond energy of the carbon-sulfur double bond in CS_2.

96.

Using the standard enthalpy of formation data in Appendix 11.7, determine which bond is stronger: the S–F bond in $SF_4(g)$ or in $SF_6(g)$?

97.

Using the standard enthalpy of formation data in Appendix 11.7, determine which bond is stronger: the P–Cl bond in $PCl_3(g)$ or in $PCl_5(g)$?

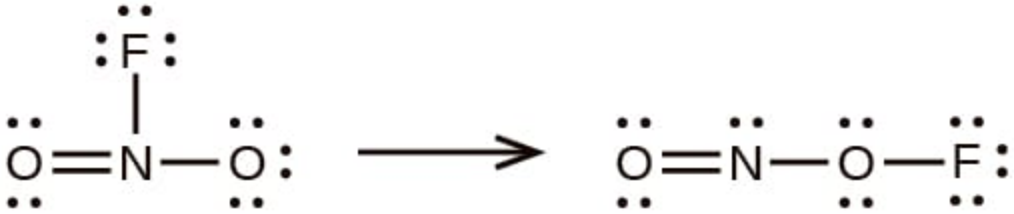
98.

Complete the following Lewis structure by adding bonds (not atoms), and then indicate the longest bond:



99.

Use the bond energy to calculate an approximate value of ΔH for the following reaction. Which is the more stable form of FNO_2?



100.

Use principles of atomic structure to answer each of the following:[4]

(a) The radius of the Ca atom is 197 pm; the radius of the Ca^{2+} ion is 99 pm. Account for the difference.

(b) The lattice energy of CaO(s) is –3460 kJ/mol; the lattice energy of K_2O is –2240 kJ/mol. Account for the difference.

(c) Given these ionization values, explain the difference between Ca and K with regard to their first and second ionization energies.

Element	First Ionization Energy (kJ/mol)	Second Ionization Energy (kJ/mol)
K	419	3050
Ca	590	1140

(d) The first ionization energy of Mg is 738 kJ/mol and that of Al is 578 kJ/mol. Account for this difference.

101.

The lattice energy of LiF is 1023 kJ/mol, and the Li–F distance is 200.8 pm. NaF crystallizes in the same structure as LiF but with a Na–F distance of 231 pm. Which of the following values most closely approximates the lattice energy of NaF: 510, 890, 1023, 1175, or 4090 kJ/mol? Explain your choice.

102.

For which of the following substances is the least energy required to convert one mole of the solid into separate ions?

(a) MgO

(b) SrO

(c) KF

(d) CsF

(e) MgF_2

103.

The reaction of a metal, M, with a halogen, X_2, proceeds by an exothermic reaction as indicated by this equation: $\mathrm{M}\,(s) + \mathrm{X}_2(g)$ ⟐MX2(s).M(s)+X2(g)⟐MX2(s). For each of the following, indicate which option will make the reaction more exothermic. Explain your answers.

(a) a large radius vs. a small radius for M^{+2}

(b) a high ionization energy vs. a low ionization energy for M

(c) an increasing bond energy for the halogen

(d) a decreasing electron affinity for the halogen

(e) an increasing size of the anion formed by the halogen

104.

The lattice energy of LiF is 1023 kJ/mol, and the Li–F distance is 201 pm. MgO crystallizes in the same structure as LiF but with a Mg–O distance of 205 pm. Which of the following values most closely approximates the lattice energy of MgO: 256 kJ/mol, 512 kJ/mol, 1023 kJ/mol, 2046 kJ/mol, or 4008 kJ/mol? Explain your choice.

105.

Which compound in each of the following pairs has the larger lattice energy? Note: Mg^{2+} and Li^{+} have similar radii; O^{2-} and F^{-} have similar radii. Explain your choices.

(a) MgO or MgSe

(b) LiF or MgO

(c) Li_2O or LiCl

(d) Li_2Se or MgO

106.

Which compound in each of the following pairs has the larger lattice energy? Note: Ba^{2+} and

K^{+} have similar radii; S^{2-} and Cl^{-} have similar radii. Explain your choices.

(a) K_2O or Na_2O

(b) K_2S or BaS

(c) KCl or BaS

(d) BaS or $BaCl_2$

107.

Which of the following compounds requires the most energy to convert one mole of the solid into separate ions?

(a) MgO

(b) SrO

(c) KF

(d) CsF

(e) MgF_2

108.

Which of the following compounds requires the most energy to convert one mole of the solid into separate ions?

(a) K_2S

(b) K_2O

(c) CaS

(d) Cs_2S

(e) CaO

109.

The lattice energy of KF is 794 kJ/mol, and the interionic distance is 269 pm. The Na–F

distance in NaF, which has the same structure as KF, is 231 pm. Which of the following values is the closest approximation of the lattice energy of NaF: 682 kJ/mol, 794 kJ/mol, 924 kJ/mol, 1588 kJ/mol, or 3175 kJ/mol? Explain your answer.

Footnotes

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6: THERMODYNAMICS

6.1: Introduction

6.2: Spontaneity

6.3: Entropy

6.4: The Second and Third Laws of Thermodynamics

6.5: Free Energy

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6.7: Key Equations

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6.1: Introduction

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.



Figure 6.1.1: Geysers are a dramatic display of thermodynamic principles in nature. Water deep within the underground channels of the geyser is under high pressure and heated to high temperature by magma. When a pocket of water near the surface reaches boiling point and is expelled, the resulting drop in pressure causes larger volumes of water to flash boil, forcefully ejecting steam and water in an impressive eruption. (credit: modification of work by Yellowstone National Park)

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6.2: Spontaneity

Learning Objectives

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

- Distinguish between spontaneous and nonspontaneous processes
- Describe the dispersal of matter and energy that accompanies certain spontaneous 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. Iron exposed to the earth's atmosphere will corrode, but rust is not converted to iron without intentional chemical treatment. 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 6.2.1).

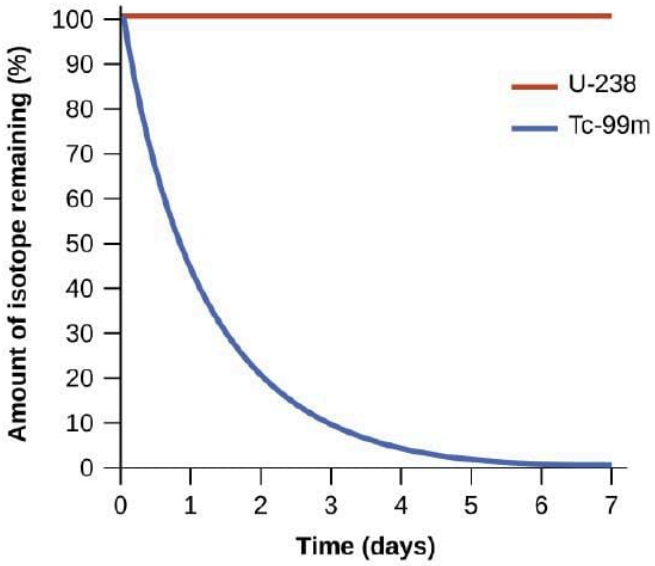


Figure 6.2.1: Both U-238 and Tc-99m undergo spontaneous radioactive decay, but at drastically different rates. Over the course of one week, essentially all of a Tc-99m sample and none of a U-238 sample will have decayed.

As another example, consider the conversion of diamond into graphite (Figure 6.2.2).

$$C(s,\text{ diamond }) \longrightarrow C(s,\text{ graphite })$$

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; 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.

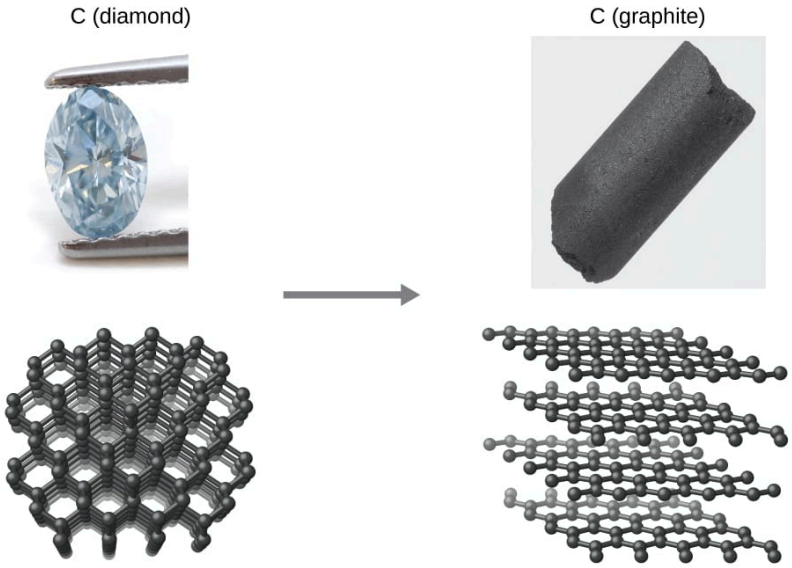


Figure 6.2.2: The conversion of carbon from the diamond allotrope to the graphite allotrope is spontaneous at ambient pressure, but its rate is immeasurably slow at low to moderate temperatures. This process is known as *graphitization*, and its rate can be increased to easily measurable values at temperatures 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)

Dispersal of Matter and Energy

Extending the 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 in one flask and the other flask is empty ($P = 0$) (Figure 6.2.3). When the valve is opened, the gas spontaneously expands to fill both flasks equally. 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=0 (P=0 \text { in a vacuum })|]

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.

$$\Delta U = q + w = 0 + 0 = 0$$

The spontaneity of this process is therefore not a consequence of any change in energy that accompanies the process. Instead, the driving force 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 expansion took place, the matter was distributed both more widely (occupying twice its original volume) and more uniformly (present in equal amounts in each flask).

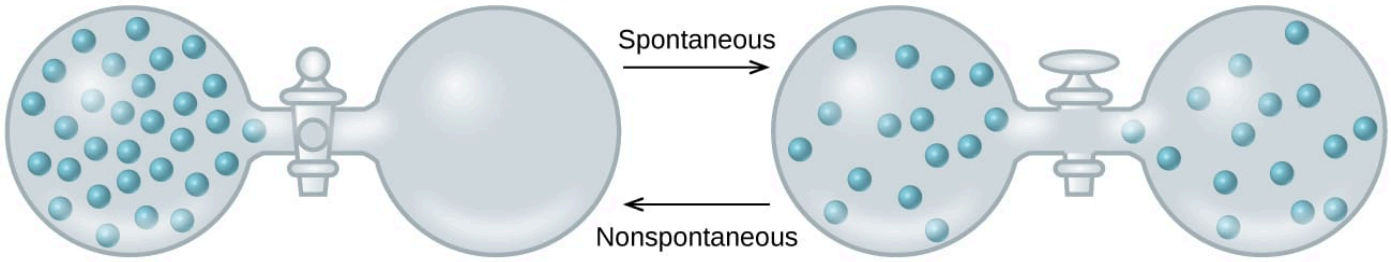


Figure 6.2.3: An isolated system consists of an ideal gas in one flask that is connected by a closed valve to a second flask containing a vacuum. Once the valve is opened, the gas spontaneously becomes evenly distributed between the flasks.

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 6.2.4). 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.

$$q_X < 0 \quad \text{and} \quad q_Y = -q_X > 0$$

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 6.2.4: When two objects at different temperatures come in contact, heat spontaneously flows from the hotter to the colder object.

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 6.2.1: Redistribution of Matter during a Spontaneous Process

Describe how matter is 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 6.2.5: (credit a: modification of work by Jenny Downing; credit b: modification of work by “Fuzzy Gerdes”/Flickr; credit c: modification of work by Paul A. Flowers)

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.
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.
c. The process in question is diffusion. This process yields a more uniform dispersal of matter, since the initial state of the system involves two regions of different dye concentrations (high in the drop of dye, zero in the water), and the final state of the system contains a single dye concentration throughout.

Exercise 6.2.1

Describe how energy is redistributed when a spoon at room temperature is placed in a cup of hot coffee.

Answer available at the end of this section.

Answers

Exercise 6.2.1

Heat will spontaneously flow from the hotter object (coffee) to the colder object (spoon), resulting in a more uniform distribution of thermal energy as the spoon warms and the coffee cools.

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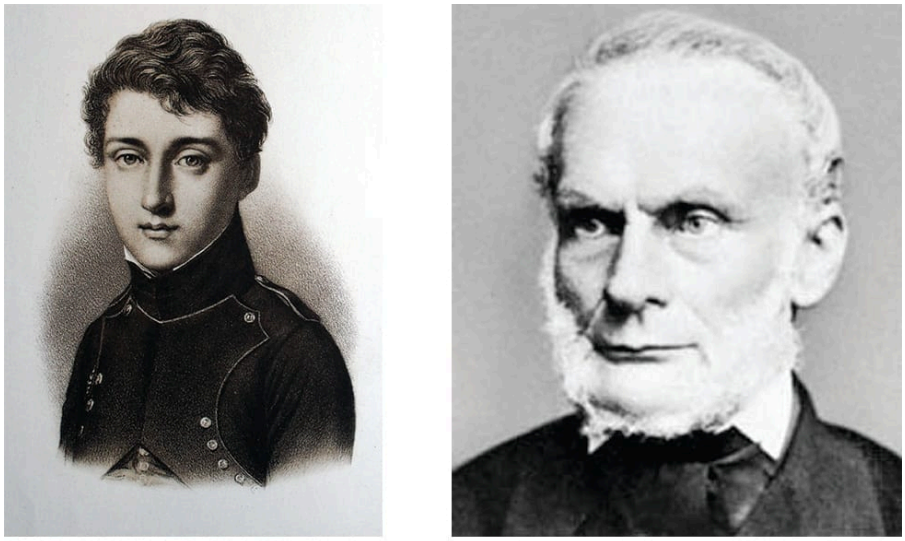
6.3: Entropy

Learning Objectives

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

- 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 6.3.1) published the results of an extensive study regarding the efficiency of steam heat engines. A later review of Carnot's findings by 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). In thermodynamics, a **reversible process** is one 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 in 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*.



(a) (b)

Figure 6.3.1: (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, 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:

$$\Delta S = \frac{q_{rev}}{T}$$

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.

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* (*W*) possible for the system. A **microstate** is a specific configuration of all the locations and energies of the atoms or molecules that make up a system. The relation between a system's entropy and the

number of possible microstates is

$$S = k \ln W$$

where k is the Boltzmann constant, 1.38 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:

$$\Delta S = S_f - S_i = k \ln W_f - k \ln W_i = k \ln \frac{W_f}{W_i}$$

For processes involving an increase in the number of microstates, $W_f > W_i$, the entropy of the system increases and $\Delta S > 0$. Conversely, processes that reduce the number of microstates, $W_f < W_i$, 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.

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 6.3.2. Microstates with equivalent particle arrangements (not considering individual particle identities) are grouped together and are called *distributions*. 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*.

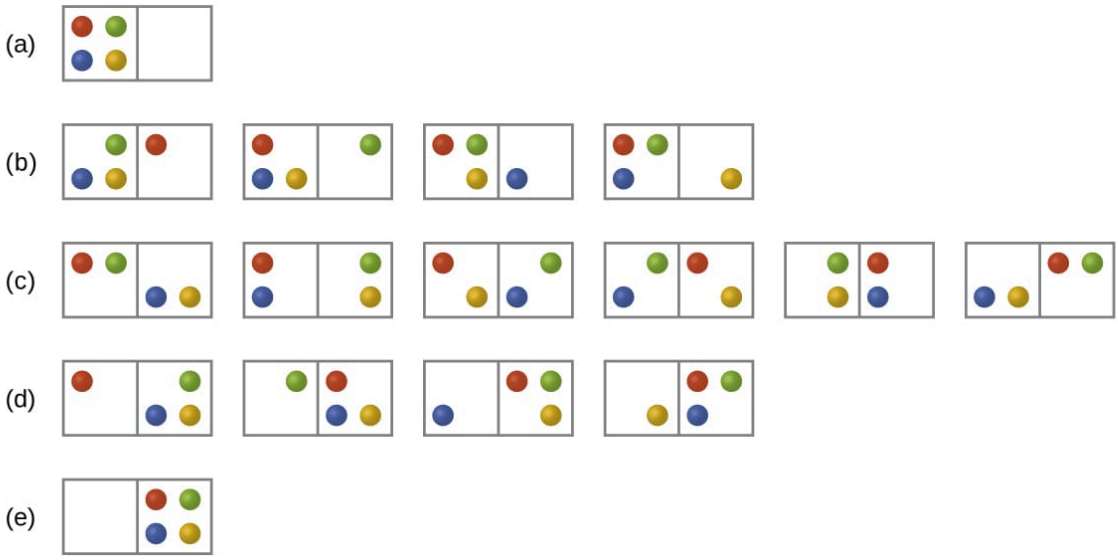


Figure 6.3.2: The sixteen microstates associated with placing four particles in two boxes are shown. The microstates are collected into five distributions—(a), (b), (c), (d), and (e)—based on the numbers of particles in each box.

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 $\frac{6}{16}$ or $\frac{3}{8}$ 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 The probability of finding all particles in only one box (either the left box or right box) is then or

$$\left(\frac{1}{16} + \frac{1}{16}\right) = \frac{2}{16} \text{ or } \frac{1}{8}$$

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.

This matter dispersal model of entropy is often described qualitatively in terms of the *disorder* of the system. By this description,

microstates in which all the particles are in a single box are the most ordered, thus possessing the least entropy. Microstates in which the particles are more evenly distributed among the boxes are more disordered, possessing greater entropy.

The previous description of an ideal gas expanding into a vacuum (Figure 16.4) 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. Initially, the gas molecules are confined to just one of the two flasks. Opening the valve between the flasks increases the volume available to the gas molecules and, correspondingly, the number of microstates possible for the system. Since $W_f > W_i$, the expansion process involves an increase in entropy ($\Delta S > 0$) and is spontaneous.

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 thermal energy (represented as "*") in Figure 6.3.3. 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. Thus, 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 $\frac{4}{10}$. 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.

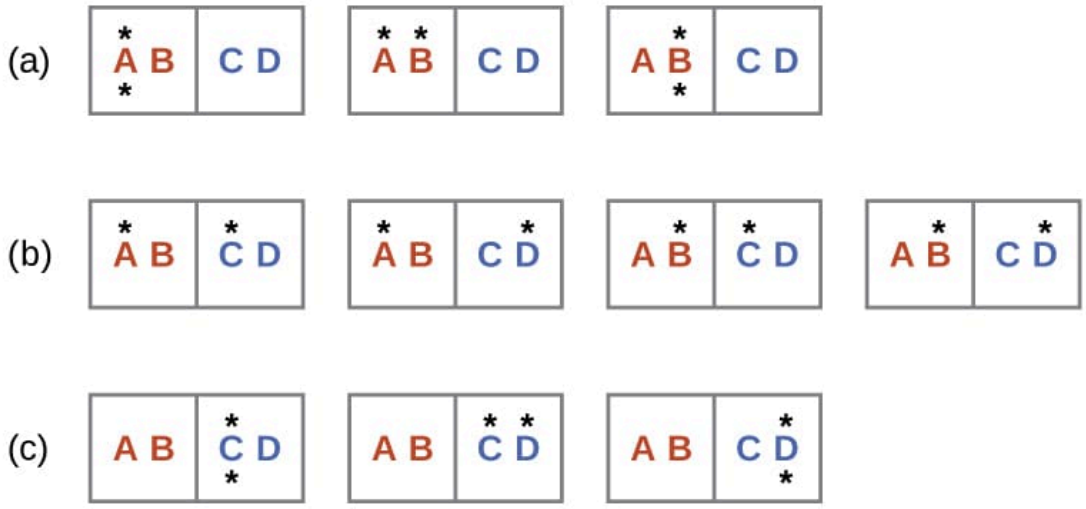
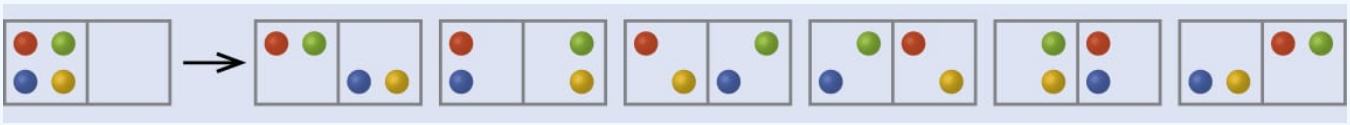


Figure 6.3.3: This shows a microstate model describing the flow of heat from a hot object to a cold object. (a) Before the heat flow occurs, the object comprised of particles **A** and **B** contains both units of energy and as represented by a distribution of three microstates. (b) If the heat flow 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.

Example 6.3.1: Determination of ΔS

Calculate the change in entropy for the process depicted below.



Solution

The initial number of microstates is one, the final six:

$$\Delta S = k \ln \frac{W_c}{W_a} = 1.38 \times 10^{-23} J/K \times \ln \frac{6}{1} = 2.47 \times 10^{-23} J/K$$

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 6.3.1

Consider the system shown in Figure 6.3.3. 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 available at the end of this section.

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 6.3.4. 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, $\Delta S < 0$.

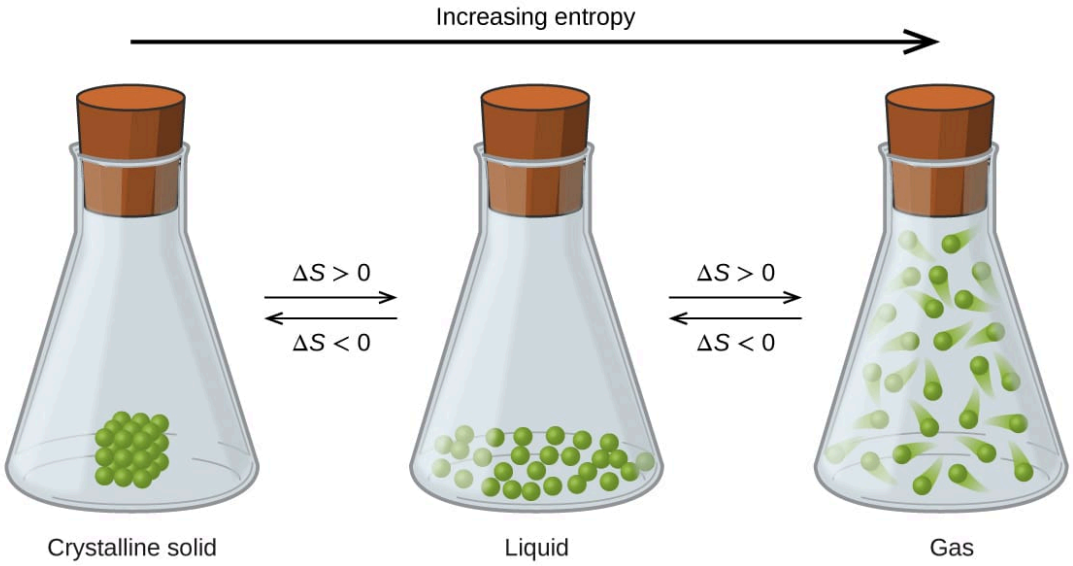


Figure 6.3.4: The entropy of a substance increases ($\Delta S > 0$) as it transforms from a relatively ordered solid, to a less-ordered liquid, and then to a still less-ordered gas. The entropy decreases ($\Delta S < 0$) as the substance transforms from a gas to a liquid and then to a solid.

Now consider the gaseous phase, in which a given number of atoms or molecules occupy a *much* greater volume than in the liquid phase. Each atom or molecule can be found in many more locations, corresponding to a much greater number of microstates. 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 6.3.5).

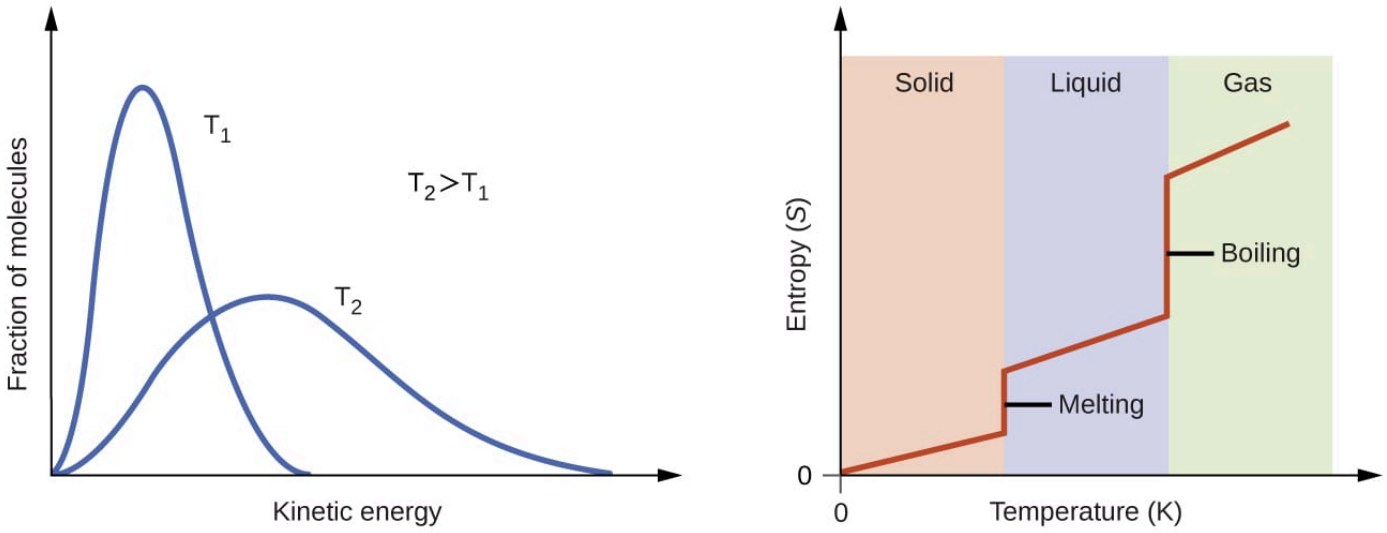


Figure 6.3.5: Entropy increases as the temperature of a substance is raised, which corresponds to the greater spread of kinetic energies. When a substance undergoes a phase transition, its entropy changes significantly.

Link to Learning

Try this simulator with interactive visualization of the dependence of particle location and freedom of motion on physical state and temperature.

The entropy of a substance is influenced by the 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 (a topic beyond the scope of this text). For molecules, greater numbers of atoms increase the number of ways in which the molecules can vibrate and thus the number of possible microstates and the entropy of the system.

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 6.3.2.

Example 6.3.2: 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 one mole liquid water at 50 °C
b. $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$
c. \(C_6 H_6(l)+\frac{15}{2} O_2(g) \longrightarrow 6 CO_2(g)+3 H_2O(l)
d. $NH_3(s) \longrightarrow NH_3(l)$

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 6.3.1

Predict the sign of the entropy change for the following processes. Give a reason for your prediction.

a. $NaNO_3(s) \longrightarrow Na^+(aq) + NO_3{}^-(aq)$
b. the freezing of liquid water
c. $CO_2(s) \longrightarrow CO_2(g)$
d. $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

Answer available at the end of this section.

Answers

Exercise 6.3.1

0 J/K

Exercise 6.3.1

(a) Positive; The solid dissolves to give an increase of mobile ions in solution.
(b) Negative; The liquid becomes a more ordered solid.
(c) Positive; The relatively ordered solid becomes a gas.
(d) Positive; There is a net increase in the amount of gaseous species.

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6.4: The Second and Third Laws of Thermodynamics

Learning Objectives

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

- State and explain the second and third laws of thermodynamics
- Calculate entropy changes for phase transitions and chemical reactions under standard conditions

The Second Law of Thermodynamics

In the quest to identify a property that may reliably predict the spontaneity of a process, a promising candidate has been identified: 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:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

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:

$$\Delta S_{sys} = \frac{-q_{rev}}{T_{sys}} \quad \text{and} \quad \Delta S_{surr} = \frac{q_{rev}}{T_{surr}}$$

   The magnitudes of $-q_{\text{rev}}$ and q_{rev} are equal, their opposite arithmetic signs denoting loss of heat by the system and gain of heat by the surroundings. Since $T_{\text{sys}} > T_{\text{surr}}$ in this scenario, the entropy *decrease* of the system will be less than the entropy *increase* of the surroundings, and so *the entropy of the universe will increase*:

$$|\Delta S_{\text{sys}}| < |\Delta S_{\text{surr}}|$$
$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

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:

$$\Delta S_{sys} = \frac{q_{rev}}{T_{sys}} \quad \text{and} \quad \Delta S_{surr} = \frac{-q_{rev}}{T_{surr}}$$

   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 (that is, *the direction of the heat flow*) will yield a negative value for ΔS_{univ}. *This process involves a decrease in the entropy of the universe.*
3. The objects are at essentially the same temperature, $T_{\text{sys}} \approx T_{\text{surr}}$, and so the magnitudes of the entropy changes are essentially the same for both the system and the surroundings. In this case, the entropy change of the universe is zero, and the system is *at equilibrium*.

$$|\Delta S_{\text{sys}}| \approx |\Delta S_{\text{surr}}|$$
$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

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 6.4.1.

Table 6.4.1: The Second Law of Thermodynamics

$\Delta S_{univ} > 0$	spontaneous
$\Delta S_{univ} < 0$	nonspontaneous (spontaneous in opposite direction)
$\Delta S_{univ} = 0$	at equilibrium

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:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = \Delta S_{sys} + \frac{q_{surr}}{T}$$

We may use this equation to predict the spontaneity of a process as illustrated in Example 6.4.1.

Example 6.4.1: Will Ice Spontaneously Melt?

The entropy change for the process

$$H_2O(s) \longrightarrow H_2O(l)$$

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:

$$\begin{aligned}\Delta S_{\text{univ}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \\ &= 22.1 J/K + \frac{-6.00 \times 10^3 J}{263.15 K} = -0.7 J/K\end{aligned}$$

$S_{univ} < 0$, 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 6.4.1

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 available at the end of this section.

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.

$$S = k \ln W = k \ln(1) = 0$$

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.*

Careful calorimetric measurements can be made to determine the temperature dependence of a substance's entropy and to derive absolute entropy values under specific conditions. **Standard entropies** ($S°$) are for one mole of substance under standard conditions (a pressure of 1 bar and a temperature of 298.15 K; see details regarding standard conditions in the thermochemistry chapter of this text). The **standard entropy change** ($\Delta S°$) for a reaction may be computed using standard entropies as shown below:

$$\Delta S^\circ = \sum \nu S^\circ(\text{ products }) - \sum \nu S^\circ(\text{ reactants })$$

where ν represents stoichiometric coefficients in the balanced equation representing the process. For example, $\Delta S°$ for the following reaction at room temperature

$$mA + nB \longrightarrow xC + yD$$

is computed as:

$$= [xS^\circ(C) + yS^\circ(D)] - [mS^\circ(A) + nS^\circ(B)]$$

A partial listing of standard entropies is provided in Table 6.4.2, and additional values are provided in Appendix 11.7. The example exercises that follow demonstrate the use of S° values in calculating standard entropy changes for physical and chemical processes.

Table 6.4.2: Standard entropies for selected substances measured at 1 atm and 298.15 K. (Values are approximately equal to those measured at 1 bar, the currently accepted standard state pressure.)

Substance	($J\ mol^{-1}\ K^{-1}$)
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	($J\ mol^{-1}\ K^{-1}$)
$H_2O(g)$	188.71
$H_2O(l)$	69.91
HCI(g)	186.8
$H_2S(g)$	205.7
oxygen	
$O_2(g)$	205.03

Example 6.4.2: Determination of ΔS°

Calculate the standard entropy change for the following process:

$$H_2O(g) \longrightarrow H_2O(l)$$

Solution

Calculate the entropy change using standard entropies as shown above:

$$\Delta S^\circ = (1mol)\left(70.0Jmol^{-1}K^{-1}\right) - (1mol)\left(188.8Jmol^{-1}K^{-1}\right) = -118.8J/K$$

The value for ΔS° is negative, as expected for this phase transition (condensation), which the previous section discussed.

Exercise 6.4.2

Calculate the standard entropy change for the following process:

$$H_2(g) + C_2H_4(g) \longrightarrow C_2H_6(g)$$

Answer available at the end of this section.

Example 6.4.3: Determination of ΔS°

Calculate the standard entropy change for the combustion of methanol, CH_3OH:

$$2CH_3OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 4H_2O(l)$$

Solution

Calculate the entropy change using standard entropies as shown above:

$$\Delta S^\circ = \sum \nu S^\circ(\text{ products }) - \sum \nu S^\circ(\text{ reactants })$$

$$[2mol \times S^\circ(CO_2(g)) + 4mol \times S^\circ(H_2O(l))] - [2mol \times S^\circ(CH_3OH(l)) + 3mol \times S^\circ(O_2(g))]$$

$$= \{[2(213.8) + 4 \times 70.0] - [2(126.8) + 3(205.2)]\} = -161.6J/K$$

Exercise 6.4.3

Calculate the standard entropy change for the following reaction:

$$Ca(OH)_2(s) \longrightarrow CaO(s) + H_2O(l)$$

Answer available at the end of this section.

Answers

Exercise 6.4.1

Entropy is a state function, so $\Delta S_{freezing} = -\Delta S_{melting} = -22.1$ J/K and $q_{surr} = +6.00$ kJ. At −10.00 °C spontaneous, +0.7 J/K; at +10.00 °C nonspontaneous, −0.9 J/K.

Exercise 6.4.2

$-120.6\ J\ K^{-1}\ mol^{-1}$

Exercise 6.4.3

24.7 J/K

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6.5: Free Energy

Learning Objectives

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

- Define Gibbs free energy, and describe its relation to spontaneity
- Calculate free energy change for a process using free energies of formation for its reactants and products
- Calculate free energy change for a process using enthalpies 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 process is spontaneous is that it requires measurements of the entropy change for the system *and* the entropy change for the surroundings. 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 free energy change (ΔG) may be expressed as the following:

$$\Delta G = \Delta H - T\Delta S$$

(For simplicity's sake, the subscript "sys" will be omitted henceforth.)

The relationship between this system property and the spontaneity of a process may be understood 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 $q_{sys} = \Delta H$, so this expression may be rewritten as:

$$\Delta S_{\text{univ}} = \Delta S - \frac{\Delta H}{T}$$

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:

$$\Delta G = -T\Delta S_{\text{univ}}$$

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 6.5.1 summarizes the relation between the spontaneity of a process and the arithmetic signs of these indicators.

Table 6.5.1: 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)

What's "Free" about ΔG?

In addition to indicating spontaneity, the free energy change also provides information regarding the amount of useful work (w) that may be accomplished by a spontaneous process. Although a rigorous treatment of this subject is beyond the scope of an introductory chemistry text, a brief discussion is helpful for gaining a better perspective on this important thermodynamic property.

For this purpose, consider a spontaneous, exothermic process that involves a decrease in entropy. The free energy, as defined by

$$\Delta G = \Delta H - T\Delta S$$

may be interpreted as representing the difference between the energy produced by the process, Δ*H*, and the energy lost to the surroundings, *T*Δ*S*. The difference between the energy produced and the energy lost is the energy available (or "free") to do useful work by the process, Δ*G*. If the process somehow could be made to take place under conditions of thermodynamic reversibility, the amount of work that could be done would be maximal:

$$\Delta G = w_{max}$$

where w_{max} refers to all types of work except expansion (pressure-volume) work.

However, as noted previously in this chapter, such conditions are not realistic. In addition, the technologies used to extract work from a spontaneous process (e.g., batteries) are never 100% efficient, and so the work done by these processes is always less than the theoretical maximum. Similar reasoning may be applied to a nonspontaneous process, for which the free energy change represents the *minimum* amount of work that must be done *on* the system to carry out the process.

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. A convenient and common approach to the calculation of free energy changes for physical 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**, ΔG^o, according to the following relation.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

It is important to understand that for phase changes, ΔG^o tells you if the phase change is spontaneous or not; will it happen, or not happen. For chemical reactions, ΔG^o tells you the **extent** of a reaction. In other words, ΔG^o for a reaction tells you how much product will be present at equilibrium. A reaction with ΔG^o < 0 is considered **product-favored at equilibrium**; there will be more products than reactants when the reaction reaches equilibrium. A reaction with ΔG^o > 0 is considered **reactant-favored at equilibrium**; there will be more reactants than products when the reaction reaches equilibrium.

Example 6.5.1: Using Standard Enthalpy and Entropy Changes to Calculate ΔG°

Use standard enthalpy and entropy data from Appendix 11.7 to calculate the standard free energy change for the vaporization of water at room temperature (298 K). What does the computed value for ΔG^o say about the spontaneity of this process?

Solution

The process of interest is the following:

$$\mathrm{H_2O\,(l)} \longrightarrow \mathrm{H_2O\,(g)}$$

The standard change in free energy may be calculated using the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

From Appendix 11.7:

Substance	$\Delta H_f^\circ (\mathrm{kJ/mol})$	$S^\circ (\mathrm{kJ/K\ mol})$
$H_2O(l)$	−285.83	70.0
$H_2O(g)$	−241.82	188.8

Using the appendix data to calculate the standard enthalpy and entropy changes yields:

$$\begin{aligned}
\Delta H^\circ &= \Delta H_f^\circ\,(\mathrm{H_2O\,(g)}) - \Delta H_f^\circ\,(\mathrm{H_2O\,(l)}) \\
&= [-241.82\ \mathrm{kJ/mol} - (-285.83)]\ \mathrm{kJ/mol} = 44.01\ \mathrm{kJ/mol} \\
\Delta S^\circ &= 1\ \mathrm{mol} \times S^\circ\,(\mathrm{H_2O\,(g)}) - 1\ \mathrm{mol} \times S^\circ\,(\mathrm{H_2O\,(l)}) \\
&= (1\ \mathrm{mol})\ 188.8 J/mol \cdot K - (1\ \mathrm{mol})\ 70.0\ \mathrm{J/mol\ K} = 118.8\ \mathrm{J\ /\ K} \\
\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ
\end{aligned}$$

Substitution into the standard free energy equation yields:

$$\begin{aligned}
\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\
&= 44.01\ \mathrm{kJ} - (298K \times 118.8\ \mathrm{J/K}) \times \frac{1\ \mathrm{kJ}}{1000\ \mathrm{J}} \\
&= 44.01\ \mathrm{kJ} - 35.4\ \mathrm{kJ} \\
&= 8.6\ \mathrm{kJ}
\end{aligned}$$

At 298 K (25 °C) so boiling is nonspontaneous (*not* spontaneous).

Exercise 6.5.1

Use standard enthalpy and entropy data from Appendix 11.7 to calculate the standard free energy change for the reaction shown here (298 K). What does the computed value for Δ*G*° say about the spontaneity of this process?

$$\mathrm{C_2H_6\,(g)} \longrightarrow \mathrm{H_2\,(g) + C_2H_4\,(g)}$$

Answer available at the end of this section.

The standard free energy change for a reaction may also be calculated from **standard free energy of formation** ΔG_f^o values 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 enthalpy of formation, ΔG_f^o is by definition zero for elemental substances in their standard states. The approach used to calculate ΔG^o for a reaction from ΔG_f^o values is the same as that demonstrated previously for enthalpy and entropy changes. For the reaction

$$mA + nB \longrightarrow xC + yD$$

the standard free energy change at room temperature may be calculated as

$$\begin{aligned}
\Delta G^\circ &= \sum \nu \Delta G^\circ(\text{ products }) - \sum \nu \Delta G^\circ(\text{ reactants }) \\
&= \left[x\Delta G_f^\circ(C) + y\Delta G_f^\circ(D)\right] - \left[m\Delta G_f^\circ(A) + n\Delta G_f^\circ(B)\right].
\end{aligned}$$

Example 6.5.2: Using Standard Free Energies of Formation to Calculate ΔG°

Consider the decomposition of yellow mercury(II) oxide.

$$\mathrm{HgO}(s,\ \text{yellow}\ ) \rightarrow \mathrm{Hg}(l) + \frac{1}{2}\mathrm{O_2}(g)$$

Calculate the standard free energy change at room temperature, using (a) standard free energies of formation and (b) standard enthalpies of formation and standard entropies. Do the results indicate the reaction to be spontaneous or nonspontaneous under standard conditions?

Solution

The required data are available in Appendix 11.7 and are shown here.

Compound	ΔG_f°(kJ / mol)	ΔH_f°(kJ / mol)	S°(kJ / 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:

$$\begin{aligned}\Delta G^\circ &= \sum \nu G_f^\circ(\ \text{products}\ ) - \sum \nu \Delta G_f^\circ(\ \text{reactants}\ ) \\ &= \left[1\Delta G_f^\circ\ \mathrm{Hg\,(l)} + \frac{1}{2}\Delta G_f^\circ\ \mathrm{O_2\,(g)}\right] - 1\Delta G_f^\circ\ \mathrm{HgO\,(s, yellow)} \\ &= \left[1\ \text{mol}(0\ \text{kJ / mol}) + \frac{1}{2}\ \text{mol}(0\ \text{kJ / mol})\right] - 1\ \text{mol}(-58.43\ \text{kJ / mol}) = 58.43\ \text{kJ / mol}\end{aligned}$$

(b) Using enthalpies and entropies of formation:

$$\begin{aligned}\Delta H^\circ &= \sum \nu \Delta H_f^\circ(\ \text{products}\ ) - \sum \nu \Delta H_f^\circ(\ \text{reactants}\ ) \\ &= \left[1\Delta H_f^\circ\ \mathrm{Hg\,(l)} + \frac{1}{2}\Delta H_f^\circ\ \mathrm{O_2\,(g)}\right] - 1\Delta H_f^\circ\ \mathrm{HgO\,(s, yellow)} \\ &= \left[1\ \text{mol}(0\ \text{kJ / mol}) + \frac{1}{2}\ \text{mol}(0\ \text{kJ / mol})\right] - 1\ \text{mol}(-90.46\ \text{kJ / mol}) = 90.46\ \text{kJ / mol} \\ \Delta S^\circ &= \sum \nu \Delta S^\circ(\ \text{products}\ ) - \sum \nu \Delta S^\circ(\ \text{reactants}\ ) \\ &= \left[1\ \Delta S^\circ\ \mathrm{Hg\,(l)} + \frac{1}{2}\Delta S^\circ\ \mathrm{O_2\,(g)}\right] - 1\Delta S^\circ\ \mathrm{HgO\,(s, yellow)} \\ &= \left[1\ \text{mol}(75.9\ \text{J / mol K}) + \frac{1}{2}\ \text{mol}(205.2\ \text{J / mol K})\right] - 1\text{mol}(71.13\ \text{J / mol K}) = 107.4\ \ \text{J / mol K}\end{aligned}$$

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = 90.46\ \text{kJ} - 298.15\ \text{K} \times 107.4\ \text{J / K} \cdot \text{mol} \times \frac{1\ \ \text{kJ}}{1000\ \text{J}} \\ &= (90.46 - 32.01)\ \text{kJ / mol} = 58.45\ \text{kJ / mol}\end{aligned}$$

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 nonspontaneous (*not* spontaneous) at room temperature.

Exercise 6.5.1

Calculate ΔG° using (a) free energies of formation and (b) enthalpies of formation and entropies (Appendix 11.7). Do the results indicate the reaction to be spontaneous or nonspontaneous at 25 °C?

$$C_2H_4\,(g) \longrightarrow H_2\,(g) + C_2H_2\,(g)$$

Answer available at the end of this section.

Free Energy Changes for Coupled Reactions

The use of free energies of formation to compute free energy changes for reactions as described above is possible because ΔG is a state function, and the approach is analogous to the use of Hess' Law in computing enthalpy changes (see the chapter on thermochemistry). Consider the vaporization of water as an example:

$$H_2O\,(l) \longrightarrow H_2O\,(g)$$

An equation representing this process may be derived by adding the formation reactions for the two phases of water (necessarily reversing the reaction for the liquid phase). The free energy change for the sum reaction is the sum of free energy changes for the two added reactions:

$$\begin{aligned} H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) &\longrightarrow H_2O\,(g) && \Delta G_f^\circ \text{ gas} \\ H_2O\,(l) &\longrightarrow H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) && -\Delta G_f^o \text{ liquid} \\ H_2O\,(l) &\longrightarrow H_2O\,(g) && \Delta G^\circ = \Delta G_f^\circ \text{ gas} - \Delta G_f^\circ \text{ liquid} \end{aligned}$$

This approach may also be used in cases where a nonspontaneous reaction is enabled by coupling it to a spontaneous reaction. For example, the production of elemental zinc from zinc sulfide is thermodynamically unfavorable, as indicated by a positive value for ΔG^o:

$$ZnS\,(s) \rightarrow Zn\,(s) + S\,(s) \quad \Delta G_1^\circ = 201.3kJ$$

The industrial process for production of zinc from sulfidic ores involves coupling this decomposition reaction to the thermodynamically favorable oxidation of sulfur:

$$S\,(s) + O_2\,(g) \rightarrow SO_2\,(g) \quad \Delta G_2^\circ = -300.1kJ$$

The coupled reaction exhibits a negative free energy change and is spontaneous:

$$ZnS\,(s) + O_2\,(g) \rightarrow Zn\,(s) + SO_2\,(g)$$

$$\Delta G^\circ = 201.3\text{ kJ} + -300.1\text{ kJ} = -98.8\text{ kJ}$$

This process is typically carried out at elevated temperatures, so this result obtained using standard free energy values is just an estimate. The gist of the calculation, however, holds true.

Example 6.5.3: Calculating Free Energy Change for a Coupled Reaction

Is a reaction coupling the decomposition of ZnS to the formation of H_2S expected to be spontaneous under standard conditions?

Solution

Following the approach outlined above and using free energy values from Appendix 11.7:

Decomposition of zinc sulfide:	$ZnS\,(s) \rightarrow Zn\,(s) + S\,(s)$	$\Delta G_1^\circ = 201.3\text{ kJ}$
Formation of hydrogen sulfide:	$S\,(s) + H_2\,(g) \rightarrow H_2S\,(g)$	$\Delta G_1^\circ = -33.4\text{ kJ}$
Coupled reaction:	$ZnS\,(s) + H_2\,(g) \rightarrow Zn\,(s) + H_2S\,(g)$	$\Delta G^\circ = 201.3\text{ kJ} + -33.4\text{ kJ} = 167.9\text{ kJ}$

The coupled reaction exhibits a positive free energy change and is thus nonspontaneous.

Exercise 6.5.3

What is the standard free energy change for the reaction below? Is the reaction expected to be spontaneous under standard conditions?

$$\mathrm{FeS(s)} + \mathrm{O_2(g)} \rightarrow \mathrm{Fe(s)} + \mathrm{SO_2(g)}$$

Answer available at the end of this section.

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 Δ*H*° and Δ*S*° are positive.** This condition describes an endothermic process that involves an increase in system entropy. In this case, Δ*G*° will be negative if the magnitude of the *T*Δ*S*° term is greater than Δ*H*°. If the *T*Δ*S*° term is less than Δ*H*°, the free energy change will be positive. Such a process is *product-favored at equilibrium at high temperatures and reactant-favored at equilibrium at low temperatures*.
2. **Both Δ*H*° and Δ*S*° are negative.** This condition describes an exothermic process that involves a decrease in system entropy. In this case, Δ*G*° will be negative if the magnitude of the *T*Δ*S*° term is less than Δ*H*°. If the *T*Δ*S*° term's magnitude is greater than Δ*H*°, the free energy change will be positive. Such a process is *product-favored at equilibrium at low temperatures* and *reactant-favored at equilibrium at high temperatures*.
3. **Δ*H*° is positive and Δ*S*° is negative.** This condition describes an endothermic process that involves a decrease in system entropy. In this case, Δ*G*° will be positive regardless of the temperature. Such a process is *reactant-favored at equilibrium at all temperatures*.
4. **Δ*H*° is negative and Δ*S*° is positive.** This condition describes an exothermic process that involves an increase in system entropy. In this case, Δ*G*° will be negative regardless of the temperature. Such a process is *product-favored at equilibrium at all temperatures*.

These four scenarios are summarized in Table 6.5.1

Table 6.5.1

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 equilibrium at all temperatures.
+	-	+	The sign of ΔG^o does not depend on the temperature.The reaction is reactant-favored at equilibrium at all temperatures.
-	-	- or +	The sign of ΔG^o **does** depend on the temperature. The reaction will be product-favored at equilibrium at lower temperatures.
+	+	- or +	The sign of ΔG^o **does** depend on the temperature. The reaction will be product-favored at equilibrium at lower temperatures.

Example 6.5.3: 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 6.5.3

Popular chemical hand warmers generate heat by the air-oxidation of iron:

$$4\,\mathrm{Fe}(s)+3\,\mathrm{O}_2(g) \longrightarrow 2\,\mathrm{Fe}_2\mathrm{O}_3(s)$$

Does the sign of ΔG^o of this process depend upon temperature?

Answer available at the end of this section.

When considering the conclusions drawn regarding the temperature dependence of the sign of $\Delta G°$, 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 $\Delta G°$) as temperature varies. This is clearly illustrated by a graphical presentation of the free energy change equation, in which $\Delta G°$ 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 6.5.2. A process whose enthalpy and entropy changes are of the same arithmetic sign will exhibit a temperature-dependence for the sign of $\Delta G°$ as depicted by the two yellow lines in the plot. Each line crosses from one spontaneity domain (positive or negative $\Delta G°$) 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 $\Delta G°$ 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 $\Delta G°$ for the process is zero.

Note

In this discussion, we have used two different descriptions for the meaning of the sign of $\Delta G°$. 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 $\Delta G°$ to tell us the same information as the equilibrium constant, K. When $\Delta G° < 0$, $K > 1$, and the reaction will be product-favored at equilibrium. When $\Delta G° > 0$, $K < 1$, and the reaction is reactant-favored at equilibrium. When $\Delta G° = 0$, $K = 1$, 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 $\Delta G°$ 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 $\Delta G° < 0$, 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 $\Delta G° > 0$, 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 $\Delta G° = 0$, we say that the neither the reactants nor the products are favored to be formed.

A detailed treatment of the meaning of $\Delta G°$ 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.

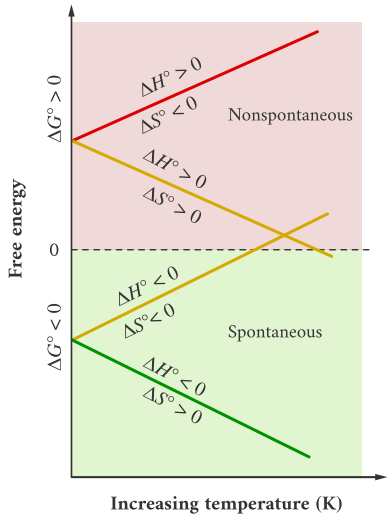


Figure 6.5.2: These plots show the variation in ΔG° with temperature for the four possible combinations of arithmetic sign for ΔH° and ΔS°. Note that in this graph of ΔG°, "spontaneous" is synonymous with "product-favored at equilibrium", and "nonspontaneous" is synonymous with "reactant-favored at equilibrium".

Example 6.5.4: 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,

$$\begin{aligned}\Delta H^\circ &= \Delta H_\mathrm{f}^\circ(\mathrm{H_2O}(g)) - \Delta H_\mathrm{f}^\circ(\mathrm{H_2O}(l)) \\ &= -241.82\ \mathrm{kJ/mol} - (-285.83\ \mathrm{kJ/mol}) = 44.01\ \mathrm{kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= \Delta S_{298}^\circ(\mathrm{H_2O}(g)) - \Delta S_{298}^\circ(\mathrm{H_2O}(l)) \\ &= 188.8\ \mathrm{J/K \cdot mol} - 70.0\ \mathrm{J/K \cdot mol} = 118.8\ \mathrm{J/K \cdot mol}\end{aligned}$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{44.01 \times 10^3\ \mathrm{J/mol}}{118.8\ \mathrm{J/K \cdot mol}} = 370.5\ \mathrm{K} = 97.3\ ^\circ\mathrm{C}$$

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 6.5.4

Use the information in Tables T1 or T2 to estimate the boiling point of CS_2.

Answer available at the end of this section.

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 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 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* (pressures other than 1 bar; concentrations other than 1 M) is related to the standard free energy change according to this equation:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

R is the gas constant (8.314 J/K mol), *T* is the kelvin or absolute temperature, and Q is the reaction quotient. For gas phase equilibria, the pressure-based reaction quotient, Q_P, is used. The concentration-based reaction quotient, Q_C, is used for condensed phase equilibria. This equation may be used to predict the spontaneity for a process under any given set of conditions as illustrated in Example 6.5.6.

Example 6.5.6: Calculating ΔG under Nonstandard Conditions

What is the free energy change for the process shown here

$$2NH_3(g) \longrightarrow 3H_2(g) + N_2(g)$$

under the specified conditions?

- $T = 25^\circ C$,
- $P_{N_2} = 0.870$ atm
- $P_{H_2} = 0.250$ atm
- $P_{NH_3} = 12.9$ atm

$$\Delta G^\circ = 33.0 kJ/mol$$

Solution

The equation relating free energy change to standard free energy change and reaction quotient may be used directly:

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT \ln Q \\ &= 33.0 \frac{\text{kJ}}{\text{mol}} + \left(8.314 \frac{\text{J}}{\text{mol K}} \times 298 K \times \ln \frac{\left(0.250^3\right) \times 0.870}{12.9^2} \right) \\ &= 9680 \frac{\text{J}}{\text{mol}} \text{ or } 9.68 \text{ kJ/mol}\end{aligned}$$

Since the computed value for ΔG is positive, the reaction is nonspontaneous under these conditions.

Exercise 6.5.6

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 available at the end of this section.

For a system at equilibrium, Q = *K* and Δ*G* = 0, and the previous equation may be written as

$$0 = \Delta G^\circ + RT \ln K \quad \text{(at equilibrium)}$$

$$\Delta G^\circ = -RT \ln K$$

or

$$K = e^{-\frac{\Delta G}{RT}}$$

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 6.5.2.

Table 6.5.2: Relations between Standard Free Energy Changes and Equilibrium Constants

K	Δ*G*°	Composition of an Equilibrium Mixture
> 1	< 0	Products are more abundant
< 1	> 0	Reactants are more abundant
= 1	= 0	Reactants and products are comparably abundant

Example 6.5.7: Calculating an 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:

$$\begin{aligned}\Delta G^\circ &= \left[\Delta G_f^\circ\left(\mathrm{Ag^+\,(aq)}\right) + \Delta G_f^\circ\left(\mathrm{Cl^-\,(aq)}\right)\right] - \left[\Delta G_f^\circ(\mathrm{AgCl\,(s)})\right] \\ &= [77.1\ \mathrm{kJ/mol} - 131.2\ \mathrm{kJ/mol}] - [-109.8\ \mathrm{kJ/mol}] = 55.7\ \mathrm{kJ/mol}\end{aligned}$$

The equilibrium constant for the reaction may then be derived from its standard free energy change:

$$K_{sp} = e^{-\frac{\Delta G^\circ}{RT}} = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(-\frac{55.7 \times 10^3 J/mol}{8.314 J/mol \cdot K \times 298.15 K}\right) = \exp(-22.470) = e^{-22.470} = 1.74 \times 10^{-10}$$

This result is in reasonable agreement with the value provided in Appendix 11.10.

Exercise 6.5.7

Use the thermodynamic data provided in Appendix 11.7 to calculate the equilibrium constant for the dissociation of dinitrogen tetroxide at 25 °C.

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

Answer available at the end of this section.

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 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 6.5.3). If a system consists of reactants and products in nonequilibrium amounts ($Q \neq K$), the reaction will proceed spontaneously in the direction necessary to establish equilibrium.

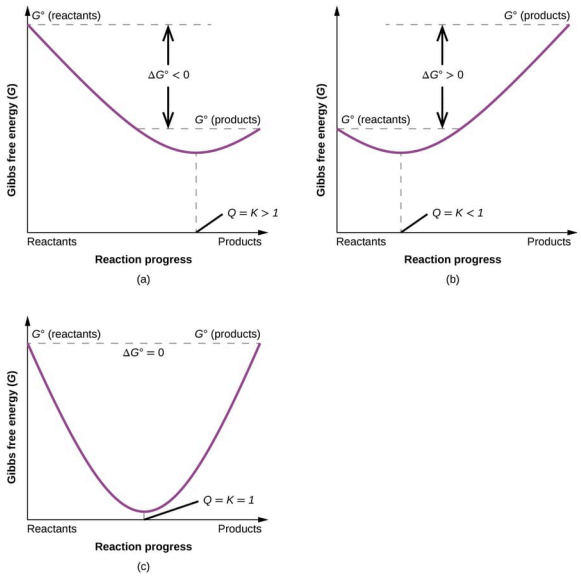


Figure 6.5.3: These plots show the free energy versus reaction progress for systems whose standard free energy changes are (a) negative, (b) positive, and (c) zero. Nonequilibrium systems will proceed spontaneously in whatever direction is necessary to minimize free energy and establish equilibrium.

Answers

Exercise 6.5.1

the reaction is nonspontaneous (*not* spontaneous) at 25 °C.

Exercise 6.5.1

a. 140.8 kJ/mol, nonspontaneous
b. 141.5 kJ/mol, nonspontaneous

Exercise 6.5.3

–199.7 kJ; spontaneous

Exercise 6.5.3

$\Delta H°$ and $\Delta S°$ are both negative; the reaction is product-favored at equilibrium at low temperatures.

Exercise 6.5.4

313 K (accepted value 319 K).

Exercise 6.5.6

ΔG = –123.5 kJ/mol; yes

Exercise 6.5.7

K = 3.1

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6.6: Key Terms

Example and Directions

Words (or words that have the same definition)	The definition is case sensitive	(Optional) Image to display with the definition [Not displayed in Glossary, only in pop-up on pages]	(Optional) Caption for Image	(Optional) External or Internal Link	(Optional) Source for Definition
(Eg. "Genetic, Hereditary, DNA ...")	(Eg. "Relating to genes or heredity")		The infamous double helix	https://bio.libretexts.org/	CC-BY-SA; Delmar Larsen

Glossary Entries

Word(s)	Definition	Image	Caption	Link	Source
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				
Gibbs free energy change (*G*)	thermodynamic property defined in terms of system enthalpy and entropy; all spontaneous processes involve a decrease in *G*				
microstate	possible configuration or arrangement of matter and energy within a system				
nonspontaneous process	process that requires continual input of energy from an external source				
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				
second law of thermodynamics	all spontaneous processes involve an increase in the entropy of the universe				
spontaneous change	process that takes place without a continuous input of energy from an external source				
standard entropy (S°)	entropy for one mole of a substance at 1 bar pressure; tabulated values are usually determined at 298.15 K				
standard entropy change ($\Delta S°$)	change in entropy for a reaction calculated using the standard entropies				
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	change in free energy accompanying the formation of one mole of substance from its elements in their standard states				
third law of thermodynamics	entropy of a perfect crystal at absolute zero (0 K) is zero				

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6.7: Key Equations

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

$$S = k \ln W$$

$$\Delta S = k \ln \frac{W_{\text{f}}}{W_{\text{i}}}$$

$$\Delta S^{\circ} = \sum \nu S^{\circ} \text{ (products) } - \sum \nu S^{\circ} \text{(reactants)}$$

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T}$$

$$\Delta G = \Delta H - T\Delta S$$

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6.8: 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.

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.

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.

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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6.9: Exercises

1.

What is a spontaneous reaction?

2.

What is a nonspontaneous reaction?

3.

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

4.

A helium-filled balloon spontaneously deflates overnight as He atoms diffuse through the wall of the balloon. Describe the redistribution of matter and/or energy that accompanies this process.

5.

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.

6.

In Figure 12.8 all possible distributions and microstates are shown for four different particles shared between two boxes. Determine the entropy change, ΔS, if the particles are initially evenly distributed between the two boxes, but upon redistribution all end up in Box (b).

7.

In Figure 12.8 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 (b) to distribution (d).

8.

How does the process described in the previous item relate to the system shown in Figure 12.4?

9.

Consider a system similar to the one in Figure 12.8, 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?

10.

Consider the system shown in Figure 12.9. What is the change in entropy for the process where the energy is initially associated only with particle A, but in the final state the energy is distributed between two different particles?

11.

Consider the system shown in Figure 12.9. What is the change in entropy for the process where the energy is initially associated with particles A and B, and the energy is distributed between two particles in different boxes (one in A-B, the other in C-D)?

12.

Arrange the following sets of systems in order of increasing entropy. Assume one mole of each substance and the same temperature for each member of a set.

(a) $H_2(g)$, $HBrO_4(g)$, $HBr(g)$

(b) $H_2O(l)$, $H_2O(g)$, $H_2O(s)$

(c) $He(g)$, $Cl_2(g)$, $P_4(g)$

13.

At room temperature, the entropy of the halogens increases from I_2 to Br_2 to Cl_2. Explain.

14.

Consider two processes: sublimation of $I_2(s)$ and melting of $I_2(s)$ (Note: the latter process can occur at the same temperature but somewhat higher pressure).

$$I_2(s) \longrightarrow I_2(g)$$

$$I_2(s) \longrightarrow I_2(l)$$

Is ΔS positive or negative in these processes? In which of the processes will the magnitude of the entropy change be greater?

15.

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) $2H(g)$ or $H(g)$

16.

Predict the sign of the entropy change for the following processes.

(a) An ice cube is warmed to near its melting point.

(b) Exhaled breath forms fog on a cold morning.

(c) Snow melts.

17.

Predict the sign of the entropy change for the following processes. Give a reason for your prediction.

(a) $\mathrm{Na^+}(aq) + \mathrm{Cl^-}(aq) \longrightarrow \mathrm{NaCl}(s)$

(b) $2\mathrm{Fe}(s) + \frac{3}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{Fe_2O_2}(s)$

(c) $2\mathrm{C_6H_{14}}(l) + 19\mathrm{O_2}(g) \longrightarrow 14\mathrm{H_2O}(g) + 12\mathrm{CO_2}(g)$

18.

Write the balanced chemical equation for the combustion of methane, $CH_4(g)$, to give carbon dioxide and water vapor. Explain why it is difficult to predict whether ΔS is positive or negative for this chemical reaction.

19.

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?

20.

What is the difference between ΔS and $\Delta S°$ for a chemical change?

21.

Calculate $\Delta S°$ 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) $\mathrm{Zn}(s) + \mathrm{CuSO_4}(s) \longrightarrow \mathrm{Cu}(s) + \mathrm{ZnSO_4}(s)$

22.

Determine the entropy change for the combustion of liquid ethanol, C_2H_5OH, under the standard conditions to give gaseous carbon dioxide and liquid water.

23.

Determine the entropy change for the combustion of gaseous propane, C_3H_8, under the standard conditions to give gaseous carbon dioxide and water.

24.

"Thermite" reactions have been used for welding metal parts such as railway rails and in metal refining. One such thermite reaction is $\mathrm{Fe_2O_3}(s) + 2\mathrm{Al}(s) \longrightarrow \mathrm{Al_2O_3}(s) + 2\mathrm{Fe}(s)$. Is the reaction spontaneous at room temperature under standard conditions? During the reaction, the surroundings absorb 851.8 kJ/mol of heat.

25.

Using the relevant $S°$ values listed in Appendix G, calculate $\Delta S°_{298}$ for the following changes:

(a) $\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \longrightarrow 2\mathrm{NH_3}(g)$

(b) $\mathrm{N_2}(g) + \frac{5}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{N_2O_5}(g)$

26.

From the following information, determine $\Delta S°$ for the following:

$\mathrm{N}(g) + \mathrm{O}(g) \longrightarrow \mathrm{NO}(g)$ $\qquad \Delta S° = ?$

$\mathrm{N_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\mathrm{NO}(g)$ $\qquad \Delta S° = 24.8\ \mathrm{J/K}$

$\mathrm{N_2}(g) \longrightarrow 2\mathrm{N}(g)$ $\qquad \Delta S° = 115.0\ \mathrm{J/K}$

$\mathrm{O_2}(g) \longrightarrow 2\mathrm{O}(g)$ $\qquad \Delta S° = 117.0\ \mathrm{J/K}$

27.

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.
$S°_{\mathrm{NaCl}(s)} = 72.11 \frac{\mathrm{J}}{\mathrm{mol \cdot K}}$ $\qquad S°_{\mathrm{NaCl}(l)} = 95.06\ \frac{\mathrm{J}}{\mathrm{mol \cdot K}}$ $\qquad \Delta H°_{\mathrm{fusion}} = 27.95\ \mathrm{kJ/mol}$

What assumptions are made about the thermodynamic information (entropy and enthalpy values) used to solve this problem?

28.

Use the standard entropy data in Appendix G to determine the change in entropy for each of the following reactions. All the processes occur at the standard conditions and 25 °C.

(a) $\mathrm{MnO_2}(s) \longrightarrow \mathrm{Mn}(s) + \mathrm{O_2}(g)$

(b) $\mathrm{H_2}(g) + \mathrm{Br_2}(l) \longrightarrow 2\mathrm{HBr}(g)$

(c) $\mathrm{Cu}(s) + \mathrm{S}(g) \longrightarrow \mathrm{CuS}(s)$

(d) $2\mathrm{LiOH}(s) + \mathrm{CO_2}(g) \longrightarrow \mathrm{Li_2CO_3}(s) + \mathrm{H_2O}(g)$

(e) $\mathrm{CH_4}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{C}(s,\ \text{graphite}) + 2\mathrm{H_2O}(g)$

(f) $\mathrm{CS_2}(g) + 3\mathrm{Cl_2}(g) \longrightarrow \mathrm{CCl_4}(g) + \mathrm{S_2Cl_2}(g)$

29.

Use the standard entropy data in Appendix G to determine the change in entropy for each of the following reactions. All the processes occur at the standard conditions and 25 °C.

(a) $\mathrm{C}(s,\ \text{graphite}) + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g)$

(b) $\mathrm{O_2}(g) + \mathrm{N_2}(g) \longrightarrow 2\mathrm{NO}(g)$

(c) $2\mathrm{Cu}(s) + \mathrm{S}(g) \longrightarrow \mathrm{Cu_2S}(s)$

(d) $\mathrm{CaO}(s) + \mathrm{H_2O}(l) \longrightarrow \mathrm{Ca(OH)_2}(s)$

(e) $\mathrm{Fe_2O_3}(s) + 3\mathrm{CO}(g) \longrightarrow 2\mathrm{Fe}(s) + 3\mathrm{CO_2}(g)$

(f) $\mathrm{CaSO_4{\cdot}2H_2O}(s) \longrightarrow \mathrm{CaSO_4}(s) + 2\mathrm{H_2O}(g)$

30.

What is the difference between ΔG and $\Delta G°$ for a chemical change?

31.

A reaction has $\Delta H°$ = 100 kJ/mol and $\Delta S° = 250\ \mathrm{J/mol{\cdot}K}$. Is the reaction spontaneous at room temperature? If not, under what temperature conditions will it become spontaneous?

32.

Explain what happens as a reaction starts with $\Delta G < 0$ (negative) and reaches the point where $\Delta G = 0$.

33.

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) $\mathrm{H_2}(g) + \mathrm{Br_2}(l) \longrightarrow 2\mathrm{HBr}(g)$

(c) $\mathrm{Cu}(s) + \mathrm{S}(g) \longrightarrow \mathrm{CuS}(s)$

(d) $2\mathrm{LiOH}(s) + \mathrm{CO_2}(g) \longrightarrow \mathrm{Li_2CO_3}(s) + \mathrm{H_2O}(g)$

(e) $\mathrm{CH_4}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{C}(s,\ \text{graphite}) + 2\mathrm{H_2O}(g)$

(f) $\mathrm{CS_2}(g) + 3\mathrm{Cl_2}(g) \longrightarrow \mathrm{CCl_4}(g) + \mathrm{S_2Cl_2}(g)$

34.

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) $\mathrm{C}(s,\ \text{graphite}) + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g)$

(b) $\mathrm{O_2}(g) + \mathrm{N_2}(g) \longrightarrow 2\mathrm{NO}(g)$

(c) $2\mathrm{Cu}(s) + \mathrm{S}(g) \longrightarrow \mathrm{Cu_2S}(s)$

(d) $\mathrm{CaO}(s) + \mathrm{H_2O}(l) \longrightarrow \mathrm{Ca(OH)_2}(s)$

(e) $\mathrm{Fe_2O_3}(s) + 3\mathrm{CO}(g) \longrightarrow 2\mathrm{Fe}(s) + 3\mathrm{CO_2}(g)$

(f) $\mathrm{CaSO_4{\cdot}2H_2O}(s) \longrightarrow \mathrm{CaSO_4}(s) + 2\mathrm{H_2O}(g)$

35.

Given:

$\mathrm{P_4}(s) + 5\mathrm{O_2}(g) \longrightarrow \mathrm{P_4O_{10}}(s) \qquad \Delta G° = -2697.0\ \mathrm{kJ/mol}$

$2\mathrm{H_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\mathrm{H_2O}(g) \qquad \Delta G° = -457.18\ \mathrm{kJ/mol}$

$6\mathrm{H_2O}(g) + \mathrm{P_4O_{10}}(s) \longrightarrow 4\mathrm{H_3PO_4}(l) \qquad \Delta G° = -428.66\ \mathrm{kJ/mol}$

(a) Determine the standard free energy of formation, $\Delta G_\mathrm{f}^\circ$, for phosphoric acid.

(b) How does your calculated result compare to the value in Appendix G? Explain.

36.

Is the formation of ozone ($O_3(g)$) from oxygen ($O_2(g)$) spontaneous at room temperature under standard state conditions?

37.

Consider the decomposition of red mercury(II) oxide under standard state conditions.

$2\mathrm{HgO}(s,\ \text{red}) \longrightarrow 2\mathrm{Hg}(l) + \mathrm{O_2}(g)$

(a) Is the decomposition spontaneous under standard state conditions?

(b) Above what temperature does the reaction become spontaneous?

38.

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: $2\mathrm{NH_3}(g) \longrightarrow \mathrm{N_2}(g) + 3\mathrm{H_2}(g)$

(b) Diborane: $\mathrm{B_2H_6}(g) \longrightarrow 2\mathrm{B}(g) + 3\mathrm{H_2}(g)$

(c) Hydrazine: $\mathrm{N_2H_4}(g) \longrightarrow \mathrm{N_2}(g) + 2\mathrm{H_2}(g)$

(d) Hydrogen peroxide: $\mathrm{H_2O_2}(l) \longrightarrow \mathrm{H_2O}(g) + \frac{1}{2}\mathrm{O_2}(g)$

39.

Calculate $\Delta G°$ for each of the following reactions from the equilibrium constant at the temperature given.

(a) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$	$T = 2000\ °C$	$K_p = 4.1 \times 10^{-4}$
(b) $H_2(g) + I_2(g) \longrightarrow 2HI(g)$	$T = 400\ °C$	$K_p = 50.0$
(c) $CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$	$T = 980\ °C$	$K_p = 1.67$
(d) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$	$T = 900\ °C$	$K_p = 1.04$
(e) $HF(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + F^-(aq)$	$T = 25\ °C$	$K_p = 7.2 \times 10^{-4}$
(f) $AgBr(s) \longrightarrow Ag^+(aq) + Br^-(aq)$	$T = 25\ °C$	$K_p = 3.3 \times 10^{-13}$

40.

Calculate $\Delta G°$ for each of the following reactions from the equilibrium constant at the temperature given.

(a) $Cl_2(g) + Br_2(g) \longrightarrow 2BrCl(g)$	$T = 25\ °C$	$K_p = 4.7 \times 10^{-2}$
(b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$	$T = 500\ °C$	$K_p = 48.2$
(c) $H_2O(l) \rightleftharpoons H_2O(g)$	$T = 60\ °C$	$K_p = 0.196$
(d) $CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g)$	$T = 550\ °C$	$K_p = 4.90 \times 10^2$
(e) $CH_3NH_2(aq) + H_2O(l) \longrightarrow CH_3NH_3{}^+(aq) + OH^-(aq)$	$T = 25\ °C$	$K_p = 4.4 \times 10^{-4}$
(f) $PbI_2(s) \longrightarrow Pb^{2+}(aq) + 2I^-(aq)$	$T = 25\ °C$	$K_p = 8.7 \times 10^{-9}$

41.

Calculate the equilibrium constant at 25 °C for each of the following reactions from the value of $\Delta G°$ given.

(a) $O_2(g) + 2F_2(g) \longrightarrow 2OF_2(g)$	$\Delta G° = -9.2\ kJ$
(b) $I_2(s) + Br_2(l) \longrightarrow 2IBr(g)$	$\Delta G° = 7.3\ kJ$
(c) $2LiOH(s) + CO_2(g) \longrightarrow Li_2CO_3(s) + H_2O(g)$	$\Delta G° = -79\ kJ$
(d) $N_2O_3(g) \longrightarrow NO(g) + NO_2(g)$	$\Delta G° = -1.6\ kJ$
(e) $SnCl_4(l) \longrightarrow SnCl_4(l)$	$\Delta G° = 8.0\ kJ$

42.

Determine $\Delta G°$ for the following reactions.

(a) Antimony pentachloride decomposes at 448 °C. The reaction is:
$SbCl_5(g) \longrightarrow SbCl_3(g) + Cl_2(g)$

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.

(b) Chlorine molecules dissociate according to this reaction:
$Cl_2(g) \longrightarrow 2Cl(g)$

1.00% of Cl_2 molecules dissociate at 975 K and a pressure of 1.00 atm.

43.

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 $PbCl_2(s)$.

44.

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 kJ/mole and –39.5 kJ/mole respectively, and the solubility product for $Ag_2S(s)$ is 8×10^{-51}.

45.

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.

46.

The evaporation of one mole of water at 298 K has a standard free energy change of 8.58 kJ.
$\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2O}(g) \qquad \Delta G° = 8.58\ \mathrm{kJ}$

(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?

47.

In glycolysis, the reaction of glucose (Glu) to form glucose-6-phosphate (G6P) requires ATP to be present as described by the following equation:
$\mathrm{Glu} + \mathrm{ATP} \longrightarrow \mathrm{G6P} + \mathrm{ADP} \qquad \Delta G° = -17\ \mathrm{kJ}$

In this process, ATP becomes ADP summarized by the following equation:
$\mathrm{ATP} \longrightarrow \mathrm{ADP} \qquad \Delta G° = -30\ \mathrm{kJ}$

Determine the standard free energy change for the following reaction, and explain why ATP is necessary to drive this process:
$\mathrm{Glu} \longrightarrow \mathrm{G6P} \qquad \Delta G° = ?$

48.

One of the important reactions in the biochemical pathway glycolysis is the reaction of glucose-6-phosphate (G6P) to form fructose-6-phosphate (F6P):
$\mathrm{G6P} \rightleftharpoons \mathrm{F6P} \qquad \Delta G° = 1.7\ \mathrm{kJ}$

(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.

49.

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) $\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \longrightarrow 2\mathrm{NH_3}(g)$

(b) $\mathrm{HCl}(g) + \mathrm{NH_3}(g) \longrightarrow \mathrm{NH_4Cl}(s)$

(c) $(\mathrm{NH_4})_2\mathrm{Cr_2O_7}(s) \longrightarrow \mathrm{Cr_2O_3}(s) + 4\mathrm{H_2O}(g) + \mathrm{N_2}(g)$

(d) $2\text{Fe}(s) + 3\text{O}_2(g) \longrightarrow \text{Fe}_2\text{O}_3(s)$

50.

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.

51.

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:
$\text{Cu}_2\text{S}(s) \longrightarrow \text{Cu}(s) + \text{S}(s)$

(a) Determine $\Delta G°$ for the decomposition of 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 $\Delta G°$ for the process.

(c) The production of copper from chalcocite is performed by roasting the 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.

52.

What happens to $\Delta G°$ (becomes more negative or more positive) for the following chemical reactions when the partial pressure of oxygen is increased?

(a) $\text{S}(s) + \text{O}_2(g) \longrightarrow \text{SO}_2(g)$

(b) $2\text{SO}_2(g) + \text{O}_2(g) \longrightarrow \text{SO}_3(g)$

(c) $\text{HgO}(s) \longrightarrow \text{Hg}(l) + \text{O}_2(g)$

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7: FUNDAMENTAL EQUILIBRIUM CONCEPTS

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7.2: Chemical Equilibria

7.3: Equilibrium Constants

7.4: Shifting Equilibria - Le Chatelier's Principle

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7.1: Introduction

Imagine a beach populated with sunbathers and swimmers. As those basking in the sun get too hot, they enter the surf to swim and cool off. As the swimmers tire, they return to the beach to rest. If the rate at which sunbathers enter the surf were to equal the rate at which swimmers return to the sand, then the numbers (though not the identities) of sunbathers and swimmers would remain constant. This scenario illustrates a dynamic phenomenon known as *equilibrium*, in which opposing processes occur at equal rates. Chemical and physical processes are subject to this phenomenon; these processes are at equilibrium when the forward and reverse reaction rates are equal. Equilibrium systems are pervasive in nature; the various reactions involving carbon dioxide dissolved in blood are examples (see Figure 7.1.1). This chapter provides a thorough introduction to the essential aspects of chemical equilibria.

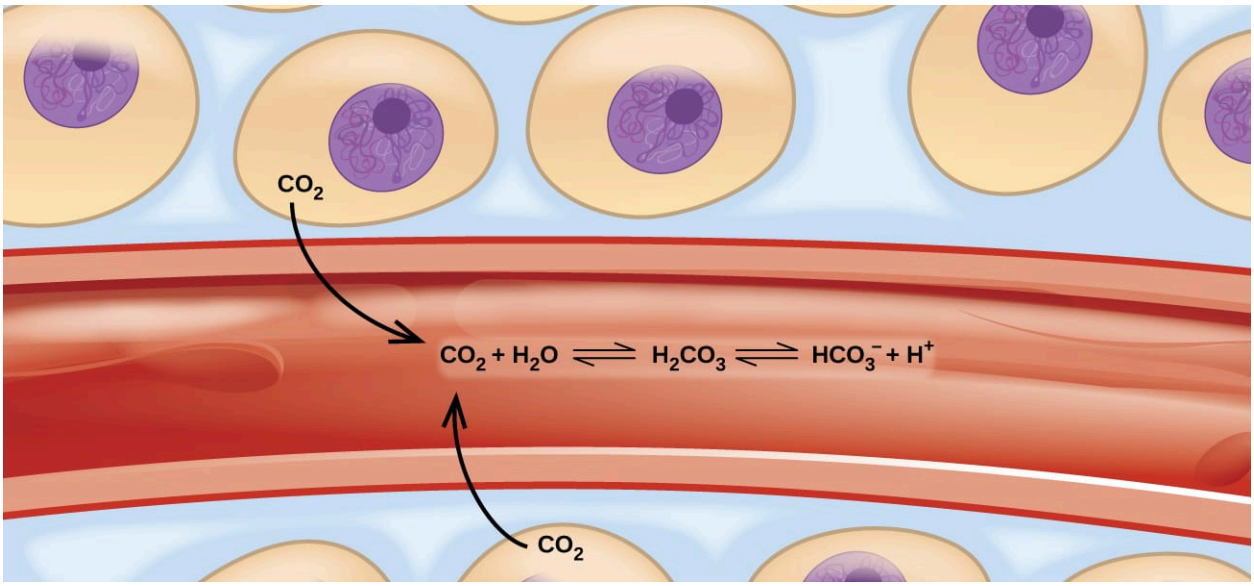


Figure 7.1.1: Transport of carbon dioxide in the body involves several reversible chemical reactions, including hydrolysis and acid ionization (among others).

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7.2: Chemical Equilibria

Learning Objectives

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

- Describe the nature of equilibrium systems
- Explain the dynamic nature of a chemical equilibrium
- Relate the magnitude of an equilibrium constant to properties of the chemical system

The convention for writing chemical equations involves placing reactant formulas on the left side of a reaction arrow and product formulas on the right side. By this convention, and the definitions of "reactant" and "product," a chemical equation represents the reaction in question as proceeding from left to right. **Reversible reactions**, however, may proceed in both forward (left to right) and reverse (right to left) directions. When the rates of the forward and reverse reactions are equal, the concentrations of the reactant and product species remain constant over time and the system is at **equilibrium**. The relative concentrations of reactants and products in equilibrium systems vary greatly; some systems contain mostly products at equilibrium, some contain mostly reactants, and some contain appreciable amounts of both.

Figure 7.2.1 illustrates fundamental equilibrium concepts using the reversible decomposition of colorless dinitrogen tetroxide to yield brown nitrogen dioxide, an elementary reaction described by the equation:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Note that a special double arrow is used to emphasize the reversible nature of the reaction.

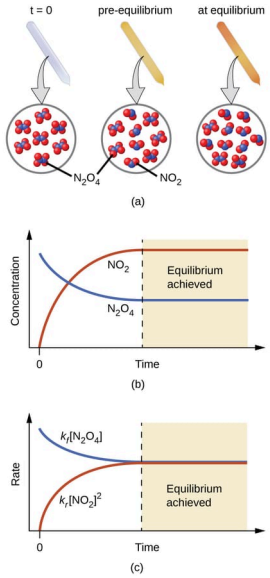


Figure 7.2.1: (a) A sealed tube containing colorless N_2O_4 darkens as it decomposes to yield brown NO_2. (b) Changes in concentration over time as the decomposition reaction achieves equilibrium. (c) At equilibrium, the forward and reverse reaction rates are equal.

For this elementary process, rate laws for the forward and reverse reactions may be derived directly from the reaction stoichiometry:

$$\text{rate}_f = k_f\,[N_2O_4]$$

$$\text{rate }_r = k_r\,[NO_2]^2$$

As the reaction begins (t = 0), the concentration of the N_2O_4 reactant is finite and that of the NO_2 product is zero, so the forward reaction proceeds at a finite rate while the reverse reaction rate is zero. As time passes, N_2O_4 is consumed and its concentration

falls, while NO_2 is produced and its concentration increases (Figure 7.2.1*b*). The decreasing concentration of the reactant slows the forward reaction rate, and the increasing product concentration speeds the reverse reaction rate (Figure 7.2.1*c*). This process continues until *the forward and reverse reaction rates become equal*, at which time the reaction has reached equilibrium, as characterized by constant concentrations of its reactants and products (shaded areas of Figure 7.2.1*b* and Figure 7.2.1*c*). It's important to emphasize that chemical equilibria are dynamic; a reaction at equilibrium has not "stopped," but is proceeding in the forward and reverse directions at the same rate. This dynamic nature is essential to understanding equilibrium behavior as discussed in this and subsequent chapters of the text.

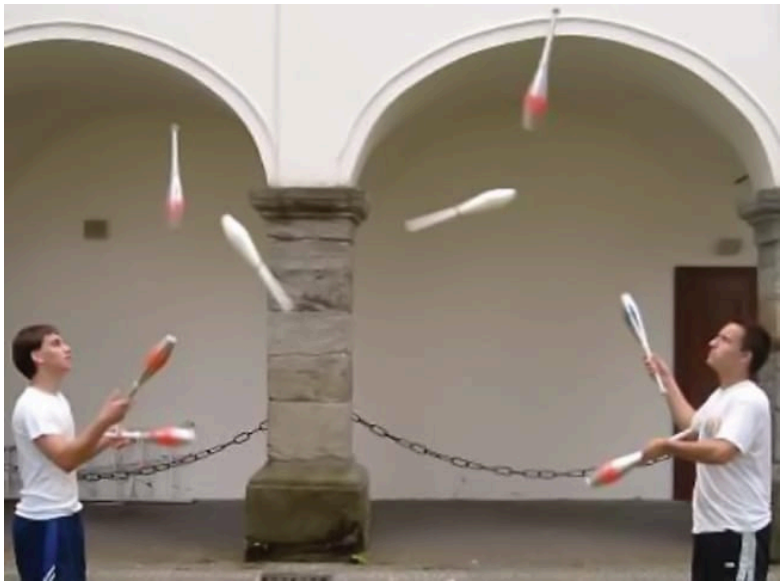


Figure 7.2.2: A two-person juggling act illustrates the dynamic aspect of chemical equilibria. Each person is throwing and catching clubs at the same rate, and each holds a (approximately) constant number of clubs.

Physical changes, such as phase transitions, are also reversible and may establish equilibria. This concept was introduced in another chapter of this text through discussion of the vapor pressure of a condensed phase (liquid or solid). As one example, consider the vaporization of bromine:

$$\mathrm{Br_2\,(l)} \rightleftharpoons \mathrm{Br_2\,(g)}$$

When liquid bromine is added to an otherwise empty container and the container is sealed, the forward process depicted above (vaporization) will commence and continue at a roughly constant rate as long as the exposed surface area of the liquid and its temperature remain constant. As increasing amounts of gaseous bromine are produced, the rate of the reverse process (condensation) will increase until it equals the rate of vaporization and equilibrium is established. A photograph showing this phase transition equilibrium is provided in Figure 7.2.3.



Figure 7.2.3: A sealed tube containing an equilibrium mixture of liquid and gaseous bromine. (credit: http://images-of-elements.com/bromine.php)

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7.3: Equilibrium Constants

Learning Objectives

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

- 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

The status of a reversible reaction is conveniently assessed by evaluating its reaction quotient (Q). For a reversible reaction described by

$$mA + nB + \rightleftharpoons xC + yD$$

the reaction quotient is derived directly from the stoichiometry of the balanced equation as

$$Q_c = \frac{[C]^x[D]^y}{[A]^m[B]^n}$$

where the subscript c denotes the use of molar concentrations in the expression. If the reactants and products are gaseous, a reaction quotient may be similarly derived using partial pressures:

$$Q_p = \frac{P_C^x P_D^y}{{P_A}^m {P_B}^n}$$

Note that the reaction quotient equations above are a simplification of more rigorous expressions that use *relative* values for concentrations and pressures rather than *absolute* values. These relative concentration and pressure values are dimensionless (they have no units); consequently, so are the reaction quotients. For purposes of this introductory text, it will suffice to use the simplified equations and to disregard units when computing Q. In most cases, this will introduce only modest errors in calculations involving reaction quotients.

Example 7.3.1: Writing Reaction Quotient Expressions

Write the concentration-based reaction quotient expression for each of the following reactions:

a. $3\,O_2\,(g) \rightleftharpoons 2\,O_3\,(g)$
b. $N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$
c. $4\,NH_3\,(g) + 7\,O_2\,(g) \rightleftharpoons 4\,NO_2\,(g) + 6\,H_2O\,(g)$

Solution

a. $$Q_c = \frac{[O_3]^2}{[O_2]^3}$$

b. $$Q_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$$

c. $$Q_c = \frac{[NO_2]^4\,[H_2O]^6}{[NH_3]^4\,[O_2]^7}$$

Exercise 7.3.1

Write the concentration-based reaction quotient expression for each of the following reactions:

a. $2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)$
b. $C_4H_8\,(g) \rightleftharpoons 2\,C_2H_4\,(g)$
c. $2\,C_4H_{10}\,(g) + 13\,O_2\,(g) \rightleftharpoons 8\,CO_2\,(g) + 10\,H_2O\,(g)$

Answer available at the end of this section.

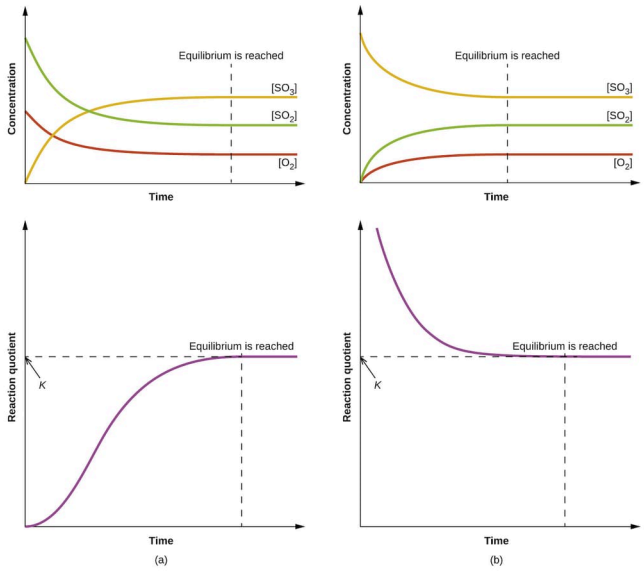


Figure 7.3.1 Changes in concentrations and Q_c for a chemical equilibrium achieved beginning with (a) a mixture of reactants only and (b) products only.

The numerical value of Q varies as a reaction proceeds towards equilibrium; therefore, it can serve as a useful indicator of the reaction's status. To illustrate this point, consider the oxidation of sulfur dioxide:

$$2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)$$

Two different experimental scenarios are depicted in Figure 7.3.1, one in which this reaction is initiated with a mixture of reactants only, SO_2 and O_2, and another that begins with only product, SO_3. For the reaction that begins with a mixture of reactants only, Q is initially equal to zero:

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]} = \frac{0^2}{[SO_2]^2\,[O_2]} = 0$$

As the reaction proceeds toward equilibrium in the forward direction, reactant concentrations decrease (as does the denominator of Q_c), product concentration increases (as does the numerator of Q_c), and the reaction quotient consequently increases. When equilibrium is achieved, the concentrations of reactants and product remain constant, as does the value of Q_c.

If the reaction begins with only product present, the value of Q_c is initially undefined (immeasurably large, or infinite):

$$Q_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]} = \frac{[SO_3]^2}{0} \rightarrow \infty$$

In this case, the reaction proceeds toward equilibrium in the reverse direction. The product concentration and the numerator of Q_c decrease with time, the reactant concentrations and the denominator of Q_c increase, and the reaction quotient consequently decreases until it becomes constant at equilibrium.

The constant value of Q exhibited by a system at equilibrium is called the equilibrium constant, K:

$$K \equiv Q \text{ at equilibrium}$$

Comparison of the data plots in Figure 7.3.1 shows that both experimental scenarios resulted in the same value for the equilibrium constant. This is a general observation for all equilibrium systems, known as the **law of mass action**.

Definition: Law of Mass Action

At a given temperature, the reaction quotient for a system at equilibrium is constant.

Example 7.3.2: 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

As for all equilibrium calculations in this text, use the simplified equations for Q and K and disregard any concentration or pressure units, as noted previously in this section.

(a) Before any product is formed

$$[NO_2] = \frac{0.10 \text{ mol}}{1.0 \text{ L}} = 0.10 \text{ M}$$

$$[N_2O_4] = 0 \text{ M}$$

Thus

$$Q_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0}{0.10^2} = 0$$

(b) 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.

Exercise 7.3.2

For the reaction

$$2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)$$

the equilibrium concentrations 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 available at the end of this section.

By its definition, the magnitude of an equilibrium constant explicitly reflects the composition of a reaction mixture at equilibrium, and it may be interpreted with regard to the extent of the forward reaction. A reaction exhibiting a large *K* will reach equilibrium when most of the reactant has been converted to product, whereas a small *K* indicates the reaction achieves equilibrium after very little reactant has been converted. It's important to keep in mind that the magnitude of *K* does *not* indicate how rapidly or slowly equilibrium will be reached. Some equilibria are established so quickly as to be nearly instantaneous, and others so slowly that no perceptible change is observed over the course of days, years, or longer.

The equilibrium constant for a reaction can be used to predict the behavior of mixtures containing its reactants and/or products. As demonstrated by the sulfur dioxide oxidation process described above, a chemical reaction will proceed in whatever direction is necessary to achieve equilibrium. Comparing *Q* to *K* for an equilibrium system of interest allows prediction of what reaction (forward or reverse), if any, will occur.

To further illustrate this important point, consider the reversible reaction shown below:

$$\mathrm{CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g)} \quad K_c = 0.640 \quad T = 800^\circ C$$

The bar charts in Figure 7.3.2 represent changes in reactant and product concentrations for three different reaction mixtures. The reaction quotients for mixtures 1 and 3 are initially lesser than the reaction's equilibrium constant, so each of these mixtures will experience a net forward reaction to achieve equilibrium. The reaction quotient for mixture 2 is initially greater than the equilibrium constant, so this mixture will proceed in the reverse direction until equilibrium is established.

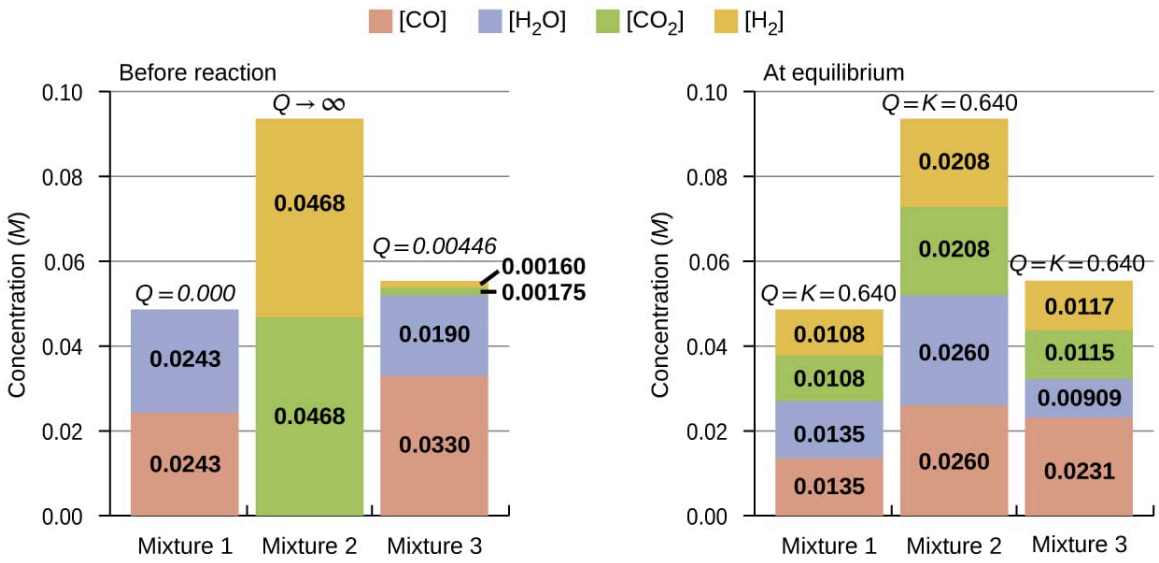


Figure 7.3.2: Compositions of three mixtures before ($Q_c \neq K_c$) and after ($Q_c = K_c$) equilibrium is established for the reaction

Example 7.3.3: Predicting the Direction of Reaction

Given here are the starting concentrations of reactants and products for three experiments involving this reaction:

$$\mathrm{CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g)} \quad K_c = 0.64$$

Determine in which direction the reaction proceeds as it goes to equilibrium in each of the three experiments shown.

Reactants/Products	Experiment 1	Experiment 2	Experiment 3
$[CO]_i$	0.020 *M*	0.011 *M*	0.0094 *M*
$[H_2O]_i$	0.020 *M*	0.0011 *M*	0.0025 *M*

Reactants/Products	Experiment 1	Experiment 2	Experiment 3
$[CO_2]_i$	0.0040 *M*	0.037 *M*	0.0015 *M*
$[H_2]_i$	0.0040 *M*	0.046 *M*	0.0076 *M*

Solution

Experiment 1:

$$Q_c = \frac{[CO_2]\,[H_2]}{[CO]\,[H_2O]} = \frac{(0.0040)(0.0040)}{(0.020)(0.020)} = 0.040$$

$Q_c < K_c$ (0.040 < 0.64)

The reaction will proceed in the forward direction.

Experiment 2:

$$Q_c = \frac{[CO_2]\,[H_2]}{[CO]\,[H_2O]} = \frac{(0.037)(0.046)}{(0.011)(0.0011)} = 1.4 \times 10^2$$

$Q_c > K_c$ (140 > 0.64)

The reaction will proceed in the reverse direction.

Experiment 3:

$$Q_c = \frac{[CO_2]\,[H_2]}{[CO]\,[H_2O]} = \frac{(0.0015)(0.0076)}{(0.0094)(0.0025)} = 0.48$$

$Q_c < K_c$ (0.48 < 0.64)

The reaction will proceed in the forward direction.

Exercise 7.3.3

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 available at the end of this section.

Homogeneous Equilibria

A homogeneous equilibrium is one in which all reactants and products (and any catalysts, if applicable) are present in the same phase. By this definition, homogeneous equilibria take place in *solutions*. These solutions are most commonly either liquid or gaseous phases, as shown by the examples below:

$$\mathrm{C_2H_2\,(aq) + 2\,Br_2\,(aq) \rightleftharpoons C_2H_2Br_4\,(aq)} \qquad K_c = \frac{[C_2H_2Br_4]}{[C_2H_2]\,[Br_2]^2}$$

$$\mathrm{I_2\,(aq) + I^-\,(aq) \rightleftharpoons I_3{}^-\,(aq)} \qquad K_c = \frac{[I_3-}{[I_2]\,[I^-]}$$

$$\mathrm{HF\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + F^-\,(aq)} \qquad K_c = \frac{[H_3O^+]\,[F^-]}{[HF]}$$

$$\mathrm{NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4{}^+\,(aq) + OH^-\,(aq)} \qquad K_c = \frac{[NH_4^+]\,[OH^-]}{[NH_3]}$$

These examples all involve aqueous solutions, those in which water functions as the solvent. In the last two examples, water also functions as a reactant, but its concentration is *not* included in the reaction quotient. The reason for this omission is related to the more rigorous form of the *Q* (or *K*) expression mentioned previously in this chapter, in which *relative concentrations for liquids and solids are equal to 1 and needn't be included*. Consequently, reaction quotients include concentration or pressure terms only for gaseous and solute species.

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 $K_a = K_{eq}$.

ıe equilibria below all involve gas-phase solutions:

$$\mathrm{C_2H_6\,(g) \rightleftharpoons C_2H_4\,(g) + H_2\,(g)} \qquad K_c = \frac{[C_2H_4]\,[H_2]}{[C_2H_6]}$$

$$\mathrm{3\,O_2\,(g) \rightleftharpoons 2\,O_3\,(g)} \qquad K_c = \frac{[O_3]^2}{[O_2]^3}$$

$$\mathrm{N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)} \qquad K_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$$

$$\mathrm{C_3H_8\,(g) + 5\,O_2\,(g) \rightleftharpoons 3\,CO_2\,(g) + 4\,H_2O\,(g)} \qquad K_c = \frac{[CO_2]^3\,[H_2O]^4}{[C_3H_8]\,[O_2]^5}$$

For gas-phase solutions, the equilibrium constant may be expressed in terms of either the molar concentrations (K_c) or partial pressures (K_p) of the reactants and products. A relation between these two *K* values may be simply derived from the ideal gas equation and the definition of molarity:

$$\begin{aligned} PV &= nRT \\ P &= \left(\frac{n}{V}\right) RT \\ &= MRT \end{aligned}$$

where P is partial pressure, V is volume, n is molar amount, R is the gas constant, T is temperature, and M is molar concentration.

For the gas-phase reaction

$$aA + bB \rightleftharpoons cC + dD$$

$$\begin{aligned} K_P &= \frac{(P_C)^c\,(P_D)^d}{(P_A)^a\,(P_B)^b} \\ &= \frac{([C]\times RT)^c([D]\times RT)^d}{([A]\times RT)^a([B]\times RT)^b} \\ &= \frac{[C]^c[D]^d}{[A]^a[B]^b}\times\frac{(RT)^{c+d}}{(RT)^{a+b}} \\ &= K_c(RT)^{(c+d)-(a+b)} \\ &= K_c(RT)^{\Delta n} \end{aligned}$$

And so, the relationship between K_c and K_P is

$$K_P = K_c(RT)^{\Delta n}$$

where Δn is the difference in the molar amounts of product and reactant gases, in this case:

$$\Delta n = (c+d)-(a+b)$$

Example 7.3.4: Calculation of K_P

Write the equations relating K_c to K_P for each of the following reactions:

a. $\mathrm{C_2H_6\,(g) \rightleftharpoons C_2H_4\,(g) + H_2\,(g)}$
b. $\mathrm{CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g)}$
c. $\mathrm{N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)}$
d. K_c is equal to 0.28 for the following reaction at 900 °C:

$$\mathrm{CS_2\,(g) + 4\,H_2\,(g) \rightleftharpoons CH_4\,(g) + 2\,H_2S\,(g)}$$

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. $$K_P = K_c(RT)^{\Delta n} = (0.28)[(0.0821)(1173)]^{-2} = 3.0\times10^{-5}$$

Exercise 7.3.4

Write the equations relating K_c to K_P for each of the following reactions:

a. $\mathrm{2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g)}$
b. $\mathrm{N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)}$
c. $\mathrm{C_3H_8\,(g) + 5\,O_2\,(g) \rightleftharpoons 3\,CO_2\,(g) + 4\,H_2O\,(g)}$
d. At 227 °C, the following reaction has K_c = 0.0952:

$$\mathrm{CH_3OH\,(g) \rightleftharpoons CO\,(g) + 2\,H_2\,(g)}$$

What would be the value of K_P at this temperature?

Answer available at the end of this section.

Heterogeneous Equilibria

A heterogeneous equilibrium involves reactants and products in two or more different phases, as illustrated by the following examples:

$$\mathrm{PbCl_2\,(s) \rightleftharpoons Pb^{2+}\,(aq) + 2\,Cl^-\,(aq)} \qquad K_c = [\blacksquare]\,[\mathrm{Cl^-}]^2$$

$$\mathrm{CaO\,(s) + CO_2\,(g) \rightleftharpoons CaCO_3\,(s)} \qquad K_c = \frac{1}{[\mathrm{CO_2}]}$$

$$\mathrm{C\,(s) + 2\,S\,(g) \rightleftharpoons CS_2\,(g)} \qquad K_c = \frac{[CS_2]}{[\mathrm{S}^2}$$

$$\mathrm{Br_2\,(l) \rightleftharpoons Br_2\,(g)} \qquad K_c = [\mathrm{Br_2\,(g)}]$$

Again, note that concentration terms are only included for gaseous and solute species, as discussed previously.

Two of the above examples include terms for gaseous species only in their equilibrium constants, and so K_p expressions may also be written:

$$\mathrm{CaO\,(s) + CO_2\,(g) \rightleftharpoons CaCO_3\,(s)} \qquad K_P = \frac{1}{P_{\mathrm{CO_2}}}$$

$$\mathrm{C\,(s) + 2\,S\,(g) \rightleftharpoons CS_2\,(g)} \qquad K_P = \frac{P_{\mathrm{CS_2}}}{(P_{\mathrm{S}})^2}$$

Coupled Equilibria

The equilibrium systems discussed so far have all been relatively simple, involving just single reversible reactions. Many systems, however, involve two or more *coupled* equilibrium reactions, those which have in common one or more reactant or product species. Since the law of mass action allows for a straightforward derivation of equilibrium constant expressions from balanced chemical equations, the K value for a system involving coupled equilibria can be related to the K values of the individual reactions. Three basic manipulations are involved in this approach, as described below.

1. Changing the direction of a chemical equation essentially swaps the identities of “reactants” and “products,” and so the equilibrium constant for the reversed equation is simply the reciprocal of that for the forward equation.

$$A \rightleftharpoons B \quad K_c = \tfrac{[B]}{[A]}$$

$$B \rightleftharpoons A \quad K_{c'} = \tfrac{[A]}{[B]}$$

$$K_{c'} = \frac{1}{K_c}$$

2. Changing the stoichiometric coefficients in an equation by some factor *x* results in an exponential change in the equilibrium constant by that same factor:

$$A \rightleftharpoons B \qquad K_c = \tfrac{[B]}{[A]}$$

$$xA \rightleftharpoons xB \quad K_c = \tfrac{[B]^x}{[A]^x}$$

$$K_{c'} = {K_c}^x$$

3. Adding two or more equilibrium equations together yields an overall equation whose equilibrium constant is the mathematical product of the individual reaction’s K values:

$$A \rightleftharpoons B \quad K_{c1} = \frac{[B]}{[A]}$$

$$B \rightleftharpoons C \quad K_{c2} = \frac{[C]}{[B]}$$

The net reaction for these coupled equilibria is obtained by summing the two equilibrium equations and canceling any redundancies:

$$A + B \rightleftharpoons B + C$$
$$A + B \rightleftharpoons B + C$$
$$A \rightleftharpoons C$$

$$K_{c'} = \frac{[C]}{[A]}$$

Comparing the equilibrium constant for the net reaction to those for the two coupled equilibrium reactions reveals the following relationship:

$$K_{c1}K_{c2} = \frac{[B]}{[A]} \times \frac{[C]}{[B]} = \frac{\cancel{[B]}\,[C]}{[A]\,\cancel{[B]}} = \frac{[C]}{[A]} = K_{c'}$$

$$K_{c'} = K_{c1}K_{c2}$$

Example 7.3.5 demonstrates the use of this strategy in describing coupled equilibrium processes.

Example 7.3.5: Equilibrium Constants for Coupled Reactions

A mixture containing nitrogen, hydrogen, and iodine established the following equilibrium at 400 °C:

$$2\,\mathrm{NH_3\,(g)} + 3\,\mathrm{I_2\,(g)} \rightleftharpoons \mathrm{N_2\,(g)} + 6\,\mathrm{HI\,(g)}$$

Use the information below to calculate Kc for this reaction.

$$\mathrm{N_2\,(g)} + 3\,\mathrm{H_2\,(g)} \rightleftharpoons 2\,\mathrm{NH_3\,(g)} K_{c1} = 0.50 \text{ at } 400^\circ C$$
$$\mathrm{H_2\,(g)} + \mathrm{I_2\,(g)} \rightleftharpoons 2\,\mathrm{HI\,(g)} K_{c2} = 50 \text{ at } 400^\circ C$$

Solution

The equilibrium equation of interest and its K value may be derived from the equations for the two coupled reactions as follows.

Reverse the first coupled reaction equation:

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g) \quad K_{c1}{}' = \frac{1}{K_{c1}} = \frac{1}{0.50} = 2.0$$

Multiply the second coupled reaction by 3:

$$3H_2(g) + 3I_2(g) \rightleftharpoons 6HI(g) \quad K_{c2}{}' = K_{c2}^3 = 50^3 = 1.2 \times 10^5$$

Finally, add the two revised equations:

$$2\,\mathrm{NH_3\,(g)} + 3\,\mathrm{H_2\,(g)} + 3\,\mathrm{I_2\,(g)} \rightleftharpoons \mathrm{N_2\,(g)} + 3\,\mathrm{H_2\,(g)} + 6\,\mathrm{HI\,(g)}$$
$$2\,\mathrm{NH_3\,(g)} + 3\,\mathrm{I_2\,(g)} \rightleftharpoons \mathrm{N_2\,(g)} + 6\,\mathrm{HI\,(g)}$$

$$K_c = K_{c1}, K_{c2}, = (2.0)\left(1.2 \times 10^5\right) = 2.5 \times 10^5$$

Exercise 7.3.5

Use the provided information to calculate Kc for the following reaction at 550 °C:

$$\mathrm{H_2\,(g) + CO_2\,(g) \rightleftharpoons CO\,(g) + H_2O\,(g)} \qquad K_c = ?$$

$$\mathrm{CoO\,(s) + CO\,(g) \rightleftharpoons Co(s)^{+}\ CO_2\,(g)} \qquad K_{c1} = 490$$

$$\mathrm{CoO\,(s) + H_2\,(g) \rightleftharpoons Co(s)^{+}\ H_2O\,(g)} \qquad K_{c1} = 67$$

Answer available at the end of this section.

Answers

Exercise 7.3.1

a. $$Q_c = \frac{[\mathrm{SO_3}]^2}{[\mathrm{SO_2}]^2\,[\mathrm{O_2}]}$$

b. $$Q_c = \frac{[\mathrm{C_2H_4}]^2}{[\mathrm{C_4H_8}]}$$

c. $$Q_c = \frac{[\mathrm{CO_2}]^8\,[\mathrm{H_2O}]^{10}}{[\mathrm{C_4H_{10}}]^2\,[\mathrm{O_2}]^{13}}$$

Exercise 7.3.2

K_c = 4.3

Exercise 7.3.3

(a) Q_c = 6.45 \times 10^{3} DELMAR, forward. (b) Q_c = 0.23, reverse. (c) Q_c = 0, forward.

Exercise 7.3.4

(a) $K_P = K_c\,(RT)^{-1}$; (b) $K_P = K_c\,(RT)$; (c) $K_P = K_c\,(RT)$; (d) 160 or 1.6 \times 10^{2} DELMAR

Exercise 7.3.5

K_c = 0.14

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7.4: Shifting Equilibria - Le Chatelier's Principle

Learning Objectives

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

- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Chatelier's principle

A system at equilibrium is in a state of dynamic balance, with forward and reverse reactions taking place at equal rates. If an equilibrium system is subjected to a change in conditions that affects these reaction rates differently (a *stress*), then the rates are no longer equal and the system is not at equilibrium. The system will subsequently experience a net reaction in the direction of greater rate (a *shift*) that will re-establish the equilibrium. This phenomenon is summarized by **Le Chatelier's principle**

Definition: Le Chatelier's Principle

if an equilibrium system is stressed, the system will experience a shift in response to the stress that re-establishes equilibrium.

Reaction rates are affected primarily by concentrations, as described by the reaction's rate law, and temperature, as described by the Arrhenius equation. Consequently, changes in concentration and temperature are the two stresses that can shift an equilibrium.

Effect of a Change in Concentration

If an equilibrium system is subjected to a change in the concentration of a reactant or product species, the rate of either the forward or the reverse reaction will change. As an example, consider the equilibrium reaction

$$\mathrm{H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)} \quad K_c = 50.0 \text{ at } 400^\circ C$$

The rate laws for the forward and reverse reactions are

$$\begin{aligned} &\text{forward} \quad \mathrm{H_2\,(g) + I_2\,(g)} \rightarrow \mathrm{2\,HI\,(g)} && \text{rate}_f = k_f[\mathrm{H_2}]^m[\mathrm{I_2}^n] \\ &\text{reverse} \quad \mathrm{2\,HI\,(g)} \rightarrow \mathrm{H_2\,(g) + I_2\,(g)} && \text{rate}_r = k_r[\mathrm{HI}]^x \end{aligned}$$

When this system is at equilibrium, the forward and reverse reaction rates are equal.

$$\text{rate}_f = \text{rate}_r$$

If the system is stressed by adding reactant, either $\mathrm{H_2}$ or $\mathrm{I_2}$, the resulting increase in concentration causes the rate of the forward reaction to increase, exceeding that of the reverse reaction:

$$\text{rate}_f > \text{rate}_r$$

The system will experience a temporary net reaction in the forward direction to re-establish equilibrium (the equilibrium will shift right). This same shift will result if some product HI is removed from the system, which decreases the rate of the reverse reaction, again resulting in the same imbalance in rates.

The same logic can be used to explain the left shift that results from either removing reactant or adding product to an equilibrium system. These stresses both result in an increased rate for the reverse reaction

$$\text{rate}_f < \text{rate}_r$$

and a temporary net reaction in the reverse direction to re-establish equilibrium.

As an alternative to this kinetic interpretation, the effect of changes in concentration on equilibria can be rationalized in terms of reaction quotients. When the system is at equilibrium,

$$Q_c = \frac{[\mathrm{HI}]^2}{[\mathrm{H_2}]\,[\mathrm{I_2}]} = K_c$$

If reactant is added (increasing the denominator of the reaction quotient) or product is removed (decreasing the numerator), then $Q_c < K_c$ and the equilibrium will shift right. Note that the three different ways of inducing this stress result in three different changes in the composition of the equilibrium mixture. If H_2 is added, the right shift will consume I_2 and produce HI as equilibrium is re-established, yielding a mixture with a greater concentrations of H_2 and HI and a lesser concentration of I_2 than was present before. If I_2 is added, the new equilibrium mixture will have greater concentrations of I_2 and HI and a lesser concentration of H_2. Finally, if HI is removed, the concentrations of all three species will be lower when equilibrium is reestablished. Despite these differences in composition, *the value of the equilibrium constant will be the same after the stress as it was before* (per the law of mass action). The same logic may be applied for stresses involving removing reactants or adding product, in which case $Q_c > K_c$ and the equilibrium will shift left.For gas-phase equilibria such as this one, some additional perspectives on changing the concentrations of reactants and products are worthy of mention. The partial pressure *P* of an ideal gas is proportional to its molar concentration M,

$$M = \frac{n}{V} = \frac{P}{RT}$$

and so changes in the partial pressures of any reactant or product are essentially changes in concentrations and thus yield the same effects on equilibria. Aside from adding or removing reactant or product, the pressures (concentrations) of species in a gas-phase equilibrium can also be changed by *changing the volume occupied by the system*. Since

all species of a gas-phase equilibrium occupy the same volume, a given change in volume will cause the same change in concentration for both reactants and products. In order to discern what shift, if any, this type of stress will induce the stoichiometry of the reaction must be considered.

At equilibrium, the reaction

$$\mathrm{H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)}$$

is described by the reaction quotient

$$Q_P = \frac{(P_{\mathrm{HI}})^2}{P_{\mathrm{H_2}} P_{\mathrm{I_2}}} = K_p$$

If the volume occupied by an equilibrium mixture of these species is decreased by a factor of 3, the partial pressures of all three species will be increased by a factor of 3:

$$\begin{aligned} Q_p{}' &= \frac{(3P_{HI})^2}{3P_{H_2} 3P_{I_2}} = \frac{9P_{H^2}}{9P_{H_2}P_{I_2}} = \frac{P_{HI^2}}{P_{H_2}P_{I_2}} \\ &= Q_P = K_P \end{aligned}$$

And so, changing the volume of this gas-phase equilibrium mixture does not result in a shift of the equilibrium.

A similar treatment of a different system,

$$\mathrm{2\,NO_2\,(g) \rightleftharpoons 2\,NO\,(g) + O_2\,(g)}$$

however, yields a different result:

$$Q_P = \frac{(P_{NO})^2}{(P_{O_2})}(P_{NO_2})^2$$

$$Q'_P = \frac{(3P_{\mathrm{NO}})^2(3P_{\mathrm{O_2}})}{3(P_{\mathrm{NO_2}})^2} = \frac{9(P_{\mathrm{NO}})^2(3P_{\mathrm{O_2}})}{9(P_{\mathrm{NO_2}})^2} = \frac{27(P_{\mathrm{NO}})^2 P_{\mathrm{O_2}}}{9(P_{\mathrm{NO_2}})^2}$$

$$= 3Q_P > K_P$$

In this case, the change in volume results in a reaction quotient greater than the equilibrium constant, and so the equilibrium will shift left.

These results illustrate the relationship between the stoichiometry of a gas-phase equilibrium and the effect of a volume-induced pressure (concentration) change. If the total molar amounts of reactants and products are equal, as in the first example, a change in volume does not shift the equilibrium. If the molar amounts of reactants and products are different, a change in volume will shift the equilibrium in a direction that better "accommodates" the volume change. In the second example, two moles of reactant (NO_2) yield three moles of product ($2NO + O_2$), and so decreasing the system volume causes the equilibrium to shift left since the reverse reaction produces less gas (2 mol) than the forward reaction (3 mol). Conversely, increasing the volume of this equilibrium system would result in a shift towards products.

Link to Learning

Check out this link to see a dramatic visual demonstration of how equilibrium changes with pressure changes.

Chemistry in Everyday Life: Equilibrium and Soft Drinks

The connection between chemistry and carbonated soft drinks goes back to 1767, when Joseph Priestley (1733–1804) developed a method of infusing water with carbon dioxide to make carbonated water. Priestley's approach involved production of carbon dioxide by reacting oil of vitriol (sulfuric acid) with chalk (calcium carbonate).

The carbon dioxide was then dissolved in water, reacting to produce hydrogen carbonate, a weak acid that subsequently ionized to yield bicarbonate and hydrogen ions:

$$\begin{aligned}
&\text{dissolution} && \mathrm{CO_2\,(g) \rightleftharpoons CO_2\,(aq)}\\
&\text{hydrolysis} && \mathrm{CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq)}\\
&\text{ionization} && \mathrm{H_2CO_3\,(aq) \rightleftharpoons HCO_3^-\,(aq) + H^+\,(aq)}
\end{aligned}$$

These same equilibrium reactions are the basis of today's soft-drink carbonation process. Beverages are exposed to a high pressure of gaseous carbon dioxide during the process to shift the first equilibrium above to

the right, resulting in desirably high concentrations of dissolved carbon dioxide and, per similar shifts in the other two equilibria, its hydrolysis and ionization products. A bottle or can is then nearly filled with the carbonated beverage, leaving a relatively small volume of air in the container above the beverage surface (the *headspace*) before it is sealed. The pressure of carbon dioxide in the container headspace is very low immediately after sealing, but it rises as the dissolution equilibrium is re-established by shifting to the left. Since the volume of the beverage is significantly greater than the volume of the headspace, only a relatively small amount of dissolved carbon dioxide is lost to the headspace.

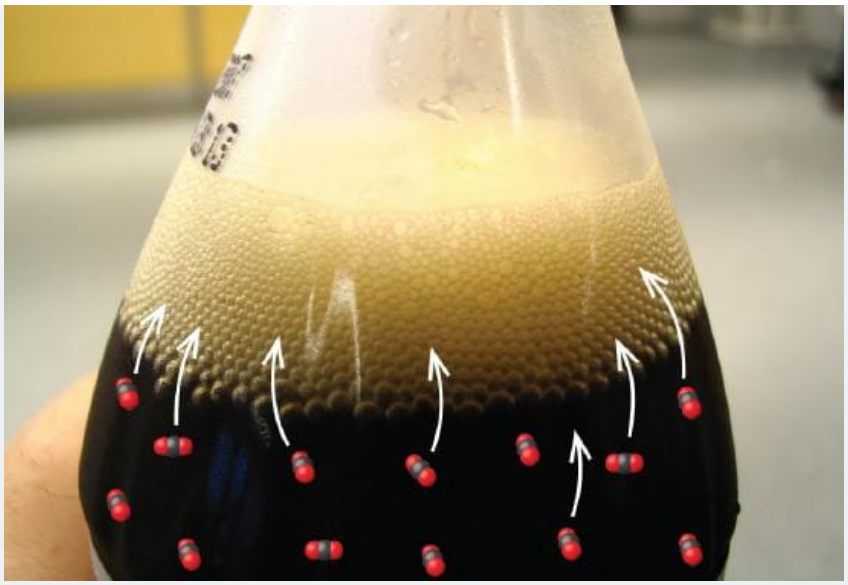


Figure 7.4.1: Opening a soft-drink bottle lowers the CO_2 pressure above the beverage, shifting the dissolution equilibrium and releasing dissolved CO_2 from the beverage. (credit: modification of work by “D Coetzee”/Flickr)

When a carbonated beverage container is opened, a hissing sound is heard as pressurized CO_2 escapes from the headspace. This causes the dissolution equilibrium to shift left, resulting in a decrease in the concentration of dissolved CO_2 and subsequent left-shifts of the hydrolysis and ionization equilibria. Fortunately for the consumer, the dissolution equilibrium is usually re-established slowly, and so the beverage may be enjoyed while its dissolved carbon dioxide concentration remains palatably high. Once the equilibria are re-established, the $CO_2(aq)$ concentration will be significantly lowered, and the beverage acquires a characteristic taste referred to as “flat.”

Effect of a Change in Temperature

Consistent with the law of mass action, an equilibrium stressed by a change in concentration will shift to re-establish equilibrium without any change in the value of the

equilibrium constant, K. When an equilibrium shifts in response to a temperature change, however, it is re-established with a different relative composition that exhibits a different value for the equilibrium constant.

To understand this phenomenon, consider the elementary reaction

$$A \rightleftharpoons B$$

Since this is an elementary reaction, the rates laws for the forward and reverse may be derived directly from the balanced equation’s stoichiometry:

$$\text{rate}_f = k_f[A]$$
$$\text{rate}_r = k_r[B]$$

When the system is at equilibrium,

$$\text{rate}_r = \text{rate}_f$$

Substituting the rate laws into this equality and rearranging gives

$$k_f[A] = k_r[B]$$
$$\frac{[B]}{[A]} = \frac{k_f}{k_r} = K_c$$

The equilibrium constant is seen to be a mathematical function of the rate constants for the forward and reverse reactions. Since the rate constants vary with temperature as

described by the Arrhenius equation, is stands to reason that the equilibrium constant will likewise vary with temperature (assuming the rate constants are affected to different extents by the temperature change). For more complex reactions involving multistep reaction mechanisms, a similar but more complex mathematical relation exists between the equilibrium constant and the rate constants of the steps in the mechanism. Regardless of how complex the reaction may be, the temperature-dependence of its equilibrium constant persists.

Predicting the shift an equilibrium will experience in response to a change in temperature is most conveniently accomplished by considering the enthalpy change of the reaction. For example, the decomposition of dinitrogen tetroxide is an endothermic (heat-consuming) process:

$$\mathrm{N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)} \quad \Delta H = +57.20\ \mathrm{kJ}$$

For purposes of applying Le Chatelier's principle, heat (q) may be viewed as a reactant:

$$\mathrm{heat + N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)}$$

Raising the temperature of the system is akin to increasing the amount of a reactant, and so the equilibrium will shift to the right. Lowering the system temperature will likewise cause the equilibrium to shift left. For exothermic processes, heat is viewed as a product of the reaction and so the opposite temperature dependence is observed.

Effect of a Catalyst

The kinetics chapter of this text identifies a *catalyst* as a substance that enables a reaction to proceed via a different mechanism with an accelerated rate. The catalyzed reaction mechanism involves a lower energy transition state than the uncatalyzed reaction, resulting in a lower activation energy, E_a, and a correspondingly greater rate constant.

To discern the effect of catalysis on an equilibrium system, consider the reaction diagram for a simple one-step (elementary) reaction shown in Figure 7.4.2. The lowered transition state energy of the catalyzed reaction results in lowered activation energies for both the forward and the reverse reactions. Consequently, both forward and reverse reactions are accelerated, and equilibrium is achieved more quickly *but without a change in the equilibrium constant*.

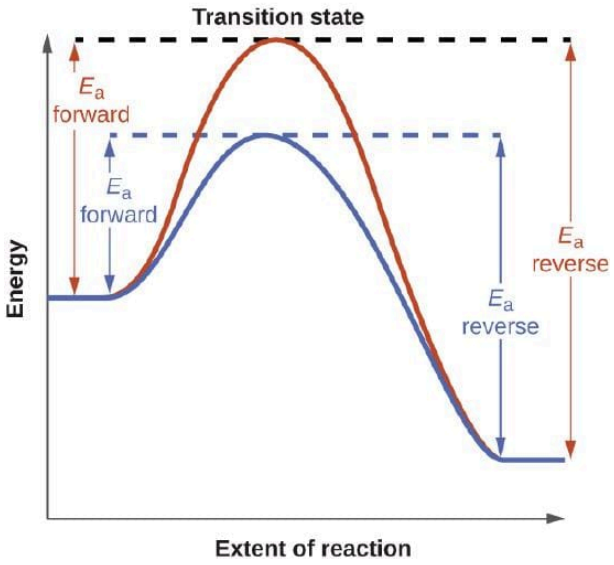


Figure 7.4.2 : Reaction diagrams for an elementary process in the absence (red) and presence (blue) of a catalyst. The presence of catalyst lowers the activation energies of both the forward and reverse reactions but does not affect the value of the equilibrium constant.

An interesting case study highlighting these equilibrium concepts is the industrial production of ammonia, NH_3. This substance is among the "top 10" industrial chemicals with regard to production, with roughly two billion pounds produced annually in the US. Ammonia is used as a chemical feedstock to synthesize a wide range of commercially useful compounds, including fertilizers,

plastics, dyes, and explosives.

Most industrial production of ammonia uses the Haber-Bosch process based on the following equilibrium reaction:

$$\mathrm{N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)} \quad \Delta H = -92.2\ \mathrm{kJ}$$

The traits of this reaction present challenges to its use in an efficient industrial process. The equilibrium constant is relatively small (Kp on the order of 10^{-5} at 25 °C), meaning very little ammonia is present in an equilibrium mixture. Also, the rate of this reaction is relatively slow at low temperatures. To raise the yield of ammonia, the industrial process is designed to operate under conditions favoring product formation:

- High pressures (concentrations) of reactants are used, ~150–250 atm, to shift the equilibrium right, favoring product formation.
- Ammonia is continually removed (collected) from the equilibrium mixture during the process, lowering its concentration and also shifting the equilibrium right.
- Although low temperatures favor product formation for this exothermic process, the reaction rate at low temperatures is inefficiently slow. A catalyst is used to accelerate the reaction to reasonable rates at relatively moderate temperatures (400–500 °C).

A diagram illustrating a typical industrial setup for production of ammonia via the Haber-Bosch process is shown in Figure 7.4.3.

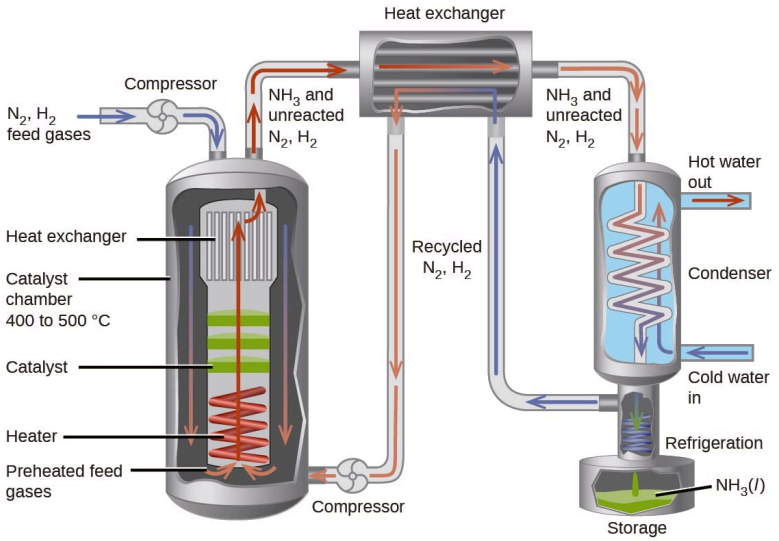


Figure 7.4.3: The figure shows a typical industrial setup for the commercial production of ammonia by the Haber-Bosch process. The process operates under conditions that stress the chemical equilibrium to favor product formation.

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7.5: Equilibrium Calculations

Learning Objectives

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

- Identify the changes in concentration or pressure that occur for chemical species in equilibrium systems
- Calculate equilibrium concentrations or pressures and equilibrium constants, using various algebraic approaches

Having covered the essential concepts of chemical equilibria in the preceding sections of this chapter, this final section will demonstrate the more practical aspect of using these concepts and appropriate mathematical strategies to perform various equilibrium calculations. These types of computations are essential to many areas of science and technology—for example, in the formulation and dosing of pharmaceutical products. After a drug is ingested or injected, it is typically involved in several chemical equilibria that affect its ultimate concentration in the body system of interest. Knowledge of the quantitative aspects of these equilibria is required to compute a dosage amount that will solicit the desired therapeutic effect.

Many of the useful equilibrium calculations that will be demonstrated here require terms representing changes in reactant and product concentrations. These terms are derived from the stoichiometry of the reaction, as illustrated by decomposition of ammonia:

$$2\,\mathrm{NH_3\,(g)} \rightleftharpoons \mathrm{N_2\,(g)} + 3\,\mathrm{H_2\,(g)}$$

As shown earlier in this chapter, this equilibrium may be established within a sealed container that initially contains either NH_3 only, or a mixture of any two of the three chemical species involved in the equilibrium. Regardless of its initial composition, a reaction mixture will show the same relationships between changes in the concentrations of the three species involved, as dictated by the reaction stoichiometry (see also the related content on expressing reaction rates in the chapter on kinetics). For example, if the nitrogen concentration increases by an amount *x*:

$$\Delta\,[N_2] = +x$$

the corresponding changes in the other species concentrations are

$$\Delta\,[\mathrm{H_2}] = \Delta\,[\mathrm{N_2}]\left(\frac{3\text{ mol }\mathrm{H_2}}{1\text{ mol }\mathrm{N_2}}\right) = +3x$$

$$\Delta\,[\mathrm{NH_3}] = -\Delta\,[\mathrm{N_2}]\left(\frac{2\text{ mol }\mathrm{NH_3}}{1\text{ mol }\mathrm{N_2}}\right) = -2x$$

where the negative sign indicates a decrease in concentration.

Example 7.5.1: Determining Relative Changes in Concentration

Derive the missing terms representing concentration changes for each of the following reactions.

a. $$\underset{x}{\mathrm{C_2H_2\,(g)}} + 2\,\underset{?}{\mathrm{Br_2\,(g)}} \rightleftharpoons \underset{?}{\mathrm{C_2H_2Br_4\,(g)}}$$

b. $$\underset{?}{\mathrm{I_2\,(aq)}} + \underset{?}{\mathrm{I^-\,(aq)}} \rightleftharpoons \underset{x}{\mathrm{I_3{}^-\,(aq)}}$$

c. $$\underset{x}{\mathrm{C_3H_8\,(g)}} + 5\,\underset{?}{\mathrm{O_2\,(g)}} \rightleftharpoons 3\,\underset{?}{\mathrm{CO_2\,(g)}} + 4\,\underset{?}{\mathrm{H_2O\,(g)}}$$

Solution

a. $$\underset{x}{\mathrm{C_2H_2\,(g)}} + 2\,\underset{2x}{\mathrm{Br_2\,(g)}} \rightleftharpoons \underset{-x}{\mathrm{C_2H_2Br_4\,(g)}}$$

b. $$\underset{-x}{\mathrm{I_2\,(aq)}} + \underset{-x}{\mathrm{I^-\,(aq)}} \rightleftharpoons \underset{x}{\mathrm{I_3{}^-\,(aq)}}$$

c. $\underset{x}{\mathrm{C_3H_8\,(g)}} + 5\,\underset{5x}{\mathrm{O_2\,(g)}} \rightleftharpoons 3\,\underset{-3x}{\mathrm{CO_2\,(g)}} + 4\,\underset{-4x}{\mathrm{H_2O\,(g)}}$

Exercise 7.5.1

Complete the changes in concentrations for each of the following reactions:

a. $2\,\underset{?}{\mathrm{SO_2\,(g)}} + \underset{x}{\mathrm{O_2\,(g)}} \rightleftharpoons 2\,\underset{?}{\mathrm{SO_3\,(g)}}$

b. $\underset{?}{\mathrm{C_4H_8\,(g)}} \rightleftharpoons 2\,\underset{-2x}{\mathrm{C_2H_4\,(g)}}$

c. $4\,\underset{?}{\mathrm{NH_3\,(g)}} + 7\,\underset{x}{\mathrm{O_2\,(g)}} \rightleftharpoons 4\,\underset{?}{\mathrm{NO_2\,(g)}} + 6\,\underset{?}{\mathrm{H_2O\,(g)}}$

Answer available at the end of this section.

Calculation of an Equilibrium Constant

The equilibrium constant for a reaction is calculated from the equilibrium concentrations (or pressures) of its reactants and products. If these concentrations are known, the calculation simply involves their substitution into the K expression, as was illustrated by Example 7.5.1. A slightly more challenging example is provided next, in which the reaction stoichiometry is used to derive equilibrium concentrations from the information provided. The basic strategy of this computation is helpful for many types of equilibrium computations and relies on the use of terms for the reactant and product concentrations *initially* present, for how they *change* as the reaction proceeds, and for what they are when the system reaches *equilibrium*. The acronym ICE is commonly used to refer to this mathematical approach, and the concentrations terms are usually gathered in a tabular format called an ICE table.

Example 7.5.2: Calculation of an Equilibrium Constant

Iodine molecules react reversibly with iodide ions to produce triiodide ions.

$$\mathrm{I_2\,(aq) + I^-\,(aq)} \rightleftharpoons \mathrm{I_3^-\,(aq)}$$

If a solution with the concentrations of $\mathrm{I_2}$ and $\mathrm{I^-}$ both equal to $1.000 \times 10^{-3}\ \mathrm{M}$ before reaction gives an equilibrium concentration of $\mathrm{I_2}$ of $6.61 \times 10^{-4}\ \mathrm{M}$, what is the equilibrium constant for the reaction?

Solution

To calculate the equilibrium constants, equilibrium concentrations are needed for all the reactants and products:

$$K_C = \frac{[\mathrm{I_3^-}]}{[\mathrm{I_2}]\,[\mathrm{I^-}]}$$

Provided are the initial concentrations of the reactants and the equilibrium concentration of the product. Use this information to derive terms for the equilibrium concentrations of the reactants, presenting all the information in an ICE table.

	I_2 + I^- ⇌ 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

At equilibrium the concentration of I_2 is 6.61×10^{-4} M so that

$$\begin{aligned} 1.000 \times 10^{-3} - x &= 6.61 \times 10^{-4} \\ x &= 1.000 \times 10^{-3} - 6.61 \times 10^{-4} \\ &= 3.39 \times 10^{-4} M \end{aligned}$$

The ICE table may now be updated with numerical values for all its concentrations:

	I_2 + I^- ⇌ I_3^-		
Initial concentration (*M*)	1.000×10^{-3}	1.000×10^{-3}	0
Change (*M*)	-3.39×10^{-4}	-3.39×10^{-4}	$+3.39 \times 10^{-4}$
Equilibrium concentration (*M*)	6.61×10^{-4}	6.61×10^{-4}	3.39×10^{-4}

Finally, substitute the equilibrium concentrations into the *K* expression and solve:

$$\begin{aligned} K_c &= \frac{[I_3^-]}{[I_2]\,[I^-]} \\ &= \frac{3.39 \times 10^{-4} M}{\left(6.61 \times 10^{-4} M\right)\left(6.61 \times 10^{-4} M\right)} = 776 \end{aligned}$$

Exercise 7.5.2

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 a solute in this reaction.)

Answer available at the end of this section.

Calculation of a Missing Equilibrium Concentration

When the equilibrium constant and all but one equilibrium concentration are provided, the other equilibrium concentration(s) may be calculated. A computation of this sort is illustrated in the next example exercise.

Example 7.5.3: 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 K_c for the reaction,

$$\mathrm{N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g)}$$

is 4.1×10^{-4}. Calculate the equilibrium concentration of NO(*g*) in air at 1 atm pressure and 2000 °C. The equilibrium concentrations of N_2 and O_2 at this pressure and temperature are 0.036 M and 0.0089 M, respectively.

Solution

Substitute the provided quantities into the equilibrium constant expression and solve for [NO]:

$$\begin{aligned} K_c &= \frac{[NO]^2}{[N_2]\,[O_2]} \\ [NO]^2 &= K_c\,[N_2]\,[O_2] \\ [NO] &= \sqrt{K_c\,[N_2]\,[O_2]} \\ &= \sqrt{\left(4.1 \times 10^{-4}\right)(0.036)(0.0089)} \\ &= \sqrt{1.31 \times 10^{-7}} \\ &= 3.6 \times 10^{-4} \end{aligned}$$

Thus [NO] is $3.6 \times 10^{-4}\ \mathrm{mol/L}$ at equilibrium under these conditions.

To confirm this result, it may be used along with the provided equilibrium concentrations to calculate a value for *K*:

$$\begin{aligned} K_c &= \frac{[NO]^2}{[N_2]\,[O_2]} \\ &= \frac{\left(3.6 \times 10^{-4}\right)^2}{(0.036)(0.0089)} \\ &= 4.0 \times 10^{-4} \end{aligned}$$

This result is consistent with the provided value for *K* within nominal uncertainty, differing by just 1 in the least significant digit's place.

Exercise 7.5.3

The equilibrium constant K_c for the reaction of nitrogen and hydrogen to produce ammonia at a certain temperature is 6.00×10^{-2}. Calculate the equilibrium concentration of ammonia if the equilibrium concentrations of nitrogen and hydrogen are 4.26 *M* and 2.09 *M*, respectively.

Answer available at the end of this section.

Calculation of Equilibrium Concentrations from Initial Concentrations

Perhaps the most challenging type of equilibrium calculation can be one in which equilibrium concentrations are derived from initial concentrations and an equilibrium constant. For these calculations, a four-step approach is typically useful:

1. Identify the direction in which the reaction will proceed to reach equilibrium.
2. Develop an ICE table.
3. Calculate the concentration changes and, subsequently, the equilibrium concentrations.
4. Confirm the calculated equilibrium concentrations.

The last two example exercises of this chapter demonstrate the application of this strategy.

Example 7.5.4: Calculation of Equilibrium Concentrations

Under certain conditions, the equilibrium constant K_c for the decomposition of $\mathrm{PCl_5\,(g)}$ into $\mathrm{PCl_3\,(g)}$ and $\mathrm{Cl_2\,(g)}$ is 0.0211. What are the equilibrium concentrations of $\mathrm{PCl_5}$, $\mathrm{PCl_3}$, and $\mathrm{Cl_2}$ in a mixture that initially contained only $\mathrm{PCl_5}$ at a concentration of 1.00 *M*?

Solution

Use the stepwise process described earlier.

Step 1.

Determine the direction the reaction proceeds.

The balanced equation for the decomposition of $\mathrm{PCl_5}$ is

$$\mathrm{PCl_5\,(g)} \rightleftharpoons \mathrm{PCl_3\,(g)} + \mathrm{Cl_2\,(g)}$$

Because only the reactant is present initially Q_c = 0 and the reaction will proceed to the right.

Step 2:

Develop an ICE table.

	$\mathrm{PCl_5}$	$\rightleftharpoons$	$\mathrm{PCl_3}$	+	$\mathrm{Cl_2}$
Initial concentration (*M*)	1.00		0		0
Change (*M*)	$-x$		$+x$		$+x$
Equilibrium concentration (*M*)	$1.00 - x$		x		x

Step 3.

Solve for the change and the equilibrium concentrations.

Substituting the equilibrium concentrations into the equilibrium constant equation gives

$$K_c = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]} = 0.0211$$

$$= \frac{(x)(x)}{(1.00 - x)}$$

$$0.0211 = \frac{(x)(x)}{(1.00 - x)}$$

$$0.0211(1.00 - x)7 = x^2$$

$$x^2 + 0.0211x - 0.0211 = 0$$

Appendix 11.2 shows 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:

$$x = \frac{-0.0211 \pm \sqrt{(0.0211)^2 - 4(1)(-0.0211)}}{2(1)}$$

$$= \frac{-0.0211 \pm \sqrt{\left(4.45 \times 10^{-4}\right) + \left(8.44 \times 10^{-2}\right)}}{2}$$

$$= \frac{-0.0211 \pm 0.291}{2}$$

The two roots of the quadratic are, therefore,

$$x = \frac{-0.0211 + 0.291}{2} = 0.135$$

and

$$x = \frac{-0.0211 - 0.291}{2} = -0.156$$

For this scenario, only the positive root is physically meaningful (concentrations are either zero or positive), and so *x* = 0.135 *M*.

The equilibrium concentrations are

$$[PCl_5] = 1.00 - 0.135 = 0.87\ \text{M}$$

$$[PCl_3] = x = 0.135\ \text{M} =$$

$$[Cl_2] = x = 0.135\ \text{M}$$

Step 4.

Confirm the calculated equilibrium concentrations.

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).

Exercise 7.5.4A

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 for a mixture that is initially 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?

Answer available at the end of this section.

Exercise 7.5.4B

A 1.00-L flask is filled with 1.00 mole of H_2 and 2.00 moles of I_2. The value of the equilibrium constant for the reaction of hydrogen and iodine reacting to form hydrogen iodide is 50.5 under the given conditions. What are the equilibrium concentrations of H_2, I_2, and HI in moles/L?

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2\,HI\,(g)$$

Answer available at the end of this section.

Example 7.5.5: Calculation of Equilibrium Concentrations Using an Algebra-Simplifying Assumption

What are the concentrations at equilibrium of a 0.15 *M* solution of HCN?

$$HCN\,(aq) \rightleftharpoons H^+\,(aq) + CN^-\,(aq) \qquad K_c = 4.9 \times 10^{-10}$$

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*

Substitute the equilibrium concentration terms into the K_c expression

$$K_c = \frac{(x)(x)}{0.15 - x}$$

rearrange to the quadratic form and solve for *x*

$$x^2 + 4.9 \times 10^{-10} - 7.35 \times 10^{-11} = 0$$

$$x = 8.56 \times 10^{-6} M(3 \text{ sig. figs. }) = 8.6 \times 10^{-6} M(2 \text{ sig. figs. })$$

Thus $[H^+] = [CN^-] = x = 8.6 \times 10^{-6}$ M and $[HCN] = 0.15–x = 0.15$ M.

Note in this case that the change in concentration is significantly less than the initial concentration (a consequence of the small *K*), and so the initial concentration experiences a negligible change:

$$\text{if } x \ll 0.15M, \text{ then } (0.15 - x) \approx 0.15$$

This approximation allows for a more expedient mathematical approach to the calculation that avoids the need to solve for the roots of a quadratic equation:

$$\begin{aligned} K_c &= \frac{(x)(x)}{0.15 - x} \approx \frac{x^2}{0.15} \\ 4.9 \times 10^{-10} &= \frac{x^2}{0.15} \\ x^2 &= (0.15)\left(4.9 \times 10^{-10}\right) \\ &= 7.4 \times 10^{-11} \\ x &= \sqrt{7.4 \times 10^{-11}} \\ &= 8.6 \times 10^{-6}\ \text{M} \end{aligned}$$

The value of x calculated is, indeed, much less than the initial concentration

$$8.6 \times 10^{-6} \ll 0.15$$

and so the approximation was justified. If this simplified approach were to yield a value for *x* that did *not* justify the approximation, the calculation would need to be repeated without making the approximation.

Exercise 7.5.5

What are the equilibrium concentrations in a 0.25 *M* NH_3 solution?

$$\text{NH}_3\,(\text{aq}) + \text{H}_2\text{O}\,(\text{l}) \rightleftharpoons \text{NH}_4{}^+\,(\text{aq}) + \text{OH}^-\,(\text{aq}) \quad K_c = 1.8 \times 10^{-5}$$

Answer available at the end of this section.

Answers

Exercise 7.5.1

(a) 2*x*, *x*, −2*x*; (b) *x*, −2*x*; (c) 4*x*, 7*x*, −4*x*, −6*x* or −4*x*, −7*x*, 4*x*, 6*x*

Exercise 7.5.2

K_c = 4

Exercise 7.5.3

1.53 mol/L

Exercise 7.5.4*A*

$[CH_3CO_2H]$ = 0.18 *M*, $[C_2H_5OH]$ = 0.18 *M*, $[CH_3CO_2C_2H_5]$ = 0.37 *M*, $[H_2O]$ = 0.37 *M*

Exercise 7.5.4*B*

$[H_2]$ = 0.06 *M*, $[I_2]$ = 1.06 *M*, [HI] = 1.88 *M*

Exercise 7.5.5

$[\text{OH}^-] = [\text{NH}_4{}^+] = 0.0021\ \text{M}$

$[\text{NH}_3] = 0.25\ \text{M}$

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7.6: Key Terms

Example and Directions

Words (or words that have the same definition)	The definition is case sensitive	(Optional) Image to display with the definition [Not displayed in Glossary, only in pop-up on pages]	(Optional) Caption for Image	(Optional) External or Internal Link	(Optional) Source for Definition
(Eg. "Genetic, Hereditary, DNA ...")	(Eg. "Relating to genes or heredity")		The infamous double helix	https://bio.libretexts.org/	CC-BY-SA; Delmar Larsen

Glossary Entries

Word(s)	Definition	Image	Caption	Link	Source
equilibrium	state of a reversible reaction in which the forward and reverse processes occur at equal rates				
equilibrium constant (K)	value of the reaction quotient for a system at equilibrium; may be expressed using concentrations (K_c) or partial pressures (K_p)				
heterogeneous equilibria	equilibria in which reactants and products occupy two or more different phases				
homogeneous equilibria	equilibria in which all reactants and products occupy the same phase				
law of mass action	when a reversible reaction has attained equilibrium at a given temperature, the reaction quotient remains constant				
Le Chatelier's principle	an equilibrium subjected to stress will shift in a way to counter the stress and re-establish equilibrium				
reaction quotient (Q)	mathematical function describing the relative amounts of reactants and products in a reaction mixture; may be expressed in terms of concentrations (Q_c) or pressures (Q_p)				
reversible reaction	chemical reaction that can proceed in both the forward and reverse directions under given conditions				

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7.7: Key Equations

$Q_c = \frac{[\mathrm{C}]^x[\mathrm{D}]^y}{[\mathrm{A}]^m[\mathrm{B}]^n}$ for the reaction $m\ \mathrm{A} + n\ \mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$

$Q_P = \frac{(P_C)^x\,(P_D)^y}{(P_A)^m\,(P_B)^n}$ for the reaction $m\ \mathrm{A} + n\ \mathrm{B} \rightleftharpoons x\mathrm{C} + y\mathrm{D}$

$P = MRT$

$K_c = Q_c$ at equilibrium

$K_p = Q_p$ at equilibrium

$K_P = K_c(RT)^{\Delta n}$

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7.8: Summary

A reversible reaction is at equilibrium when the forward and reverse processes occur at equal rates. Chemical equilibria are dynamic processes characterized by constant amounts of reactant and product species.

The composition of a reaction mixture may be represented by a mathematical function known as the reaction quotient, *Q*. For a reaction at equilibrium, the composition is constant, and *Q* is called the equilibrium constant, *K*.

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.

Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure. The system's response to these disturbances is described by Le Chatelier's principle: An equilibrium system subjected to a disturbance will shift in a way that counters the disturbance and re-establishes equilibrium. A catalyst will increase the rate of both the forward and reverse reactions of a reversible process, increasing the rate at which equilibrium is reached but not altering the equilibrium mixture's composition (*K* does not change).

Calculating values for equilibrium constants and/or equilibrium concentrations is of practical benefit to many applications. A mathematical strategy that uses initial concentrations, changes in concentrations, and equilibrium concentrations (and goes by the acronym ICE) is useful for several types of equilibrium calculations.

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7.9: Exercises

1.

What does it mean to describe a reaction as “reversible”?

2.

When writing an equation, how is a reversible reaction distinguished from a nonreversible reaction?

3.

If a reaction is reversible, when can it be said to have reached equilibrium?

4.

Is a system at equilibrium if the rate constants of the forward and reverse reactions are equal?

5.

If the concentrations of products and reactants are equal, is the system at equilibrium?

6.

Explain why there may be an infinite number of values for the reaction quotient of a reaction at a given temperature but there can be only one value for the equilibrium constant at that temperature.

7.

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 in Figure 13.4.

8.

If you observe the following reaction at equilibrium, is it possible to tell whether the reaction started with pure NO_2 or with pure N_2O_4?
$2\mathrm{NO}_2(g) \rightleftharpoons \mathrm{N}_2\mathrm{O}_4(g)$

9.

Among the solubility rules previously discussed is the statement: All chlorides are soluble except Hg_2Cl_2, AgCl, $PbCl_2$, and CuCl.

(a) Write the expression for the equilibrium constant for the reaction represented by the equation $\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag}^{+}(aq) + \mathrm{Cl}^{-}(aq)$. 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 $\mathrm{Pb}^{2+}(aq) + 2\mathrm{Cl}^{-}(aq) \rightleftharpoons \mathrm{PbCl}_2(s)$. Is $K_c > 1, < 1$, or ≈ 1 ? Explain your answer.

10.

Among the solubility rules previously discussed is the statement: Carbonates, phosphates, borates, and arsenates—except those of the ammonium ion and the alkali metals—are insoluble.

(a) Write the expression for the equilibrium constant for the reaction represented by the equation $\mathrm{CaCO}_3(s) \rightleftharpoons \mathrm{Ca}^{2+}(aq) + \mathrm{CO}_3^{2-}(aq)$. 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 $3\mathrm{Ba}^{2+}(aq) + 2{\mathrm{PO}_4}^{3-}(aq) \rightleftharpoons \mathrm{Ba}_3\left(\mathrm{PO}_4\right)_2(s)$. Is $K_c > 1, < 1$, or ≈ 1 ? Explain your answer.

11.

Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene: $3C_2H_2(g) \rightleftharpoons C_6H_6(g)$. 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.

12.

Show that the complete chemical equation, the total ionic equation, and the net ionic equation for the reaction represented by the equation $KI(aq) + I_2(aq) \rightleftharpoons KI_3(aq)$ give the same expression for the reaction quotient. KI_3 is composed of the ions K^+ and I_3^-.

13.

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?

14.

For a precipitation reaction to be useful in a gravimetric analysis, the product of the reaction must be insoluble. Is $K_c > 1$, < 1, or ≈ 1 for a useful precipitation reaction?

15.

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) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

(c) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

(d) $BaSO_3(s) \rightleftharpoons BaO(s) + SO_2(g)$

(e) $P_4(g) + 5O_2(g) \rightleftharpoons P_4O_{10}(s)$

(f) $Br_2(g) \rightleftharpoons 2Br(g)$

(g) $CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(l)$

(h) $CuSO_4 \cdot 5H_2O(s) \rightleftharpoons CuSO_4(s) + 5H_2O(g)$

16.

Write the mathematical expression for the reaction quotient, Q_c, for each of the following reactions:

(a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(b) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$

(c) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

(d) $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$

(e) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$

(f) $2Pb(NO_3)_2(s) \rightleftharpoons 2PbO(s) + 4NO_2(g) + O_2(g)$

(g) $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(l)$

(h) $S_8(g) \rightleftharpoons 8S(g)$

17.

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) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_c = 17; [NH_3] = 0.20\ M, [N_2] = 1.00\ M, [H_2] = 1.00\ M$
(b) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_P = 6.8 \times 10^4; NH_3 = 3.0\ \text{atm}, N_2 = 2.0\ \text{atm}, H_2 = 1.0\ \text{atm}$
(c) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_c = 0.230; [SO_3] = 0.00\ M, [SO_2] = 1.00\ M, [O_2] = 1.00\ M$
(d) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_P = 16.5; SO_3 = 1.00\ \text{atm}, SO_2 = 1.00\ \text{atm}, O_2 = 1.00\ \text{atm}$
(e) $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ $K_c = 4.6 \times 10^4; [NO] = 1.00\ M, [Cl_2] = 1.00\ M, [NOCl] = 0\ M$
(f) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K_P = 0.050; NO = 10.0\ \text{atm}, N_2 = O_2 = 5\ \text{atm}$

18.

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) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_c = 17; [NH_3] = 0.50\ M, [N_2] = 0.15\ M, [H_2] = 0.12\ M$
(b) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_P = 6.8 \times 10^4; NH_3 = 2.00\ \text{atm}, N_2 = 10.00\ \text{atm}, H_2 = 10.00\ \text{atm}$
(c) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_c = 0.230; [SO_3] = 2.00\ M, [SO_2] = 2.00\ M, [O_2] = 2.00\ M$
(d) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_P = 6.5\ \text{atm}; SO_2 = 1.00\ \text{atm}, O_2 = 1.130\ \text{atm}, SO_3 = 0\ \text{atm}$
(e) $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ $K_P = 2.5 \times 10^3; NO = 1.00\ \text{atm}, Cl_2 = 1.00\ \text{atm}, NOCl = 0\ \text{atm}$
(f) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K_c = 0.050; [N_2] = 0.100\ M, [O_2] = 0.200\ M, [NO] = 1.00\ M$

19.

The following reaction has $K_P = 4.50 \times 10^{-5}$ at 720 K.
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

If a reaction vessel is filled with each gas to the partial pressures listed, in which direction will it shift to reach equilibrium? $P(NH_3)$ = 93 atm, $P(N_2)$ = 48 atm, and $P(H_2)$ = 52 atm

20.

Determine if the following system is at equilibrium. If not, in which direction will the system need to shift to reach equilibrium?
$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$

$[SO_2Cl_2]$ = 0.12 *M*, $[Cl_2]$ = 0.16 *M* and $[SO_2]$ = 0.050 *M*. K_c for the reaction is 0.078.

21.

Which of the systems described in Exercise 13.15 are homogeneous equilibria? Which are heterogeneous equilibria?

22.

Which of the systems described in Exercise 13.16 are homogeneous equilibria? Which are heterogeneous equilibria?

23.

For which of the reactions in Exercise 13.15 does K_C (calculated using concentrations) equal K_P (calculated using pressures)?

24.

For which of the reactions in Exercise 13.16 does K_C (calculated using concentrations) equal K_P (calculated using pressures)?

25.

(a) $\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \rightleftharpoons 2\mathrm{NH_3}(g) \quad K_c = 0.50$ at $400^\circ\mathrm{C}$

(b) $\mathrm{H_2}(g) + \mathrm{I_2}(g) \rightleftharpoons 2\mathrm{HI}(g) \quad K_c = 50.2$ at $448^\circ\mathrm{C}$

(c) $\mathrm{Na_2SO_4 \cdot 10H_2O}(s) \rightleftharpoons \mathrm{Na_2SO_4}(s) + 10\mathrm{H_2O}(g) \quad K_P = 4.08 \times 10^{-25}$ at $25^\circ\mathrm{C}$

(d) $\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2O}(g) \quad K_P = 0.122$ at $50^\circ\mathrm{C}$

26.

a) $\mathrm{Cl_2}(g) + \mathrm{Br_2}(g) \rightleftharpoons 2\mathrm{BrCl}(g) \quad K_c = 4.7 \times 10^{-2}$ at $25^\circ\mathrm{C}$

(b) $2\mathrm{SO_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\mathrm{SO_3}(g) \quad K_P = 48.2$ at $500^\circ\mathrm{C}$

(c) $\mathrm{CaCl_2 \cdot 6H_2O}(s) \rightleftharpoons \mathrm{CaCl_2}(s) + 6\mathrm{H_2O}(g) \quad K_P = 5.09 \times 10^{-44}$ at $25^\circ\mathrm{C}$

(d) $\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2O}(g) \quad K_P = 0.196$ at $60^\circ\mathrm{C}$

27.

What is the value of the equilibrium constant expression for the change $\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2O}(g)$ at $30^\circ\mathrm{C}$? (See Appendix E.)

28.

Write the expression of the reaction quotient for the ionization of HOCN in water.

29.

Write the reaction quotient expression for the ionization of NH_3 in water.

30.

What is the approximate value of the equilibrium constant K_P for the change $\mathrm{C_2H_5OC_2H_5}(l) \rightleftharpoons \mathrm{C_2H_5OC_2H_5}(g)$ at 25 °C. (The equilibrium vapor pressure for this substance is 570 torr at 25 °C.)

31.

The following equation represents a reversible decomposition:
$\mathrm{CaCO_3}(s) \rightleftharpoons \mathrm{CaO}(s) + \mathrm{CO_2}(g)$

Under what conditions will decomposition in a closed container proceed to completion so that no $CaCO_3$ remains?

32.

Explain how to recognize the conditions under which changes in volume will affect gas-phase systems at equilibrium.

33.

What property of a reaction can we use to predict the effect of a change in temperature on the value of an equilibrium constant?

34.

The following reaction occurs when a burner on a gas stove is lit:

$$\mathrm{CH_4}(g) + 2\mathrm{O_2}(g) \rightleftharpoons \mathrm{CO_2}(g) + 2\mathrm{H_2O}(g)$$

Is an equilibrium among CH_4, O_2, CO_2, and H_2O established under these conditions? Explain your answer.

35.

A necessary step in the manufacture of sulfuric acid is the formation of sulfur trioxide, SO_3, from sulfur dioxide, SO_2, and oxygen, O_2, shown here. At high temperatures, the rate of formation of SO_3 is higher, but the equilibrium amount (concentration or partial pressure) of SO_3 is lower than it would be at lower temperatures.

$$2\mathrm{SO_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\mathrm{SO_3}(g)$$

(a) Does the equilibrium constant for the reaction increase, decrease, or remain about the same as the temperature increases?

(b) Is the reaction endothermic or exothermic?

36.

Suggest four ways in which the concentration of hydrazine, N_2H_4, could be increased in an equilibrium described by the following equation:

$$\mathrm{N_2}(g) + 2\mathrm{H_2}(g) \rightleftharpoons \mathrm{N_2H_4}(g) \quad \Delta H = 95\ \mathrm{kJ}$$

37.

Suggest four ways in which the concentration of PH_3 could be increased in an equilibrium described by the following equation:

$$\mathrm{P_4}(g) + 6\mathrm{H_2}(g) \rightleftharpoons 4\mathrm{PH_3}(g) \quad \Delta H = 110.5\ \mathrm{kJ}$$

38.

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) $\mathrm{CaO}(s) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{CaCO_3}(s) \quad \Delta H = -176\ \mathrm{kJ}$

39.

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) $2\mathrm{H_2O}(g) \rightleftharpoons 2\mathrm{H_2}(g) + \mathrm{O_2}(g) \quad \Delta H = 484\ \mathrm{kJ}$

(b) $\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \rightleftharpoons 2\mathrm{NH_3}(g) \quad \Delta H = -92.2\ \mathrm{kJ}$

(c) $2\mathrm{Br}(g) \rightleftharpoons \mathrm{Br_2}(g) \quad \Delta H = -224\ \mathrm{kJ}$

(d) $\mathrm{H_2}(g) + \mathrm{I_2}(s) \rightleftharpoons 2\mathrm{HI}(g) \quad \Delta H = 53\ \mathrm{kJ}$

40.

Methanol can be prepared from carbon monoxide 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

$2\mathrm{H_2}(g) + \mathrm{CO}(g) \rightleftharpoons \mathrm{CH_3OH}(g) \quad \Delta H = -90.2\ \mathrm{kJ}$

(b) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more H_2 is added?

(c) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CO is removed?

(d) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CH_3OH is added?

(e) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if the temperature of the system is increased?

41.

Nitrogen and oxygen react at high temperatures.

(a) Write the expression for the equilibrium constant (K_c) for the reversible reaction

$\mathrm{N_2}(g) + \mathrm{O_2}(g) \rightleftharpoons 2\mathrm{NO}(g) \quad \Delta H = 181\ \mathrm{kJ}$

(b) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if more O_2 is added?

(c) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if N_2 is removed?

(d) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if NO is added?

(e) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if the volume of the reaction vessel is decreased?

(f) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if the temperature of the system is increased?

42.

Water gas, a mixture of H_2 and CO, is an important industrial fuel produced by the reaction of steam with red hot coke, essentially pure carbon.

(a) Write the expression for the equilibrium constant for the reversible reaction

$\mathrm{C}(s) + \mathrm{H_2O}(g) \rightleftharpoons \mathrm{CO}(g) + \mathrm{H_2}(g) \quad \Delta H = 131.30\ \mathrm{kJ}$

(b) What will happen to the concentration of each reactant and product at equilibrium if more C is added?

(c) What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?

(d) What will happen to the concentration of each reactant and product at equilibrium if CO is added?

(e) What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

43.

Pure iron metal can be produced by the reduction of iron(III) oxide with hydrogen gas.

(a) Write the expression for the equilibrium constant (K_c) for the reversible reaction

$$\mathrm{Fe_2O_3}(s) + 3\mathrm{H_2}(g) \rightleftharpoons 2\mathrm{Fe}(s) + 3\mathrm{H_2O}(g) \quad \Delta H = 98.7 \text{ kJ}$$

(b) What will happen to the concentration of each reactant and product at equilibrium if more Fe is added?

(c) What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?

(d) What will happen to the concentration of each reactant and product at equilibrium if H_2 is added?

(e) What will happen to the concentration of each reactant and product at equilibrium if the volume of the reaction vessel is decreased?

(f) What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

44.

Ammonia is a weak base that reacts with water according to this equation:

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

Will any of the following increase the percent of ammonia that is converted to the ammonium ion in water?

(a) Addition of NaOH

(b) Addition of HCl

(c) Addition of NH_4Cl

45.

Acetic acid is a weak acid that reacts with water according to this equation:
$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(l)$

Will any of the following increase the percent of acetic acid that reacts and produces $\mathrm{CH_3CO_2}^-$ion?

(a) Addition of HCl

(b) Addition of NaOH

(c) Addition of $NaCH_3CO_2$

46.

Suggest two ways in which the equilibrium concentration of Ag^+ can be reduced in a solution of Na^+, Cl^-, Ag^+, and $\mathrm{NO_3}^-$, in contact with solid AgCl.

$\mathrm{Ag^+}$, and $\mathrm{NO_3}^-$, in contact with solid AgCl .

$\mathrm{Na^+}(aq) + \mathrm{Cl^-}(aq) + \mathrm{Ag^+}(aq) + \mathrm{NO_3}^-(aq) \rightleftharpoons \mathrm{AgCl}(s) + \mathrm{Na^+}(aq) + \mathrm{NO_3}^-(aq)$
$\Delta H = -65.9 \text{ kJ}$

47.

How can the pressure of water vapor be increased in the following equilibrium?

$\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2O}(g) \quad \Delta H = 41\ \mathrm{kJ}$

48.

A solution is saturated with silver sulfate and contains excess solid silver sulfate:

$\mathrm{Ag_2SO_4}(s) \rightleftharpoons 2\mathrm{Ag^+}(aq) + \mathrm{SO_4^{2-}}(aq)$

a small amount of solid silver sulfate containing a radioactive isotope of silver is added to this solution. Within a few minutes, a portion of the solution phase is sampled and tests positive for radioactive Ag^+ ions. Explain this observation.

49.

When equal molar amounts of HCl and HOCl are dissolved separately in equal amounts of water, the solution of HCl freezes at a lower temperature. Which compound has the larger equilibrium constant for acid ionization?

(a) HCl

(b) $\mathrm{H^+ + Cl^-}$

(c) HOCl
(d) $\mathrm{H^+ + OCl^-}$

50.

A reaction is represented by this equation: $\mathrm{A}(aq) + 2\mathrm{B}(aq) \rightleftharpoons 2\mathrm{C}(aq) \qquad K_c =$

(a) Write the mathematical expression for the equilibrium constant.

(b) Using concentrations ≤1 *M*, identify two sets of concentrations that describe a mixture of A, B, and C at equilibrium.

51.

A reaction is represented by this equation: $2\mathrm{W}(aq) \rightleftharpoons \mathrm{X}(aq) + 2\mathrm{Y}(aq) \qquad K_c = 5 \times 10^-$

(a) Write the mathematical expression for the equilibrium constant.

(b) Using concentrations of ≤1 *M*, identify two sets of concentrations that describe a mixture of W, X, and Y at equilibrium.

52.

What is the value of the equilibrium constant at 500 °C for the formation of NH_3 according to the following equation?

$\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \rightleftharpoons 2\mathrm{NH_3}(g)$

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.

53.

Hydrogen is prepared commercially by the reaction of methane and water vapor at elevated temperatures.

$\mathrm{CH_4}(g) + \mathrm{H_2O}(g) \rightleftharpoons 3\mathrm{H_2}(g) + \mathrm{CO}(g)$

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?

54.

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.

55.

At 1 atm and 25 °C, NO_2 with an initial concentration of 1.00 *M* is 0.0033% decomposed into NO and O_2. Calculate the value of the equilibrium constant for the reaction.

$$2\mathrm{NO}_2(g) \rightleftharpoons 2\mathrm{NO}(g) + \mathrm{O}_2(g)$$

56.

Calculate the value of the equilibrium constant K_P for the reaction $2\mathrm{NO}(g) + \mathrm{Cl}_2(g) \rightleftharpoons 2\mathrm{NOCl}(g)$ from these equilibrium pressures: NO, 0.050 atm; Cl_2, 0.30 atm; NOCl, 1.2 atm.

57.

When heated, iodine vapor dissociates according to this equation:

$$\mathrm{I}_2(g) \rightleftharpoons 2\mathrm{I}(g)$$

At 1274 K, a sample exhibits a partial pressure of I_2 of 0.1122 atm and a partial pressure due to I atoms of 0.1378 atm. Determine the value of the equilibrium constant, K_P, for the decomposition at 1274 K.

58.

A sample of ammonium chloride was heated in a closed container.

$$\mathrm{NH_4Cl}(s) \rightleftharpoons \mathrm{NH_3}(g) + \mathrm{HCl}(g)$$

At equilibrium, the pressure of $NH_3(g)$ was found to be 1.75 atm. What is the value of the equilibrium constant K_P for the decomposition at this temperature?

59.

At a temperature of 60 °C, the vapor pressure of water is 0.196 atm. What is the value of the equilibrium constant K_P for the vaporization equilibrium at 60 °C?

$$\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2O}(g)$$

60.

Complete the following partial ICE tables.

(a)

	$2\mathrm{SO}_3(g)$	$\rightleftharpoons$	$2\mathrm{SO}_2(g)+$	$\mathrm{O}_2(g)$
change	___		___	$+x$

(b)

$$\begin{array}{lcccc} & 4NH_3(g) & +\,3O_2(g) & \rightleftharpoons & 2N_2(g) + \quad 6H_2O(g) \\ \text{change} & \_\_ & +x & & \_\_ \quad \_\_ \end{array}$$

(c)

$$\begin{array}{lccc} & 2CH_4(g) & \rightleftharpoons & C_2H_2(g) + \quad 3H_2(g) \\ \text{change} & \_\_ & & +x \quad \_\_ \end{array}$$

(d)

$$\begin{array}{lcccc} & CH_4(g) + & H_2O(g) & \rightleftharpoons & CO(g) + \quad 3H_2(g) \\ \text{change} & \_\_ & +x & & \_\_ \quad \_\_ \end{array}$$

(e)

$$\begin{array}{lccc} & NH_4Cl(s) & \rightleftharpoons & NH_3(g) + \quad HCl(g) \\ \text{change} & & +x & \_\_ \end{array}$$

(f)

$$\begin{array}{lccc} & Ni(s) + & 4CO(g) & \rightleftharpoons & Ni(CO)_4(g) \\ \text{change} & +x & & \_\_ \end{array}$$

61.

Complete the following partial ICE tables.

(a)

$$\begin{array}{lccc} & 2H_2(g) + & O_2(g) & \rightleftharpoons & 2H_2O(g) \\ \text{change} & \_\_ & \_\_ & & +x \end{array}$$

(b)

$$\begin{array}{lcccc} & CS_2(g) + & 4H_2(g) & \rightleftharpoons & CH_4(g) + \quad 2H_2S(g) \\ \text{change} & +x & \_\_ & & \_\_ \quad \_\_ \end{array}$$

(c)

$$\begin{array}{lccc} & H_2(g) + & Cl_2(g) & \rightleftharpoons & 2HCl(g) \\ \text{change} & +x & \_\_ & & \_\_ \end{array}$$

(d)

$$\begin{array}{lcccc} & 2NH_3(g) & +\,2O_2(g) & \rightleftharpoons & N_2O(g) + \quad 3H_2O(g) \\ \text{change} & \_\_ & \_\_ & & \_\_ \quad +x \end{array}$$

(e)

$$\begin{array}{lccc} & NH_4HS(s) & \rightleftharpoons & NH_3(g) + \quad H_2S(g) \\ \text{change} & & +x & \_\_ \end{array}$$

(f)

$$\begin{array}{lccc} & Fe(s) + & 5CO(g) & \rightleftharpoons & Fe(CO)_5(g) \\ \text{change} & & \_\_ & & +x \end{array}$$

62.

Why are there no changes specified for Ni in Exercise 13.60, part (f)? What property of Ni does change?

63.

Why are there no changes specified for NH_4HS in Exercise 13.61, part (e)? What property of NH_4HS does change?

64.

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*.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K_c = 0.50 \text{ at } 400\ ^\circ\text{C}$$

Calculate the equilibrium molar concentration of NH_3.

65.

Calculate the number of moles of HI that are at equilibrium with 1.25 mol of H_2 and 1.25 mol of I_2 in a 5.00–L flask at 448 °C.

$$H_2 + I_2 \rightleftharpoons 2HI \qquad K_c = 50.2 \text{ at } 448\ ^\circ\text{C}$$

66.

What is the pressure of BrCl in an equilibrium mixture of Cl_2, Br_2, and BrCl if the pressure of Cl_2 in the mixture is 0.115 atm and the pressure of Br_2 in the mixture is 0.450 atm?

$$Cl_2(g) + Br_2(g) \rightleftharpoons 2BrCl(g) \qquad K_P = 4.7 \times 10^{-2}$$

67.

What is the pressure of CO_2 in a mixture at equilibrium that contains 0.50 atm H_2, 2.0 atm of H_2O, and 1.0 atm of CO at 990 °C?

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g) \qquad K_P = 1.6 \text{ at } 990\ ^\circ\text{C}$$

68.

Cobalt metal can be prepared by reducing cobalt(II) oxide with carbon monoxide.

$$CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g) \qquad K_c = 4.90 \times 10^2 \text{at } 550\ ^\circ\text{C}$$

What concentration of CO remains in an equilibrium mixture with [CO_2] = 0.100 *M*?

69.

Carbon reacts with water vapor at elevated temperatures.

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \qquad K_c = 0.2 \text{ at } 1000\ ^\circ\text{C}$$

Assuming a reaction mixture initially contains only reactants, what is the concentration of CO in an equilibrium mixture with [H_2O] = 0.500 *M* at 1000 °C?

70.

Sodium sulfate 10–hydrate, $Na_2SO_4{\cdot}10H_2O$, dehydrates according to the equation

$$Na_2SO_4{\cdot}10H_2O(s) \rightleftharpoons Na_2SO_4(s) + 10H_2O(g) \qquad K_P = 4.08 \times 10^{-25} \text{ at } 25\ ^\circ\text{C}$$

What is the pressure of water vapor at equilibrium with a mixture of $Na_2SO_4{\cdot}10H_2O$ and $NaSO_4$?

71.

Calcium chloride 6–hydrate, $CaCl_2{\cdot}6H_2O$, dehydrates according to the equation

$$CaCl_2{\cdot}6H_2O(s) \rightleftharpoons CaCl_2(s) + 6H_2O(g) \qquad K_P = 5.09 \times 10^{-44} \text{ at } 25\ ^\circ\text{C}$$

What is the pressure of water vapor at equilibrium with a mixture of $CaCl_2{\cdot}6H_2O$ and $CaCl_2$ at 25 °C?

72.

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:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad K_c = 4.32$$

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*?

73.

A student solved the following problem and found $[N_2O_4]$ = 0.16 *M* at equilibrium. How could this student recognize that the answer was wrong without reworking the problem? The problem was: What is the equilibrium concentration of N_2O_4 in a mixture formed from a sample of NO_2 with a concentration of 0.10 *M*?

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad K_c = 160$$

74.

Assume that the change in concentration of N_2O_4 is small enough to be neglected in the following problem.

(a) Calculate the equilibrium concentration of both species in 1.00 L of a solution prepared from 0.129 mol of N_2O_4 with chloroform as the solvent.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K_c = 1.07 \times 10^{-} \text{ in chloroform}$$

(b) Confirm that the change is small enough to be neglected.

75.

Assume that the change in concentration of $COCl_2$ is small enough to be neglected in the following problem.

(a) Calculate the equilibrium concentration of all species in an equilibrium mixture that results from the decomposition of $COCl_2$ with an initial concentration of 0.3166 *M*.

$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g) \qquad K_c = 2.2 \times 10^{-10}$$

(b) Confirm that the change is small enough to be neglected.

76.

Assume that the change in pressure of H_2S is small enough to be neglected in the following problem.

(a) Calculate the equilibrium pressures of all species in an equilibrium mixture that results from the decomposition of H_2S with an initial pressure of 0.824 atm.

$2\mathrm{H_2S}(g) \rightleftharpoons 2\mathrm{H_2}(g) + \mathrm{S_2}(g) \qquad K_P = 2.2 \times 10^{-6}$

(b) Confirm that the change is small enough to be neglected.

77.

What are all concentrations after a mixture that contains [H_2O] = 1.00 *M* and [Cl_2O] = 1.00 *M* comes to equilibrium at 25 °C?

$\mathrm{H_2O}(g) + \mathrm{Cl_2O}(g) \rightleftharpoons 2\mathrm{HOCl}(g) \qquad K_c = 0.0900$

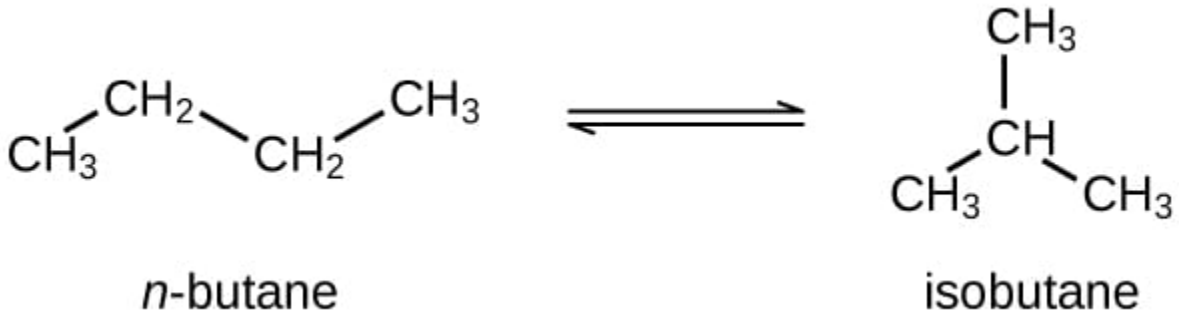
78.

Calculate the number of grams of HI that are at equilibrium with 1.25 mol of H_2 and 63.5 g of iodine at 448 °C.

$\mathrm{H_2} + \mathrm{I_2} \rightleftharpoons 2\mathrm{HI} \qquad K_c = 50.2 \text{ at } 448\ ^\circ\mathrm{C}$

79.

Butane exists as two isomers, *n*–butane and isobutane.



n-butane isobutane

K_P = 2.5 at 25 °C

What is the pressure of isobutane in a container of the two isomers at equilibrium with a total pressure of 1.22 atm?

80.

What is the minimum mass of $CaCO_3$ required to establish equilibrium at a certain temperature in a 6.50-L container if the equilibrium constant (K_c) is 0.50 for the decomposition reaction of $CaCO_3$ at that temperature?

$\mathrm{CaCO_3}(s) \rightleftharpoons \mathrm{CaO}(s) + \mathrm{CO_2}(g)$

81.

The equilibrium constant (K_c) for this reaction is 1.60 at 990 °C:

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$

Calculate the number of moles of each component in the final equilibrium mixture obtained from adding 1.00 mol of H_2, 2.00 mol of CO_2, 0.750 mol of H_2O, and 1.00 mol of CO to a 5.00-L container at 990 °C.

82.

In a 3.0-L vessel, the following equilibrium partial pressures are measured: N_2, 190 torr; H_2, 317 torr; NH_3, 1.00×10^3 torr.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(a) How will the partial pressures of H_2, N_2, and NH_3 change if H_2 is removed from the system? Will they increase, decrease, or remain the same?

(b) Hydrogen is removed from the vessel until the partial pressure of nitrogen, at equilibrium, is 250 torr. Calculate the partial pressures of the other substances under the new conditions.

83.

The equilibrium constant (K_c) for this reaction is 5.0 at a given temperature.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

(a) On analysis, an equilibrium mixture of the substances present at the given temperature was found to contain 0.20 mol of CO, 0.30 mol of water vapor, and 0.90 mol of H_2 in a liter. How many moles of CO_2 were there in the equilibrium mixture?

(b) Maintaining the same temperature, additional H_2 was added to the system, and some water vapor was removed by drying. A new equilibrium mixture was thereby established containing 0.40 mol of CO, 0.30 mol of water vapor, and 1.2 mol of H_2 in a liter. How many moles of CO_2 were in the new equilibrium mixture? Compare this with the quantity in part (a), and discuss whether the second value is reasonable. Explain how it is possible for the water vapor concentration to be the same in the two equilibrium solutions even though some vapor was removed before the second equilibrium was established.

84.

Antimony pentachloride decomposes according to this equation:

$$SbCl_5(g) \rightleftharpoons SbCl_3(g) + Cl_2(g)$$

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. How many grams of each will be found if the mixture is transferred into a 2.00-L flask at the same temperature?

85.

Consider the equilibrium

$$4NO_2(g) + 6H_2O(g) \rightleftharpoons 4NH_3(g) + 7O_2(g)$$

(a) What is the expression for the equilibrium constant (K_c) of the reaction?

(b) How must the concentration of NH_3 change to reach equilibrium if the reaction quotient is less than the equilibrium constant?

(c) If the reaction were at equilibrium, how would an increase in the volume of the reaction vessel affect the pressure of NO_2?

(d) If the change in the pressure of NO_2 is 28 torr as a mixture of the four gases reaches equilibrium, how much will the pressure of O_2 change?

86.

The binding of oxygen by hemoglobin (Hb), giving oxyhemoglobin (HbO_2), is partially regulated by the concentration of H_3O^+ and dissolved CO_2 in the blood. Although the equilibrium is complicated, it can be summarized as

$$\mathrm{HbO_2}(aq) + \mathrm{H_3O^+}(aq) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{CO_2{-}Hb{-}H^+} + \mathrm{O_2}(g) + \mathrm{H_2O}(l)$$

(a) Write the equilibrium constant expression for this reaction.

(b) Explain why the production of lactic acid and CO_2 in a muscle during exertion stimulates release of O_2 from the oxyhemoglobin in the blood passing through the muscle.

87.

Liquid N_2O_3 is dark blue at low temperatures, but the color fades and becomes greenish at higher temperatures as the compound decomposes to NO and NO_2. At 25 °C, a value of K_P = 1.91 has been established for this decomposition. If 0.236 moles of N_2O_3 are placed in a 1.52-L vessel at 25 °C, calculate the equilibrium partial pressures of $N_2O_3(g)$, $NO_2(g)$, and NO(*g*).

88.

A 1.00-L vessel at 400 °C contains the following equilibrium concentrations: N_2, 1.00 *M*; H_2, 0.50 *M*; and NH_3, 0.25 *M*. How many moles of hydrogen must be removed from the vessel to increase the concentration of nitrogen to 1.1 *M*? The equilibrium reaction is

$$\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \rightleftharpoons 2\mathrm{NH_3}(g)$$

89.

Calculate the equilibrium constant at 25 °C for each of the following reactions from the value of $\Delta G°$ given.

(a) $\mathrm{I_2}(s) + \mathrm{Cl_2}(g) \longrightarrow 2\mathrm{ICl}(g) \qquad \Delta G° = -10.88$

(b) $\mathrm{H_2}(g) + \mathrm{I_2}(s) \longrightarrow 2\mathrm{HI}(g) \qquad \Delta G° = 3.4$

(c) $\mathrm{CS_2}(g) + 3\mathrm{Cl_2}(g) \longrightarrow \mathrm{CCl_4}(g) + \mathrm{S_2Cl_2}(g) \qquad \Delta G° = -39$

(d) $2\mathrm{SO_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\mathrm{SO_3}(g) \qquad \Delta G° = -141.82$

(e) $\mathrm{CS_2}(g) \longrightarrow \mathrm{CS_2}(l) \qquad \Delta G° = -1.88$

90.

Calculate the equilibrium constant at the temperature given.

(a) $\mathrm{O_2}(g) + 2\mathrm{F_2}(g) \longrightarrow 2\mathrm{F_2O}(g) \qquad (\mathrm{T} = 100\ °\mathrm{C})$

(b) $\mathrm{I_2}(s) + \mathrm{Br_2}(l) \longrightarrow 2\mathrm{IBr}(g) \qquad (\mathrm{T} = 0.0\ °\mathrm{C})$

(c) $2\mathrm{LiOH}(s) + \mathrm{CO_2}(g) \longrightarrow \mathrm{Li_2CO_3}(s) + \mathrm{H_2O}(g) \qquad (\mathrm{T} = 575\ °\mathrm{C})$

(d) $\mathrm{N_2O_3}(g) \longrightarrow \mathrm{NO}(g) + \mathrm{NO_2}(g) \qquad (\mathrm{T} = -10.0\ °\mathrm{C})$

(e) $\mathrm{SnCl_4}(l) \longrightarrow \mathrm{SnCl_4}(g) \qquad (\mathrm{T} = 200\ °\mathrm{C})$

91.

Calculate the equilibrium constant at the temperature given.

(a) $\mathrm{I_2}(s) + \mathrm{Cl_2}(g) \longrightarrow 2\mathrm{ICl}(g) \qquad (\mathrm{T} = 100\ ^\circ\mathrm{C})$

(b) $\mathrm{H_2}(g) + \mathrm{I_2}(s) \longrightarrow 2\mathrm{HI}(g) \qquad (\mathrm{T} = 0.0\ ^\circ\mathrm{C})$

(c) $\mathrm{CS_2}(g) + 3\mathrm{Cl_2}(g) \longrightarrow \mathrm{CCl_4}(g) + \mathrm{S_2Cl_2}(g) \qquad (\mathrm{T} = 125\ ^\circ\mathrm{C})$

(d) $2\mathrm{SO_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\mathrm{SO_3}(g) \qquad (\mathrm{T} = 675\ ^\circ\mathrm{C})$

(e) $\mathrm{CS_2}(g) \longrightarrow \mathrm{CS_2}(l) \qquad (\mathrm{T} = 90\ ^\circ\mathrm{C})$

92.

Consider the following reaction at 298 K:
$\mathrm{N_2O_4}(g) \rightleftharpoons 2\mathrm{NO_2}(g) \qquad K_P = 0.142$

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.

93.

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.

94.

Under what conditions is $\mathrm{N_2O_3}(g) \longrightarrow \mathrm{NO}(g) + \mathrm{NO_2}(g)$ spontaneous?

95.

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.)

96.

Hydrogen sulfide is a pollutant found in natural gas. Following its removal, it is converted to sulfur by the reaction $2\mathrm{H_2S}(g) + \mathrm{SO_2}(g) \rightleftharpoons \frac{3}{8}\mathrm{S_8}(s,\ \mathrm{rhombic}) + 2\mathrm{H_2O}(l)$. What is the equilibrium constant for this reaction? Is the reaction endothermic or exothermic?

97.

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?

98.

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.)

99.

Benzene can be prepared from acetylene. $3C_2H_2(g) \rightleftharpoons C_6H_6(g)$. 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?

100.

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?

101.

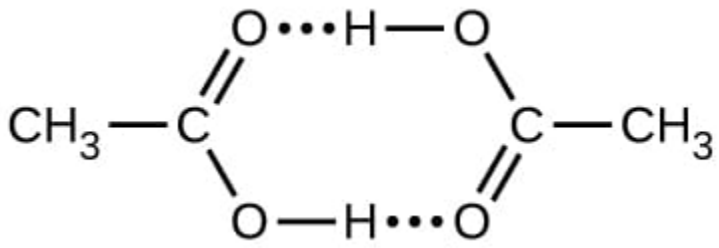
Carbon tetrachloride, an important industrial solvent, is prepared by the chlorination of methane at 850 K.
$CH_4(g) + 4Cl_2(g) \longrightarrow CCl_4(g) + 4HCl(g)$

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?

102.

Acetic acid, CH_3CO_2H, can form a dimer, $(CH_3CO_2H)_2$, in the gas phase.
$2CH_3CO_2H(g) \longrightarrow (CH_3CO_2H)_2(g)$

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?

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8: ACID-BASE EQUILIBRIA

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8.1: Introduction

Liquid water is essential to life on our planet, and chemistry involving the characteristic ions of water, $\mathrm{H^+}$ and $\mathrm{OH^-}$, is widely encountered in nature and society. As introduced in another chapter of this text, acid-base chemistry involves the transfer of hydrogen ions from donors (acids) to acceptors (bases). These $\mathrm{H^+}$ transfer reactions are reversible, and the equilibria established by acid-base systems are essential aspects of phenomena ranging from sinkhole formation (Figure $8.1.1$) to oxygen transport in the human body. This chapter will further explore acid-base chemistry with an emphasis on the equilibrium aspects of this important reaction class.



Figure $8.1.1$: Sinkholes such as this are the result of reactions between acidic groundwaters and basic rock formations, like limestone. (credit: modification of work by Emil Kehnel)

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8.2: Brønsted-Lowry Acids and Bases

Learning Objectives

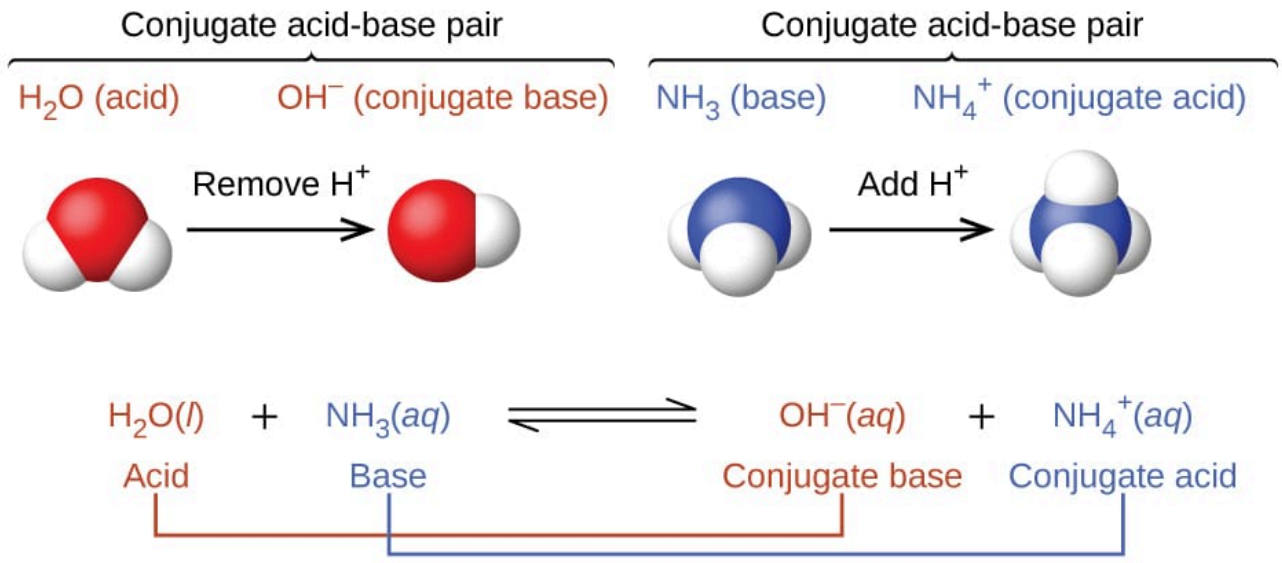
By the end of this section, you will be able to:

- 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

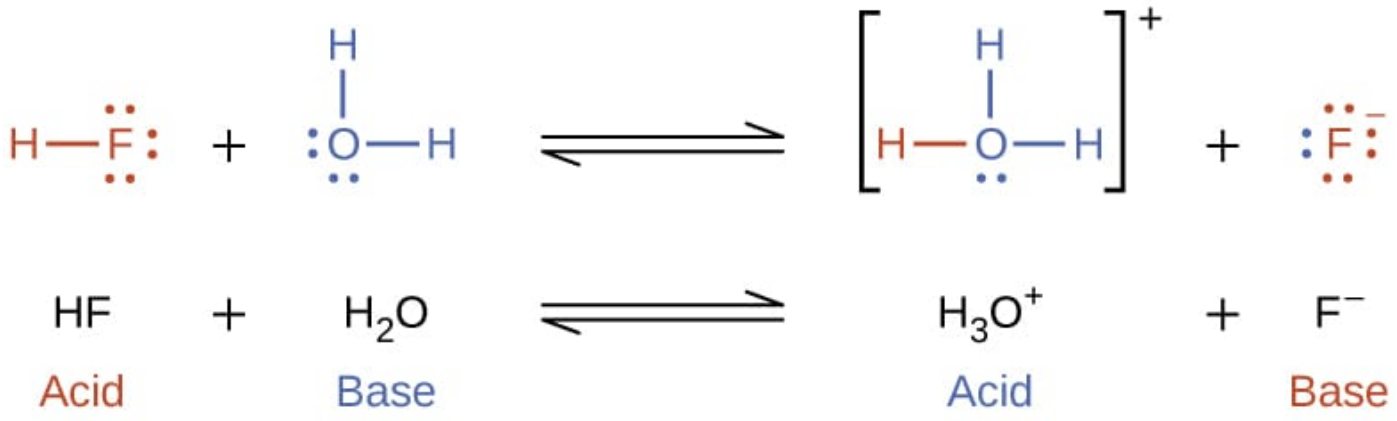
The acid-base reaction class has been studied for quite some time. In 1680, Robert Boyle reported traits of acid solutions that included their ability to dissolve many substances, to change the colors of certain natural dyes, and to lose these traits after coming in contact with alkali (base) solutions. 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.

Johannes Brønsted and Thomas Lowry proposed a more general description in 1923 in which acids and bases were defined in terms of the transfer of hydrogen ions, H^+. (Note that these hydrogen ions are often referred to simply as *protons*, since that subatomic particle is the only component of cations derived from the most abundant hydrogen isotope, ^1H.) A compound that donates a proton to another compound is called a Brønsted-Lowry acid, and a compound that accepts a proton is called a Brønsted-Lowry base. An acid-base reaction is, thus, the transfer of a proton from a donor (acid) to an acceptor (base).

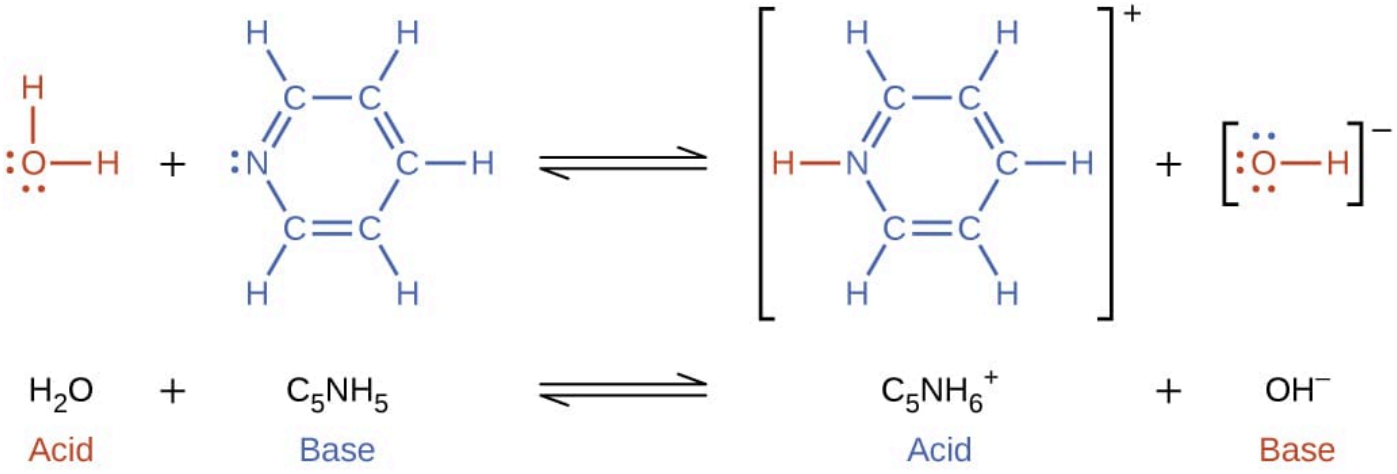
The concept of *conjugate pairs* is useful in describing Brønsted-Lowry acid-base reactions (and other reversible reactions, as well). When an acid donates H^+, the species that remains is called the **conjugate base** of the acid because it reacts as a proton acceptor in the reverse reaction. Likewise, when a base accepts H^+, it is converted to its **conjugate acid**. The reaction between water and ammonia illustrates this idea. In the forward direction, water acts as an acid by donating a proton to ammonia and subsequently becoming a hydroxide ion, OH^-, the conjugate base of water. The ammonia acts as a base in accepting this proton, becoming an ammonium ion, NH_4^+, the conjugate acid of ammonia. In the reverse direction, a hydroxide ion acts as a base in accepting a proton from ammonium ion, which acts as an acid.



The reaction between a Brønsted-Lowry acid and water is called acid ionization. For example, when hydrogen fluoride dissolves in water and ionizes, protons are transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions:



Base ionization of a species occurs when it accepts protons from water molecules. In the example below, pyridine molecules, C_5NH_5, undergo base ionization when dissolved in water, yielding hydroxide and pyridinium ions:



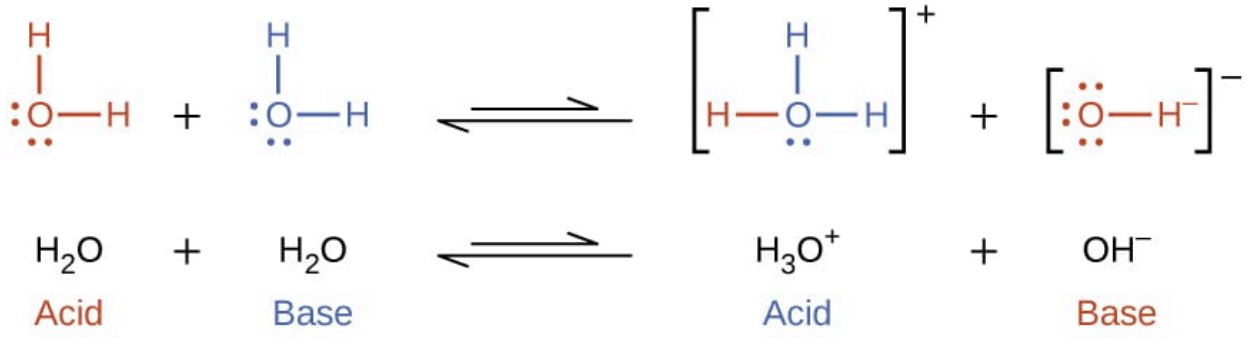
The preceding ionization reactions suggest that water may function as both a base (as in its reaction with hydrogen fluoride) and an acid (as in its reaction with ammonia). Species capable of either donating or accepting protons are called amphiprotic, or more generally, amphoteric, a term that may be used for acids and bases per definitions other than the Brønsted-Lowry one. The equations below show the two possible acid-base reactions for two amphiprotic species, bicarbonate ion and water:

$$\mathrm{HCO_3^-\,(aq) + H_2O\,(l) \rightleftharpoons CO_3^{2-}\,(aq) + H_3O^+\,(aq)}$$

$$\mathrm{HCO_3^-\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq) + OH^-\,(aq)}$$

The first equation represents the reaction of bicarbonate as an acid with water as a base, whereas the second represents reaction of bicarbonate as a base with water as an acid. When bicarbonate is added to water, both these equilibria are established simultaneously and the composition of the resulting solution may be determined through appropriate equilibrium calculations, as described later in this chapter.

In the liquid state, molecules of an amphiprotic substance can react with one another as illustrated for water in the equations below:



The process in which like molecules react to yield ions is called autoionization. Liquid water undergoes autoionization to a very slight extent; at 25 °C, approximately two out of every billion water molecules are ionized. The extent of the water autoionization process is reflected in the value of its equilibrium constant, the ion-product constant for water, K_w:

$$\mathrm{2\,H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)} \tag{8.2.1}$$

with

$$K_w = [\mathrm{H_3O^+}][\mathrm{OH^-}] \tag{8.2.2}$$

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, K_w has a value of 1.0×10^{-14}. The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and hydroxide ion increase with temperature. For example, at 100 °C, the value for K_w is about 5.6×10^{-13}, roughly 50 times larger than the value at 25 °C.

Example 8.2.1: 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, [H_3O^+] = [OH^-] = *x*. At 25 °C:

$$K_w = [H_3O^+]\,[OH^-] = (x)(x) = x^2 = 1.0 \times 10^{-14}$$

So:

$$x = [H_3O^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} M$$

The hydronium ion concentration and the hydroxide ion concentration are the same, $1.0 \times 10^{-7}\ M$.

Exercise 8.2.1

The ion product of water at 80 °C is 2.4 \times 10^{–13}. What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

Answer available at the end of this section.

Example 8.2.2: The Inverse Relation between [H_3O^+] and [OH^-]

A solution of an acid 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

Use the value of the ion-product constant for water at 25 °C (Equations 8.2.1 and 8.2.2) to calculate the missing equilibrium concentration.

$$2\,\mathrm{H_2O\,(l)} \rightleftharpoons \mathrm{H_3O^+\,(aq)} + \mathrm{OH^-\,(aq)}$$

with $K_w = [\mathrm{H_3O^+}][\mathrm{OH^-}]$.

Rearrangement of the K_w expression shows that [OH^-] is inversely proportional to [H_3O^+]:

$$K_w = [\mathrm{H_3O^+}]\,[\mathrm{OH^-}] = \left(2.0 \times 10^{-6}\right)\left(5.0 \times 10^{-9}\right) = 1.0 \times 10^{-14}$$

Compared with pure water, a solution of acid exhibits a higher concentration of hydronium ions (due to ionization of the acid) and a proportionally lower concentration of hydroxide ions. This may be explained via Le Chatelier's principle as a left shift in the water autoionization equilibrium resulting from the stress of increased hydronium ion concentration.

Substituting the ion concentrations into the K_w expression confirms this calculation, resulting in the expected value:

$$K_w = [\mathrm{H_3O^+}][\mathrm{OH^-}] = (2.0 \times 10^{-6})(5.0 \times 10^{-9}) = 1.0 \times 10^{-14}$$

Exercise 8.2.2

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 *M* at 25 °C?

Answer available at the end of this section.

Example 8.2.3: Representing 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. $\mathrm{HSO_3^-(aq) + OH^-(aq) \rightleftharpoons SO_3^{2-}(aq) + H_2O(l)}$
b. $\mathrm{HSO_3^-(aq) + HI(aq) \rightleftharpoons H_2SO_3(aq) + I^-(aq)}$

Exercise 8.2.3

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 available at the end of this section.

Answers

Exercise 8.2.1

$$[\mathrm{H_3O^+}] = [\mathrm{OH^-}] = 4.9 \times 10^{-7}\,M$$

Exercise 8.2.2

$$[\mathrm{H_3O^+}] = 1 \times 10^{-11}\ \mathrm{M}$$

Exercise 8.2.3

a. $\mathrm{H_2PO_4^-(aq) + HBr(aq) \rightleftharpoons H_3PO_4(aq) + Br^-(aq)}$
b. $\mathrm{H_2PO_4^-(aq) + OH^-(aq) \rightleftharpoons HPO_4^{2-}(aq) + H_2O(l)}$

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8.3: pH and pOH

Learning Objectives

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

- 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 that may span many orders of magnitude is to use a logarithmic scale. One such scale that is very popular for chemical concentrations and equilibrium constants is based on the p-function, defined as shown where "X" is the quantity of interest and "log" is the base-10 logarithm:

$$pX = -\log X$$

The pH of a solution is therefore defined as shown here, where [H_3O^+] is the molar concentration of hydronium ion in the solution:

$$pH = -\log\left[H_3O^+\right]$$

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

$$\left[H_3O^+\right] = 10^{-pH}$$

Likewise, the hydroxide ion molarity may be expressed as a p-function, or pOH:

$$pOH = -\log\left[OH^-\right]$$

or

$$\left[OH^-\right] = 10^{-pOH}$$

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the K_w expression:

$$\begin{aligned} K_w &= \left[\mathrm{H_3O^+}\right]\left[\mathrm{OH^-}\right] \\ -\log K_w &= -\log\left(\left[\mathrm{H_3O^+}\right]\left[\mathrm{OH^-}\right]\right) \\ &= -\log\left[\mathrm{H_3O^+}\right] + -\log\left[\mathrm{OH^-}\right] \\ pK_w &= pH + pOH \end{aligned} \tag{8.3.1}$$

At 25 °C, the value of K_w is 1.0×10^{-14}, and so:

$$14.00 = pH + pOH$$

As was demonstrated previously, the hydronium ion molarity in pure water (or any neutral solution) is 1.0×10^{-7} M at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

$$pH = -\log\left[H_3O^+\right] = -\log\left(1.0 \times 10^{-7}\right) = 7.00$$

$$pOH = -\log\left[OH^-\right] = -\log\left(1.0 \times 10^{-7}\right) = 7.00$$

And so, *at this temperature*, acidic solutions are those with hydronium ion molarities greater than 1.0×10^{-7} M and hydroxide ion molarities less than 1.0×10^{-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 1.0×10^{-7} M and hydroxide ion molarities greater than 1.0×10^{-7} M (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

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, Exercise 8.3.1 showed the hydronium molarity of pure water at 80 °C is 4.9×10^{-7} M, which corresponds to pH and pOH values of:

$$pH = -\log\left[H_3O^+\right] = -\log\left(4.9 \times 10^{-7}\right) = 6.31$$

$$pOH = -\log\left[OH^-\right] = -\log\left(4.9 \times 10^{-7}\right) = 6.31$$

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 other temperatures, such as enzyme reactions in warm-blooded organisms at a temperature around 36–40 °C. Unless otherwise noted, references to pH values are presumed to be those at 25 °C (Table 8.3.1).

Table 8.3.1: 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 8.3.1: shows the relationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH for solutions classified as acidic, basic, and neutral.

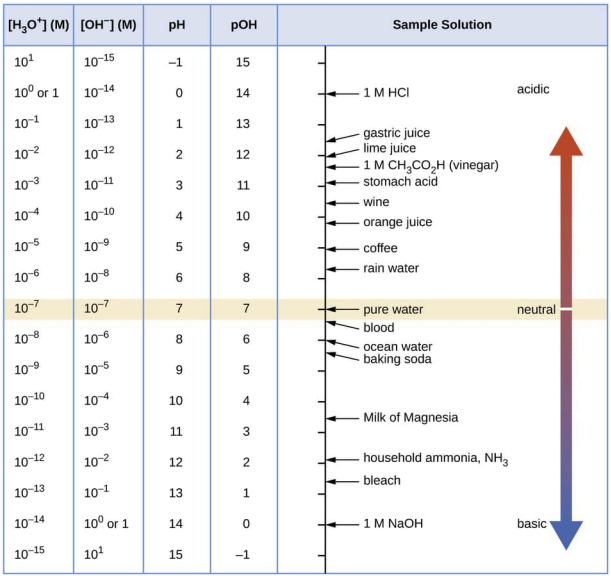


Figure 8.3.1: The pH and pOH scales represent concentrations of H_3O^+ and OH^-, respectively. The pH and pOH values of some common substances at 25 °C are shown in this chart.

Example 8.3.1: Calculation of pH from $[H_3O^+]$

What is the pH of stomach acid, a solution of HCl with a hydronium ion concentration of 1.2×10^{-3} M?

Solution

$$\begin{aligned} pH &= -\log\left[\mathrm{H_3O^+}\right] \\ &= -\log\left(1.2 \times 10^{-3}\right) \\ &= -(-2.92) = 2.92 \end{aligned}$$

(The use of logarithms is explained in Appendix 11.2. When taking the log of a value, keep as many decimal places in the result as there are significant figures in the value.)

Exercise 8.3.1

Water exposed to air contains carbonic acid, $\mathrm{H_2CO_3}$, due to the reaction between carbon dioxide and water:

$$\mathrm{CO_2\,(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq)}$$

Air-saturated water has a hydronium ion concentration caused by the dissolved $\mathrm{CO_2}$ of 2.0×10^{-6} M, about 20-times larger than that of pure water. Calculate the pH of the solution at 25 °C.

Answer available at the end of this section.

Example 8.3.2: Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3.

Solution

$$\begin{aligned} pH = -\log\left[H_3O^+\right] &= 7.3 \\ \log\left[H_3O^+\right] &= -7.3 \\ \left[H_3O^+\right] &= 10^{-7.3} \end{aligned}$$

or

$$\begin{aligned} \left[\mathrm{H_3O^+}\right] &= \text{antilog of } -7.3 \\ &= 5 \times 10^{-8} M \end{aligned}$$

(On a calculator take the antilog, or the "inverse" log, of –7.3, or calculate $10^{-7.3}$.)

Exercise 8.3.2

Calculate the hydronium ion concentration of a solution with a pH of –1.07.

Answer available at the end of this section.

How Sciences Interconnect: Environmental Science

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved $\mathrm{CO_2}$ which forms carbonic acid:

$$\mathrm{H_2O\,(l) + CO_2\,(g) \longrightarrow H_2CO_3\,(aq)}$$
$$\mathrm{H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq)}$$

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:

$$H_2O\,(l) + SO_3\,(g) \longrightarrow H_2SO_4\,(aq)$$
$$H_2SO_4\,(aq) \longrightarrow H^+\,(aq) + HSO_4{}^-\,(aq)$$

Carbon dioxide is naturally present in the atmosphere because most organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also originates 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 8.3.2). 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.

For further information on acid rain, visit this website hosted by the US Environmental Protection Agency.



Figure 8.3.2: (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 8.3.3: Calculation of pOH

What are the pOH and the \(\text{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*:

$$\begin{aligned}\text{pOH} &= -\log\left[OH^-\right] = -\log 0.0125\\ &= -(-1.903) = 1.903\end{aligned}$$

The pH can be found from the pOH:

$$\begin{aligned}\text{pH} + \text{pOH} &= 14.00\\ pH &= 14.00 - pOH\\ &= 14.00 - 1.903 = 12.10\end{aligned}$$

Exercise 8.3.3

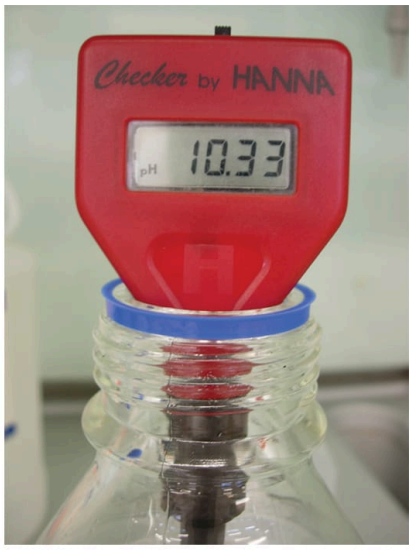
The hydronium ion concentration of vinegar is approximately 4×10^{-3} M. What are the corresponding values of pOH and pH ?

Answer available at the end of this section.

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 8.3.3).



(a)



(b)

Figure 8.3.3: (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 8.3.4). The acid-base equilibria that enable use of these indicator dyes for pH measurements are described in a later section of this chapter.



Figure 8.3.4: (a) A solution containing a dye mixture, called universal indicator, takes on different colors depending upon its pH. (b) Convenient test strips, called pH paper, contain embedded indicator dyes that yield pH-dependent color changes on contact with aqueous solutions.(credit: modification of work by Sahar Atwa)

Answers

Exercise 8.3.1

5.70

Exercise 8.3.2

12 *M*

Exercise 8.3.3

pOH = 11.6, pH = 2.4

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8.4: Relative Strengths of Acids and Bases

Learning Objectives

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

- 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

Acid and Base Ionization Constants

The relative strength of an acid or base is the extent to which it ionizes when dissolved in water. If the ionization reaction is essentially complete, the acid or base is termed *strong*; if relatively little ionization occurs, the acid or base is weak. As will be evident throughout the remainder of this chapter, there are many more weak acids and bases than strong ones. The most common strong acids and bases are listed in Figure 8.4.1.

6 Strong Acids		6 Strong Bases	
$HClO_4$	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$Ca(OH)_2$	calcium hydroxide
HNO_3	nitric acid	$Sr(OH)_2$	strontium hydroxide
H_2SO_4	sulfuric acid	$Ba(OH)_2$	barium hydroxide

Figure 8.4.1: Some of the common strong acids and bases are listed here.

The relative strengths of acids may be quantified by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions than do weaker acids. The equilibrium constant for an acid is called the acid-ionization constant, K_a. For the reaction of an acid HA:

$$\mathrm{HA\,(aq) + H_2O\,(l)} \rightleftharpoons \mathrm{H_3O^+\,(aq) + A^-\,(aq)}$$

the acid ionization constant is written

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

where the concentrations are those at equilibrium. Although water is a reactant in the reaction, it is the solvent as well, so we do not include $[\mathrm{H_2O}]$ in the equation.

Note

Equilibrium constant expressions are actually ratios of activities, and the value of *K* is determined at the limit of infinite dilution of the solutes. In these very dilute solutions, the activity of the solvent has a value of unity (1) and the activity of each solute can be approximated by its molar concentration.

The larger the K_a of an acid, the larger the concentration of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$ relative to the concentration of the nonionized acid, HA, in an equilibrium mixture, and the stronger the acid. An acid is classified as "strong" when it undergoes complete ionization, in which case the concentration of HA is zero and the acid ionization constant is immeasurably large ($K_a \approx \infty$). Acids that are partially ionized are called "weak," and their acid ionization constants may be experimentally measured. A table of ionization constants for weak acids is provided in Appendix 11.8.

To illustrate this idea, three acid ionization equations and K_a values are shown below. The ionization constants increase from first to last of the listed equations, indicating the relative acid strength increases in the order:

$$\mathrm{CH_3CO_2H} < \mathrm{HNO_2} < \mathrm{HSO_4^-}$$

as demonstrated with the equations below:

$$\mathrm{CH_3CO_2H\,(aq) + H_2O\,(l)} \rightleftharpoons \mathrm{H_3O^+\,(aq) + CH_3CO_2^-\,(aq)} \qquad K_a = 1.8 \times 10^{-5}$$

$$\mathrm{HNO_2\,(aq) + H_2O\,(l)} \rightleftharpoons \mathrm{H_3O^+\,(aq) + NO_2^-\,(aq)} \qquad K_a = 4.6 \times 10^{-4}$$

$$\mathrm{HSO_4^-\,(aq) + H_2O\,(aq)} \rightleftharpoons \mathrm{H_3O^+\,(aq) + SO_4^{2-}\,(aq)} \qquad K_a = 1.2 \times 10^{-2}$$

Another measure of the strength of an acid is its percent ionization. The percent ionization of a weak acid is defined in terms of the composition of an equilibrium mixture:

$$\%\text{ ionization } = \frac{[\mathrm{H_3O^+}]_{eq}}{[\mathrm{HA}]_0} \times 100$$

where the numerator is equivalent to the concentration of the acid's conjugate base (per stoichiometry, $[A^-] = [H_3O^+]$). Unlike the K_a value, the percent ionization of a weak acid varies with the initial concentration of acid, typically decreasing as concentration increases. Equilibrium calculations of the sort described later in this chapter can be used to confirm this behavior.

Example 8.4.1: 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:

$$\frac{[\mathrm{H_3O^+}]_{eq}}{[\mathrm{HNO_2}]_0} \times 100$$

Converting the provided pH to hydronium ion molarity yields

$$[\mathrm{H_3O^+}] = 10^{-2.09} = 0.0081M$$

Substituting this value and the provided initial acid concentration into the percent ionization equation gives

$$\frac{8.1 \times 10^{-3}}{0.125} \times 100 = 6.5\%$$

(Recall the provided pH value of 2.09 is logarithmic, and so it contains just two significant digits, limiting the certainty of the computed percent ionization.)

Exercise 8.4.1

Calculate the percent ionization of a 0.10-*M* solution of acetic acid with a pH of 2.89.

Answer available at the end of this section.

Link to Learning

View the simulation of strong and weak acids and bases at the molecular level.

Just as for acids, the relative strength of a base is reflected in the magnitude of its base-ionization constant (K_b) in aqueous solutions. In solutions of the same concentration, stronger bases ionize to a greater extent, and so yield higher hydroxide ion concentrations than do weaker bases. A stronger base has a larger ionization constant than does a weaker base. For the reaction of a base, B:

$$\mathrm{B\,(aq) + H_2O\,(l) \rightleftharpoons HB^+\,(aq) + OH^-\,(aq)},$$

the ionization constant is written as

$$K_b = \frac{[\mathrm{HB^+}]\,[\mathrm{OH^-}]}{[\mathrm{B}]}$$

Inspection of the data for three weak bases presented below shows the base strength increases in the order: $\mathrm{NO_2^- < CH_2CO_2^- < NH_3}$

$$\mathrm{NO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons HNO_2\,(aq) + OH^-\,(aq)} \qquad K_b = 2.17 \times 10^{-11}$$
$$\mathrm{CH_3\ CO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons CH_3\ CO_2\ H\,(aq) + OH^-\,(aq)} \qquad K_b = 5.6 \times 10^{-10}$$
$$\mathrm{NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)} \qquad K_b = 1.8 \times 10^{-5}$$

A table of ionization constants for weak bases appears in Appendix 11.9. As for acids, the relative strength of a base is also reflected in its percent ionization, computed as

$$\%\ \text{ionization} = \left(\frac{[\mathrm{OH^-}_{eq}]}{[\mathrm{B}]_0}\right) \times 100\%$$

but will vary depending on the base ionization constant and the initial concentration of the solution.

Relative Strengths of Conjugate Acid-Base Pairs

Brønsted-Lowry acid-base chemistry is the transfer of protons; thus, logic suggests a relation between the relative strengths of conjugate acid-base pairs. The strength of an acid or base is quantified in its ionization constant, K_a or K_b, which represents the extent of the acid or base ionization reaction. For the conjugate acid-base pair $\mathrm{HA\ /\ A^-}$, ionization equilibrium equations and ionization constant expressions are

$$\mathrm{HA\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq)}$$

with

$$K_a = \frac{[H3O^+][A^-]}{[HA]}$$

and

$$\mathrm{A^-\,(aq) + H_2O\,(l) \rightleftharpoons OH^-\,(aq) + HA\,(aq)}$$

with

$$K_b = \frac{[HA][OH-]}{[A-]}$$

Adding these two chemical equations yields the equation for the autoionization for water:

$$\cancel{HA(aq)} + \mathrm{H_2O\,(l)} + \cancel{A^-(aq)} + \mathrm{H_2O\,(l)} \rightleftharpoons \mathrm{H_3O^+\,(aq)} + \cancel{A^-(aq)} + \mathrm{OH^-\,(aq)} + \cancel{HA(aq)}$$

$$\mathrm{2\,H_2O\,(l)} \rightleftharpoons \mathrm{H_3O^+\,(aq)} + \mathrm{OH^-\,(aq)}$$

As discussed in another chapter on equilibrium, the equilibrium constant for a summed reaction is equal to the mathematical product of the equilibrium constants for the added reactions, and so

$$K_a \times K_b = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]} \times \frac{[\mathrm{HA}][\mathrm{OH^-}]}{[\mathrm{A^-}]} = [\mathrm{H_3O^+}][\mathrm{OH^-}] = K_w$$

This equation states the relation between ionization constants for any conjugate acid-base pair, namely, their mathematical product is equal to the ion product of water, K_w. By rearranging this equation, a reciprocal relation between the strengths of a conjugate acid-base pair becomes evident:

$$K_a = \frac{K_w}{K_b}$$

or

$$K_b = \frac{K_w}{K_a}$$

The inverse proportional relation between K_a and K_b means the stronger the acid or base, the weaker its **conjugate partner**. Figure 8.4.2: illustrates this relation for several conjugate acid-base pairs.

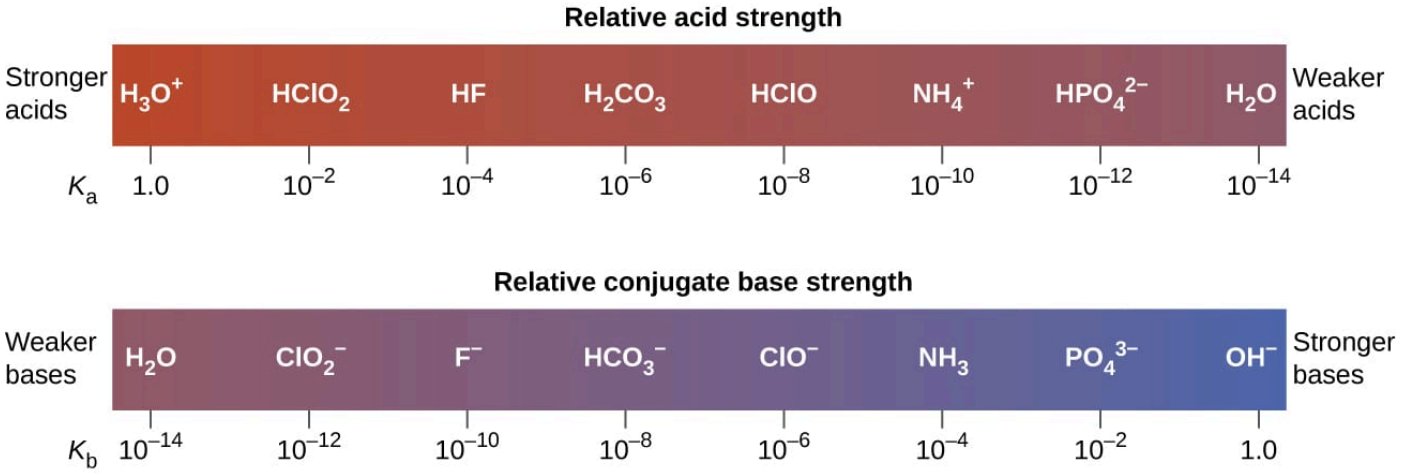


Figure 8.4.2: Relative strengths of several conjugate acid-base pairs are shown.

The listing of conjugate acid–base pairs shown in Figure 8.4.3: is arranged to show the relative strength of each species as compared with water, whose entries are highlighted in each of the table's columns. In the acid column, those species listed below water are weaker acids than water. These species do not undergo acid ionization in water; they are not Bronsted-Lowry acids. All the species listed above water are stronger acids, transferring protons to water to some extent when dissolved in an aqueous solution to generate hydronium ions. Species above water but below hydronium ion are *weak acids*, undergoing partial acid ionization, wheres those above hydronium ion are *strong acids* that are completely ionized in aqueous solution.

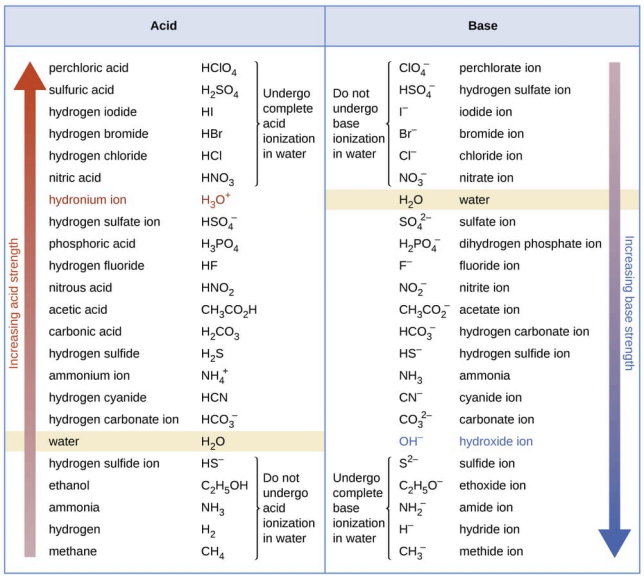


Figure 8.4.3: This figure shows strengths of conjugate acid-base pairs relative to the strength of water as the reference substance.

If all these strong acids are completely ionized in water, why does the column indicate they vary in strength, with nitric acid being the weakest and perchloric acid the strongest? Notice that the sole acid species present in an aqueous solution of any strong acid is $H_3O^+(aq)$, meaning that hydronium ion is the strongest acid that may exist in water; any stronger acid will react completely with water to generate hydronium ions. This limit on the acid strength of solutes in a solution is called a **leveling effect**. To measure the differences in acid strength for "strong" acids, the acids must be dissolved in a solvent that is *less basic* than water. In such solvents, the acids will be "weak," and so any differences in the extent of their ionization can be determined. For example, the binary hydrogen halides HCl, HBr, and HI are strong acids in water but weak acids in ethanol (strength increasing HCl < HBr < HI).

The right column of Figure 8.4.3 lists a number of substances in order of increasing base strength from top to bottom. Following the same logic as for the left column, species listed above water are weaker bases and so they don't undergo base ionization when dissolved in water. Species listed between water and its conjugate base, hydroxide ion, are weak bases that partially ionize. Species listed below hydroxide ion are strong bases that completely ionize in water to yield hydroxide ions (i.e., they are *leveled* to hydroxide). A comparison of the acid and base columns in this table supports the reciprocal relation between the strengths of conjugate acid-base pairs. For example, the conjugate bases of the strong acids (top of table) are all of negligible strength. A strong acid exhibits an immeasurably large K_a, and so its conjugate base will exhibit a K_b that is essentially zero:

- strong acid: $K_a \approx \infty$
- conjugate base: $K_b = K_w/K_a = K_w/\infty \approx 0$

A similar approach can be used to support the observation that conjugate acids of strong bases ($K_b \approx \infty$) are of negligible strength ($K_a \approx 0$).

Example 8.4.2: Calculating Ionization Constants for Conjugate Acid-Base Pairs

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 yields

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{2.17 \times 10^{-11}} = 4.6 \times 10^{-4}$$

This answer can be verified by finding the Ka for $\mathrm{HNO_2}$ in Appendix 11.8.

Exercise 8.4.2

Determine the relative acid strengths of $\mathrm{NH\ 4^+}$ and HCN by comparing their ionization constants. The ionization constant of HCN is given in Appendix 11.8 as 4.9×10^{-10}. The ionization constant of $\mathrm{NH\ 4^+}$ is not listed, but the ionization constant of its conjugate base, $\mathrm{NH_3}$, is listed as 1.8×10^{-5}.

Answer available at the end of this section.

Acid-Base Equilibrium Calculations

The chapter on chemical equilibria introduced several types of equilibrium calculations and the various mathematical strategies that are helpful in performing them. These strategies are generally useful for equilibrium systems regardless of chemical reaction class, and so they may be effectively applied to acid-base equilibrium problems. This section presents several example exercises involving equilibrium calculations for acid-base systems.



Litmus paper in action

Example 8.4.3: Determination of K_a from Equilibrium Concentrations

Acetic acid is the principal ingredient in vinegar (Figure 8.4.4) that provides its sour taste. At equilibrium, a solution contains $[\mathrm{CH_3CO_2H}] = 0.0787\ M$: and $\mathrm{H_3O^+}] = [\mathrm{CH_3CO_2}^-] = 0.00118\ M$. What is the value of K_a for acetic acid?



Figure 8.4.4: Vinegar contains acetic acid, a weak acid. (credit: modification of work by "HomeSpot HQ"/Flickr)

Solution

The relevant equilibrium equation and its equilibrium constant expression are shown below. Substitution of the provided equilibrium concentrations permits a straightforward calculation of the Ka for acetic acid.

$$\mathrm{CH_3CO_2H\,(aq) + H_2O\,(l) \;\rightleftharpoons\; H_3O^+\,(aq) + CH_3CO_2{}^-\,(aq)}$$

$$K_a = \frac{[\mathrm{H_3O^+}]\,[\mathrm{CH_3CO_2{}^-}]}{[\mathrm{CH_3CO_2H}]} = \frac{(0.00118)(0.00118)}{0.0787} = 1.77 \times 10^{-5}$$

Exercise 8.4.3

The $\mathrm{HSO_4{}^-}$ ion, weak acid used in some household cleansers:

$$\mathrm{HSO_4{}^-\,(aq) + H_2O\,(l) \;\rightleftharpoons\; H_3O^+\,(aq) + SO_4{}^{2-}\,(aq)}$$

What is the acid ionization constant for this weak acid if an equilibrium mixture has the following composition: $[\mathrm{H_3O^+}] = 0.027\ M$; $[\mathrm{HSO_4{}^-}] = 0.29\ M$; $[\mathrm{HSO_4{}^-}] = 0.29\ M$; and $[\mathrm{SO_4{}^{2-}}] = 0.13\ M$?

Answer available at the end of this section.

Example 8.4.4: Determination of K_b from Equilibrium Concentrations

Caffeine, $\mathrm{C_8H_{10}N_4O_2}$ is a weak base. What is the value of K_b for caffeine if a solution at equilibrium has $[\mathrm{C_8H_{10}N_4O_2}] = 0.050\ \mathrm{M}$, $[\mathrm{C_8H_{10}N_4O_2H^+}] = 5.0 \times 10^{-3}\ \mathrm{M}$, and $[\mathrm{OH^-}] = 2.5 \times 10^{-3}\ \mathrm{M}$?

Solution

The relevant equilibrium equation and its equilibrium constant expression are shown below. Substitution of the provided equilibrium concentrations permits a straightforward calculation of the K_b for caffeine.

$$\mathrm{C_8H_{10}N_4O_2\,(aq) + H_2O\,(l) \;\rightleftharpoons\; C_8H_{10}N_4O_2H^+\,(aq) + OH^-\,(aq)}$$

$$\begin{aligned} K_b &= [\mathrm{C_8H_{10}N_4O_2H^+}][\mathrm{OH^-}][\mathrm{C_8H_{10}N_4O_2}] \\ &= (5.0 \times 10^{-3})(2.5 \times 10^{-3})(0.050) \\ &= 2.5 \times 10^{-4} \end{aligned}$$

Exercise 8.4.4

What is the equilibrium constant for the ionization of the $\mathrm{HPO_4^{2-}}$ ion, a weak base

$$\mathrm{HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_2PO_4^{-}(aq) + OH^{-}(aq)}$$

if the composition of an equilibrium mixture is as follows: $[\mathrm{OH^-}] = 1.3 \times 10^{-6} M$; $[\mathrm{H_2PO_4^-}] = 0.042 M$; and $[\mathrm{HPO_4^{2-}}] = 0.341 M$?

Answer available at the end of this section.

Example 8.4.5: Determination of K_a or K_b from pH

The pH of a 0.0516-M solution of nitrous acid, $\mathrm{HNO_2}$, is 2.34. What is its K_a?

$$\mathrm{HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)}$$

Solution

The nitrous acid concentration provided is a *formal* concentration, one that does not account for any chemical equilibria that may be established in solution. Such concentrations are treated as "initial" values for equilibrium calculations using the ICE table approach. Notice the initial value of hydronium ion is listed as *approximately* zero because a small concentration of $\mathrm{H_3O^+}$ is present ($1 \times \times 10^{-7}$ M) due to the autoprotolysis of water. In many cases, such as all the ones presented in this chapter, this concentration is much less than that generated by ionization of the acid (or base) in question and may be neglected.

The pH provided is a logarithmic measure of the hydronium ion concentration resulting from the acid ionization of the nitrous acid, and so it represents an "equilibrium" value for the ICE table:

$$[\mathrm{H_3O^+}] = 10^{-2.34} = 0.0046 \text{ M}$$

The ICE table for this system is then

	$\mathrm{HNO_2}$ + $\mathrm{H_2O}$ $\rightleftharpoons$ $\mathrm{H_3O^+}$ + $\mathrm{NO_2^-}$			
Initial concentration (*M*)	0.0516		~0	0
Change (*M*)	−0.0046		+0.0046	+0.0046
Equilibrium concentration (*M*)	0.0470		0.0046	0.0046

Finally, calculate the value of the equilibrium constant using the data in the table:

$$K_a = \frac{[\mathrm{H_3O^+}]\,[\mathrm{NO_2^-}]}{[\mathrm{HNO_2}]} = \frac{(0.0046)(0.0046)}{(0.0470)} = 4.6 \times 10^{-4}$$

Exercise 8.4.5

The pH of a solution of household ammonia, a 0.950-M solution of $\mathrm{NH_3}$, is 11.612. What is K_b for $\mathrm{NH_3}$.

Answer available at the end of this section.

Example 8.4.6: Calculating Equilibrium Concentrations in a Weak Acid Solution

Formic acid, $\mathrm{HCO_2H}$, is one irritant that causes the body's reaction to some ant bites and stings (Figure 8.4.5).



Figure 8.4.5: The pain of some ant bites and stings is caused by formic acid. (credit: John Tann)

What is the concentration of hydronium ion and the pH of a 0.534-*M* solution of formic acid?

$$\mathrm{HCO_2H\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + HCO_2^-\,(aq)} \quad K_a = 1.8 \times 10^{-4}$$

Solution

The ICE table for this system is

	$\mathrm{HCO_2H}$ +	$\mathrm{H_2O}$ $\rightleftharpoons$	$\mathrm{H_3O^+}$ +	$\mathrm{HCO_2^-}$
Initial concentration (*M*)	0.534		~0	0
Change (*M*)			$+x$	$+x$
Equilibrium concentration (*M*)	$0.534 - x$		x	x

Substituting the equilibrium concentration terms into the K_a expression gives

$$K_a = 1.8 \times 10^{-4} = \frac{[\mathrm{H_3O^+}]\,[\mathrm{HCO_2^-}]}{[\mathrm{HCO_2H}]}$$

$$= \frac{(x)(x)}{0.534 - x} = 1.8 \times 10^{-4}$$

The relatively large initial concentration and small equilibrium constant permits the simplifying assumption that *x* will be much lesser than 0.534, and so the equation becomes

$$K_a = 1.8 \times 10^{-4} = \frac{x^2}{0.534}$$

Solving the equation for x yields

$$\begin{aligned} x^2 &= 0.534 \times \left(1.8 \times 10^{-4}\right) = 9.6 \times 10^{-5} \\ x &= \sqrt{9.6 \times 10^{-5}} \\ &= 9.8 \times 10^{-3} M \end{aligned}$$

To check the assumption that *x* is small compared to 0.534, its relative magnitude can be estimated:

$$\frac{x}{0.534} = \frac{9.8 \times 10^{-3}}{0.534} = 1.8 \times 10^{-2} (1.8\% \text{ of } 0.534)$$

Because *x* is less than 5% of the initial concentration, the assumption is valid.

As defined in the ICE table, *x* is equal to the equilibrium concentration of hydronium ion:

$$x = \left[\mathrm{H_3O^+}\right] = 0.0098 \text{ M}$$

Finally, the pH is calculated to be

$$\mathrm{pH} = -\log\left[\mathrm{H_3O^+}\right] = -\log(0.0098) = 2.01$$

Exercise 8.4.6

Only a small fraction of a weak acid ionizes in aqueous solution. What is the percent ionization of a 0.100-*M* solution of acetic acid, CH_3CO_2H?

$$\mathrm{CH_3CO_2H\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + CH_3CO_2^-\,(aq)} \quad K_a = 1.8 \times 10^{-5}$$

Answer available at the end of this section.

Example 8.4.7: Calculating Equilibrium Concentrations in a Weak Base Solution

Find the concentration of hydroxide ion, the pOH, and the pH of a 0.25-*M* solution of trimethylamine, a weak base:

$$\mathrm{(CH_3)_3N\,(aq) + H_2O\,(l) \rightleftharpoons (CH_3)_3NH^+\,(aq) + OH^-\,(aq)} \quad K_b = 6.3 \times 10^{-5}$$

Solution

The ICE table for this system is

	$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$			
Initial concentration (*M*)	0.25		0	~0
Change (*M*)	−*x*		*x*	*x*
Equilibrium concentration (*M*)	0.25 + (−*x*)		0 + *x*	~0 + *x*

Substituting the equilibrium concentration terms into the K_b expression gives

$$K_b = \frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]} = \frac{(x)(x)}{0.25 - x} = 6.3 \times 10^{-5}$$

Assuming $x \ll 0.25$ and solving for x yields

$$x = 4.0 \times 10^{-3}\ \text{M}$$

This value is less than 5% of the initial concentration (0.25), so the assumption is justified. As defined in the ICE table, x is equal to the equilibrium concentration of hydroxide ion:

$$\begin{aligned}[OH^-] &=\sim 0 + x \\ &= x = 4.0 \times 10^{-3} M\end{aligned}$$

The pOH is calculated to be

$$\text{pOH} = -\log\left(4.0 \times 10^{-3}\right) = 2.40$$

Using the relation introduced in the previous section of this chapter:

$$\text{pH} + \text{pOH} = pK_w = 14.00$$

permits the computation of pH:

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.40 = 11.60$$

Exercise 8.4.7

Calculate the hydroxide ion concentration and the percent ionization of a 0.0325-*M* solution of ammonia, a weak base with a K_b of 1.76×10^{-5}.

Answer available at the end of this section.

In some cases, the strength of the weak acid or base and its formal (initial) concentration result in an appreciable ionization. Though the ICE strategy remains effective for these systems, the algebra is a bit more involved because the simplifying assumption that *x* is negligible cannot be made. Calculations of this sort are demonstrated in Example 8.4.8 below.

Example 8.4.8: Calculating Equilibrium Concentrations without Simplifying Assumptions

Sodium bisulfate, NaHSO4, is used in some household cleansers as a source of the HSO_4^- ion, a weak acid. What is the pH of a 0.50-M solution of HSO_4^-?

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq) \quad K_a = 1.2 \times 10^{-2}$$

Solution

The ICE table for this system is

	HSO_4^- + H_2O ⇌	H_3O^+ +	SO_4^{2-}
Initial concentration (*M*)	0.50	~0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$0.50 - x$	x	x

Substituting the equilibrium concentration terms into the K_a expression gives

$$K_a = 1.2 \times 10^{-2} = \frac{[H_3O^+]\,[SO_4^{2-}]}{[HSO_4^-]} = \frac{(x)(x)}{0.50 - x}$$

If the assumption that $x \ll 0.5$ is made, simplifying and solving the above equation yields

$$x = 0.077 \text{ M}$$

This value of x is clearly not significantly less than 0.50 *M*; rather, it is approximately 15% of the initial concentration: When we check the assumption, we calculate:

$$\frac{x}{[HSO_4^-]_i}$$

$$\frac{x}{0.50} = \frac{7.7 \times 10^{-2}}{0.50} = 0.15(15\%)$$

Because the simplifying assumption is not valid for this system, the equilibrium constant expression is solved as follows:

$$K_a = 1.2 \times 10^{-2} = \frac{(x)(x)}{0.50 - x}$$

Rearranging this equation yields

$$6.0 \times 10^{-3} - 1.2 \times 10^{-2}x = x^2$$

Writing the equation in quadratic form gives

$$x^2 + 1.2 \times 10^{-2}x - 6.0 \times 10^{-3} = 0$$

Solving for the two roots of this quadratic equation results in a negative value that may be discarded as physically irrelevant and a positive value equal to *x*. As defined in the ICE table, x is equal to the hydronium concentration.

$$x = [H3O^+] = 0.072 \text{ M}$$

$$\text{pH} = -\log[H_3O^+] = -\log(0.072) = 1.14$$

Exercise 8.4.8

Calculate the pH in a 0.010-*M* solution of caffeine, a weak base:

$$C_8H10N_4O_2\,(aq) + H_2O\,(l) \rightleftharpoons C_8H10N_4O_2H^+\,(aq) + OH^-\,(aq) \quad K_b = 2.5 \times 10^{-4}$$

Answer available at the end of this section.

Effect of Molecular Structure on Acid-Base Strength

Binary Acids and Bases

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 8.4.6).

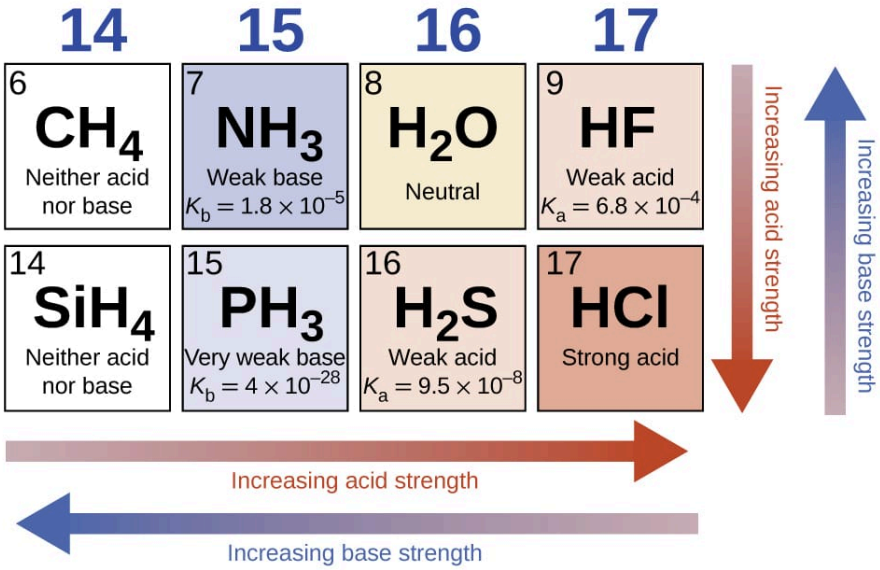
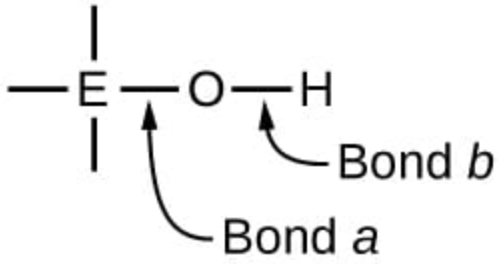


Figure 8.4.6: The figure shows trends in the strengths of binary acids and bases.

Ternary Acids and Bases

Ternary compounds composed of hydrogen, oxygen, and some third element ("E") may be structured as depicted in the image below. In these compounds, the central E atom is bonded to one or more O atoms, and at least one of the O atoms is also bonded to an H atom, corresponding to the general molecular formula $O_mE(OH)_n$. These compounds may be acidic, basic, or amphoteric depending on the properties of the central E atom. Examples of such compounds 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 $8.4.7$).

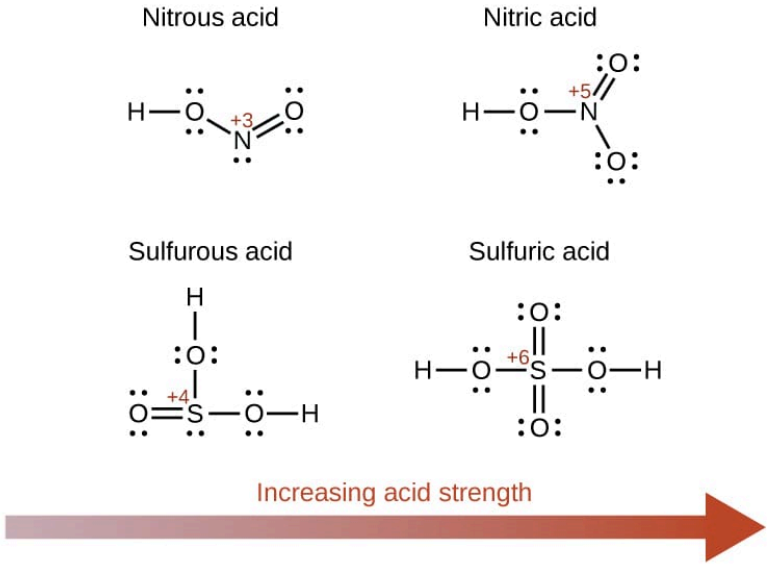


Figure $8.4.7$: As the oxidation number of the central atom E increases, the acidity also increases.

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 $Al(H_2O)_3(OH)_3$, is reflected in its solubility in both strong acids and strong bases. In strong bases, the relatively insoluble hydrated aluminum hydroxide, $Al(H_2O)_3(OH)_3$, is converted into the soluble ion, $[Al(H_2O)_2(OH)_4]^-$, by reaction with hydroxide ion:

$$Al(H_2O)_3(OH)_3\,(aq) + OH^-\,(aq) \rightleftharpoons H_2O\,(l) + [Al(H_2O)_2(OH)_4]^-\,(aq)$$

In this reaction, a proton is transferred from one of the aluminum-bound H2O molecules to a hydroxide ion in solution. The

$Al(H_2O)_3(OH)_3$ 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 $[Al(H_2O)_6]^{3+}$ by reaction with hydronium ion:

$$3\,H_3O^+\,(aq) + Al(H_2O)_3(OH)_3\,(aq) \rightleftharpoons Al(H_2O)_6{}^{3+}\,(aq) + 3\,H_2O\,(l)$$

In this case, protons are transferred from hydronium ions in solution to $Al(H_2O)_3(OH)_3$, and the compound functions as a base.

Answers

Exercise 8.4.1

1.3% ionized

Exercise 8.4.2

$NH_4{}^+$ is the slightly stronger acid (K_a for $NH_4{}^+$ is 5.6×10^{-10}).

Exercise 8.4.3

K_a for $HSO_4{}^- = 1.2 \times 10^{-2}$

Exercise 8.4.4

K_b for $HPO_4{}^{2-}$ is 1.6×10^{-7}

Exercise 8.4.5

$K_b = 1.8 \times 10^{-5}$

Exercise 8.4.6

percent ionization = 1.3%

Exercise 8.4.7

7.56×10^{-4} M, 2.33%

Exercise 8.4.8

pH = 11.16

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8.5: Hydrolysis of Salt

Learning Objectives

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

- Predict whether a salt solution will be acidic, basic, or neutral
- Calculate the concentrations of the various species in a salt solution
- Describe the acid ionization of hydrated metal ions

Salts with Acidic Ions

Salts are ionic compounds composed of cations and anions, either of which may be capable of undergoing an acid or base ionization reaction with water. Aqueous salt solutions, therefore, may be acidic, basic, or neutral, depending on the relative acid-base strengths of the salt's constituent ions. For example, dissolving ammonium chloride in water results in its dissociation, as described by the equation

$$\mathrm{NH_4Cl\,(s)} \rightleftharpoons \mathrm{NH_4{}^+\,(aq)} + \mathrm{Cl^-\,(aq)}$$

The ammonium ion is the conjugate acid of the base ammonia, NH_3; its acid ionization (or acid hydrolysis) reaction is represented by

$$\mathrm{NH_4{}^+\,(aq)} + \mathrm{H_2O\,(l)} \rightleftharpoons \mathrm{H_3O^+\,(aq)} + \mathrm{NH_3\,(aq)} \quad K_a = K_w/K_b$$

Since ammonia is a weak base, K_b is measurable and $K_a > 0$ (ammonium ion is a weak acid).

The chloride ion is the conjugate base of hydrochloric acid, and so its base ionization (or *base hydrolysis*) reaction is represented by

$$\mathrm{Cl^-\,(aq)} + \mathrm{H_2O\,(l)} \rightleftharpoons \mathrm{HCl\,(aq)} + \mathrm{OH^-\,(aq)} \quad K_b = K_w/K_a$$

Since HCl is a strong acid, K_a is immeasurably large and $K_b \approx 0$ (chloride ions don't undergo appreciable hydrolysis).

Thus, dissolving ammonium chloride in water yields a solution of weak acid cations (NH_4^+) and inert anions (Cl^-), resulting in an acidic solution.

Example 8.5.1: Calculating the pH of an Acidic Salt Solution

Aniline is an amine that is used to manufacture dyes. It is isolated as anilinium chloride, 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 anilinium chloride

$$\mathrm{C_6H_5NH_3{}^+\,(aq)} + \mathrm{H_2O\,(l)} \rightleftharpoons \mathrm{H_3O^+\,(aq)} + \mathrm{C_6H_5NH_2\,(aq)}$$

Solution

The K_a for anilinium ion is derived from the K_b for its conjugate base, aniline (see Appendix 11.8):

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.3 \times 10^{-10}} = 2.3 \times 10^{-5}$$

Using the provided information, an ICE table for this system is prepared:

	$C_6H_5NH_3^+$ + H_2O ⇌	$C_6H_5NH_2$ +	H_3O^+
Initial concentration (*M*)	0.233	0	~0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$0.233 - x$	x	x

Substituting these equilibrium concentration terms into the K_a expression gives

$$K_a = \frac{[C_6H_5NH_2]\,[H_3O^+]}{[C_6H_5NH_3^+]}$$

$$2.3 \times 10^{-5} = \frac{(x)(x)}{0.233 - x}$$

Assuming $x \ll 0.233$, the equation is simplified and solved for x:

$$2.3 \times 10^{-5} = \frac{x^2}{0.233}$$

$$x = 0.0023\ \text{M}$$

The ICE table defines x as the hydronium ion molarity, and so the pH is computed as

$$\text{pH} = -\log\left[H_3O^+\right] = -\log(0.0023) = 2.64$$

Exercise 8.5.1

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^- and.

Which is the stronger acid $C_6H_5NH_3^+$ or NH_4^+?

Answer available at the end of this section.

Salts with Basic Ions

As another example, consider dissolving sodium acetate in water:

$$NaCH_3CO_2\,(s) \rightleftharpoons Na^+\,(aq) + CH_3CO_2^-\,(aq)$$

The sodium ion does not undergo appreciable acid or base ionization and has no effect on the solution pH. This may seem obvious from the ion's formula, which indicates no hydrogen or oxygen atoms, but some dissolved metal ions function as weak acids, as addressed later in this section.

The acetate ion, $CH_3CO_2^-\,(aq)$, is the conjugate base of acetic acid, CH_3CO_2H, and so its base ionization (or *base hydrolysis*) reaction is represented by

$$CH_3CO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons CH_3\ CO_2\ H\,(aq) + OH\,-(aq) \quad K_b = K_w/K_a$$

Because acetic acid is a weak acid, its K_a is measurable and $K_b > 0$ (acetate ion is a weak base).

Dissolving sodium acetate in water yields a solution of inert cations (Na^+) and weak base anions $(CH_3CO_2^-)$, resulting in a basic solution.

Example 8.5.2: Equilibrium in a Solution of a Salt of a Weak Acid and a Strong Base

Determine the acetic acid concentration in a solution with and $[\mathrm{OH}^-] = 0.050\ \mathrm{M}$ and $[\mathrm{OH}^-] = 2.5 \times 10^{-6} M$ at equilibrium. The reaction is:

$$\mathrm{CH_3CO_2}^-(\mathrm{aq}) + \mathrm{H_2O}(\mathrm{l}) \rightleftharpoons \mathrm{CH_3CO_2H}(\mathrm{aq}) + \mathrm{OH}^-(\mathrm{aq})$$

Solution

The provided equilibrium concentrations and a value for the equilibrium constant will permit calculation of the missing equilibrium concentration. The process in question is the base ionization of acetate ion, for which

$$\mathrm{CH_3CO_2}^-(\mathrm{aq}) + \mathrm{H_2O}(\mathrm{l}) \rightleftharpoons \mathrm{CH_3CO_2H}(\mathrm{aq}) + \mathrm{OH}^-(\mathrm{aq})$$

Substituting the available values into the K_b expression gives

$$K_b = \frac{[CH_3CO_2H]\,[\mathrm{OH}^-]}{[\mathrm{CH_3CO_2}^-]} = 5.6 \times 10^{-10}$$

$$= \frac{[\mathrm{CH_3CO_2H}]\,(2.5 \times 10^{-6})}{(0.050)} = 5.6 \times 10^{-10}$$

Solving the above equation for the acetic acid molarity yields $[\mathrm{CH_3CO_2H}] = 1.1 \times 10^{-5}\ \mathrm{M}$.

Exercise 8.5.2

What is the pH of a 0.083-*M* solution of NaCN?

Answer available at the end of this section.

Salts with Acidic and Basic Ions

Some salts are composed of both acidic and basic ions, and so the pH of their solutions will depend on the relative strengths of these two species. Likewise, some salts contain a single ion that is amphiprotic, and so the relative strengths of this ion's acid and base character will determine its effect on solution pH. For both types of salts, a comparison of the K_a and K_b values allows prediction of the solution's acid-base status, as illustrated in the following example exercise.

Example 8.5.3: 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. Na_2HPO_4
d. 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 is inert and will not affect pH. The bromide ion is the conjugate base of a strong acid, and so it is of negligible base strength (no appreciable base ionization). The solution is neutral.

(b) The $\mathrm{Na^+}$ cation is inert and will not affect the pH of the solution; while the $\mathrm{HCO_3^-}$ anion is amphiprotic. The K_a of $\mathrm{HCO_3^-}$ is 4.7×10^{-11}, and its K_b is:

$$\frac{1.0 \times 10^{-14}}{4.3 \times 10^{-7}} = 2.3 \times 10^{-8}$$

Since $K_b \gg K_a$, the solution is basic.

(c) The $\mathrm{Na^+}$ cation is inert and will not affect the pH of the solution, while the $\mathrm{HPO_4^{2-}}$ anion is amphiprotic. The K_a of $\mathrm{HPO_4^{2-}}$ is 4.2×10^{-13}, and its K_b is:

$$\frac{1.0 \times 10^{-14}}{6.2 \times 10^{-8}} = 1.6 \times 10^{-7}$$

Because $K_b \gg K_a$, the solution is basic.

(d) The $\mathrm{NH_4^+}$ ion is acidic (see above discussion) and the $\mathrm{F^-}$ ion is basic (conjugate base of the weak acid HF). Comparing the two ionization constants: K_a of $\mathrm{NH_4^+}$ is 5.6 × 10−10 and the K_b of $\mathrm{F^-}$ is 1.6×10^{-11}, so the solution is acidic, since $K_a > K_b$.

Exercise 8.5.3

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. $(NH_4)_2CO_3$

Answer available at the end of this section.

The Ionization of Hydrated Metal Ions

Unlike the group 1 and 2 metal ions of the preceding examples (Na^+, Ca^{2+}, etc.), some metal ions function as acids in aqueous solutions. These ions are not just loosely solvated by water molecules when dissolved, instead they are covalently bonded to a fixed number of water molecules to yield a complex ion (see chapter on coordination chemistry). As an example, the dissolution of aluminum nitrate in water is typically represented as

$$\mathrm{Al(NO_3)_3\,(s)} \rightleftharpoons \mathrm{Al^{3+}\,(aq) + 3\,NO_3^-\,(aq)}$$

However, the aluminum(III) ion actually reacts with six water molecules to form a stable complex ion, and so the more explicit representation of the dissolution process is

$$\mathrm{Al(NO_3)_3\,(s) + 6\,H_2O\,(l)} \rightleftharpoons \mathrm{Al(H_2O)_6^{3+}\,(aq) + 3\,NO_3^-\,(aq)}$$

As shown in Figure 8.5.1, the ions involve bonds between a central Al atom and the O atoms of the six water molecules. Consequently, the bonded water molecules' O–H bonds are more polar than in nonbonded water molecules, making the bonded molecules more prone to donation of a hydrogen ion:

$$\mathrm{Al(H_2O)_6^{3+}\,(aq) + H_2O\,(l)} \rightleftharpoons \mathrm{H_3O^+\,(aq) + Al(H_2O)_5(OH)^{2+}\,(aq)} \qquad K_a = 1.4 \times 10^{-5}$$

The conjugate base produced by this process contains five other bonded water molecules capable of acting as acids, and so the sequential or step-wise transfer of protons is possible as depicted in few equations below:

$$\mathrm{Al(H_2O)_6}^{3+}\,(\mathrm{aq}) + \mathrm{H_2O}\,(\mathrm{l}) \rightleftharpoons \mathrm{H_3O^+}\,(\mathrm{aq}) + \mathrm{Al(H_2O)_5(OH)}^{2+}\,(\mathrm{aq})$$
$$\mathrm{Al(H_2O)_5(OH)}^{2+}\,(\mathrm{aq}) + \mathrm{H_2O}\,(\mathrm{l}) \rightleftharpoons \mathrm{H_3O^+}\,(\mathrm{aq}) + \mathrm{Al(H_2O)_4(OH)_2}^{+}\,(\mathrm{aq})$$
$$\mathrm{Al(H_2O)_4(OH)_2}^{+}\,(\mathrm{aq}) + \mathrm{H_2O}\,(\mathrm{l}) \rightleftharpoons \mathrm{H_3O^+}\,(\mathrm{aq}) + \mathrm{Al(H_2O)_3(OH)_3}\,(\mathrm{aq})$$

This is an example of a polyprotic acid, the topic of discussion in a later section of this chapter.

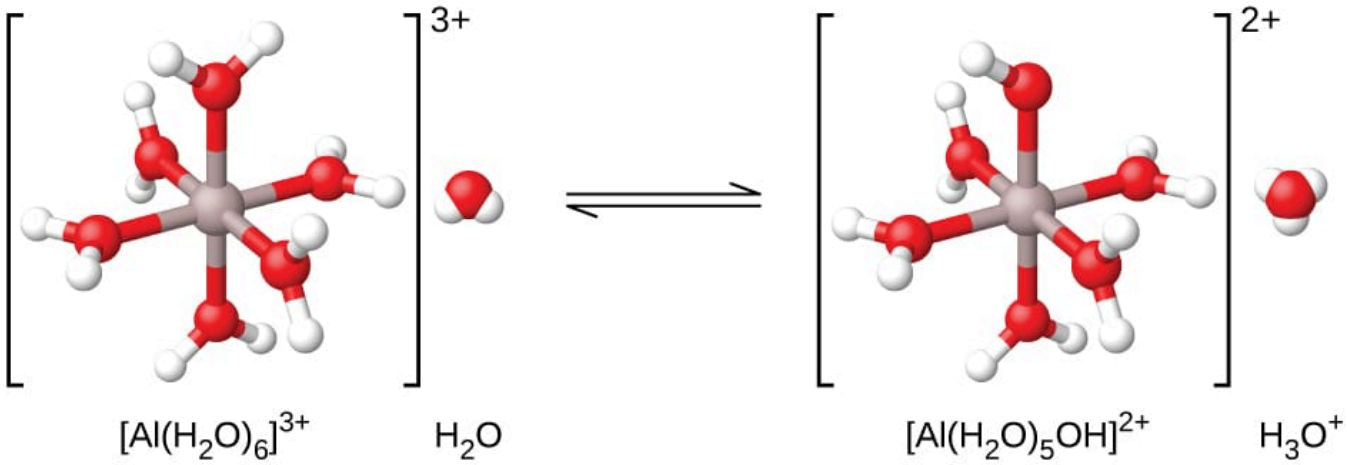


Figure 8.5.1: When an aluminum ion reacts with water, the hydrated aluminum ion becomes a weak acid.

Aside from the alkali metals (group 1) and some alkaline earth metals (group 2), most other metal ions will undergo acid ionization to some extent when dissolved in water. The acid strength of these complex ions typically increases with increasing charge and decreasing size of the metal ions. The first-step acid ionization equations for a few other acidic metal ions are shown below:

$$\mathrm{Fe(H_2O)_6}^{3+}\,(\mathrm{aq}) + \mathrm{H_2O}\,(\mathrm{l}) \rightleftharpoons \mathrm{H_3O^+}\,(\mathrm{aq}) + \mathrm{Fe(H_2O)_5(OH)}^{2+}\,(\mathrm{aq}) \qquad pK_a = 2.74$$
$$\mathrm{Cu(H_2O)_6}^{2+}\,(\mathrm{aq}) + \mathrm{H_2O}\,(\mathrm{l}) \rightleftharpoons \mathrm{H_3O^+}\,(\mathrm{aq}) + \mathrm{Cu(H_2O)_5(OH)}^{+}\,(\mathrm{aq}) \qquad pK_a = \sim 6.3$$
$$\mathrm{Zn(H_2O)_4}^{2+}\,(\mathrm{aq}) + \mathrm{H_2O}\,(\mathrm{l}) \rightleftharpoons \mathrm{H_3O^+}\,(\mathrm{aq}) + \mathrm{Zn(H_2O)_3(OH)}^{+}\,(\mathrm{aq}) \qquad pK_a = 9.6$$

Example 8.5.4: 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

The equation for the reaction and K_a are:

$$\mathrm{Al(H_2O)_6}^{3+}\,(\mathrm{aq}) + \mathrm{H_2O}\,(\mathrm{l}) \rightleftharpoons \mathrm{H_3O^+}\,(\mathrm{aq}) + \mathrm{Al(H_2O)_5(OH)}^{2+}\,(\mathrm{aq}) \qquad K_a = 1.4 \times 10^{-5}$$

An ICE table with the provided information is

	$Al(H_2O)_6^{3+} + H_2O \rightleftharpoons H_3O^+ + Al(H_2O)_5(OH)^{2+}$		
Initial concentration (*M*)	0.10	~0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$0.10 - x$	x	x

Substituting the expressions for the equilibrium concentrations into the equation for the ionization constant yields:

$$K_a = \frac{[H_3O^+]\,[Al(H_2O)_5(OH)^{2+}]}{[Al(H_2O)_6{}^{3+}]}$$

$$= \frac{(x)(x)}{0.10 - x} = 1.4 \times 10^{-5}$$

Assuming $x \ll 0.10$ and solving the simplified equation gives:

$$x = 1.2 \times 10^{-3}\ \text{M}$$

The ICE table defined x as equal to the hydronium ion concentration, and so the pH is calculated to be

$$[H_3O^+] = 0 + x = 1.2 \times 10^{-3}\ \text{M}$$

$$\text{pH} = -\log\left[H_3O^+\right] = 2.92$$

Therefore this is an acidic solution.

Exercise 8.5.4

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 available at the end of this section.

Answers

Exercise 8.5.1

$[H_3O^+] = 7.5 \times 10^{-6}$ M; is the stronger acid.

Exercise 8.5.2

11.11

Exercise 8.5.3

(a) basic; (b) neutral; (c) acidic; (d) basic

Exercise 8.5.4

$2.1 \times 10^{-5} M$

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8.6: Polyprotic Acids

Learning Objectives

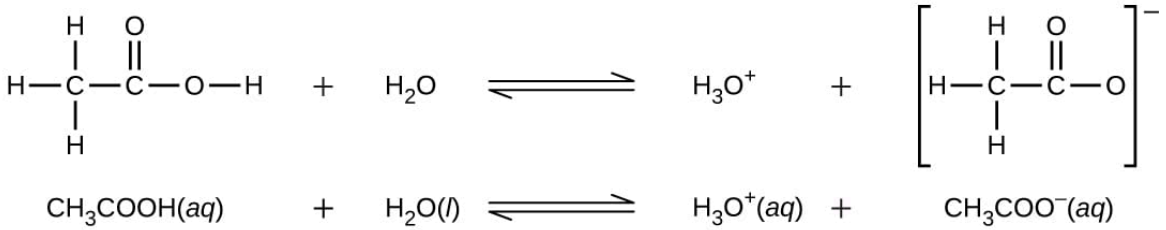
By the end of this section, you will be able to:

- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton

Acids are classified by the number of protons per molecule that they can give up in a reaction. Acids such as HCl, $\mathrm{HNO_3}$, and HCN that contain one ionizable hydrogen atom in each molecule are called **monoprotic acids**. Their reactions with water are:

$$\mathrm{HCl\,(aq) + H_2\,O\,(l) \longrightarrow H_3O^+\,(aq) + Cl^-\,(aq)}$$
$$\mathrm{HNO_3\,(aq) + H_2\,O\,(l) \longrightarrow H_3O^+\,(aq) + NO_3{}^-\,(aq)}$$
$$\mathrm{HCN\,(aq) + H_2\,O\,(l) \rightleftharpoons H_3O^+\,(aq) + CN^-\,(aq)}$$

Even though it contains four hydrogen atoms, acetic acid, $\mathrm{CH_3CO_2H}$, is also monoprotic because only the hydrogen atom from the carboxyl group ($-\mathrm{COOH}$) reacts with bases:



Similarly, monoprotic bases are bases that will accept a single proton.

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:

$$\mathrm{H_2\,SO_4\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + HSO_4{}^-\,(aq)} \qquad \text{(First ionization)}$$

with $K_{a1} > 10^2$.

$$\mathrm{HSO_4{}^-\,(aq) + H_2\,O\,(l) \rightleftharpoons H_3O^+\,(aq) + SO_4{}^{2-}\,(aq)} \qquad \text{(Second ionization)}$$

with $K_{a2} = 1.2 \times 10^{-2}$.

This stepwise ionization process occurs for all polyprotic acids. Carbonic acid, $\mathrm{H_2CO_3}$, is an example of a weak diprotic acid. The first ionization of carbonic acid yields hydronium ions and bicarbonate ions in small amounts.

$$\mathrm{H_2\,CO_3\,(aq) + H_2\,O\,(l) \rightleftharpoons H_3O^+\,(aq) + HCO_3{}^-\,(aq)} \qquad \text{(First ionization)}$$

with

$$K_{H_2CO_3} = \frac{[\mathrm{H_3O^+}]\,[\mathrm{HCO_3{}^-}]}{[\mathrm{H_2CO_3}]} = 4.3 \times 10^{-7}$$

The bicarbonate ion can also act as an acid. It ionizes and forms hydronium ions and carbonate ions in even smaller quantities.

$$\mathrm{HCO_3{}^-\,(aq) + H_2\,O\,(l) \rightleftharpoons H_3O^+\,(aq) + CO_3{}^{2-}\,(aq)} \qquad \text{(Second ionization)}$$

with

$$K_{HCO_3^-} = \frac{[H_3O^+]\,[CO_3^{2-}]}{[HCO_3^-]} = 4.7 \times 10^{-11}$$

$K_{H_2CO_3}$ is larger than $K_{HCO_3^-}$ 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 formed by the ionization of H_2CO_3 ionizes to give hydronium ions (and carbonate ions), and the concentrations of H_3O^+ and 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 approach is demonstrated in the following example and exercise.

Example 8.6.1: Ionization of a Diprotic Acid

"Carbonated water" contains a palatable amount of dissolved carbon dioxide. The solution is acidic because CO_2 reacts with water to form carbonic acid, H_2CO_3. What are and in a saturated solution of CO_2 with an initial $[H_2CO_3] = 0.033\,M$?

$$H_2\,CO_3\,(aq) + H_2\,O\,(l) \rightleftharpoons H_3O^+\,(aq) + HCO_3^-\,(aq) \quad K_{a1} = 4.3 \times 10^{-7}$$

$$HCO_3^-\,(aq) + H_2\,O\,(l) \rightleftharpoons H_3O^+\,(aq) + CO_3^{2-}\,(aq) \quad K_{a2} = 4.7 \times 10^{-11}$$

Solution

As indicated by the ionization constants, H_2CO_3 is a much stronger acid than so the stepwise ionization reactions may be treated separately.

The first ionization reaction is

$$H_2\,CO_3\,(aq) + H_2\,O\,(l) \rightleftharpoons H_3O^+\,(aq) + HCO_3^-\,(aq) \quad K_{a1} = 4.3 \times 10^{-7}$$

Using provided information, an ICE table for this first step is prepared:

	H_2CO_3 +	H_2O $\rightleftharpoons$	H_3O^+ +	HCO_3^-
Initial concentration (*M*)	0.033		~0	0
Change (*M*)	$-x$		$+x$	$+x$
Equilibrium concentration (*M*)	$0.033 - x$		x	x

Substituting the equilibrium concentrations into the equilibrium equation gives

$$K_{H_2CO_3} = \frac{[H3O^+]\,[HCO_3^-]}{[H_2CO_3]} = \frac{(x)(x)}{0.033 - x} = 4.3 \times 10^{-7}$$

Assuming $x \ll 0.033$ and solving the simplified equation yields

$$x = 1.2 \times 10^{-4}$$

The ICE table defined *x* as equal to the bicarbonate ion molarity and the hydronium ion molarity:

$$[H_2CO_3] = 0.033M$$

$$[H3O^+] = [HCO_3^-] = 1.2 \times 10^{-4}M$$

Using the bicarbonate ion concentration computed above, the second ionization is subjected to a similar equilibrium calculation:

$$\mathrm{HCO_3}^-(\mathrm{aq}) + \mathrm{H_2\ O(l)} \rightleftharpoons \mathrm{H_3O^+(aq)} + \mathrm{CO_3}^{2-}(\mathrm{aq})$$

$$K_{HCO_3^-} = \frac{[H3O^+]\left[CO_3^{2-}\right]}{\left[HCO_3^-\right]} = \frac{\left(1.2 \times 10^{-4}\right)\left[CO_3^{2-}\right]}{1.2 \times 10^{-4}}$$

$$\left[CO_3^{2-}\right] = \frac{\left(4.7 \times 10^{-11}\right)\left(1.2 \times 10^{-4}\right)}{1.2 \times 10^{-4}} = 4.7 \times 10^{-11} M$$

To summarize: at equilibrium $[\mathrm{H_2CO_3}] = 0.033M$; $[\mathrm{H_3O^+}] = 1.2 \times 10^{-4}$; $[\mathrm{HCO_3}^-] = 1.2 \times 10^{-4}\ M$; $[\mathrm{CO_{32}}^-] = 4.7 \times 10^{-11}\ M$.

Exercise 8.6.1

The concentration of $\mathrm{H_2S}$ in a saturated aqueous solution at room temperature is approximately 0.1 M. Calculate, $\mathrm{H_3O^+}$, $[\mathrm{HS}^-]$, and $[\mathrm{S}^{2-}]$ in the solution:

$$\mathrm{H_2\ S(aq)} + \mathrm{H_2\ O(l)} \rightleftharpoons \mathrm{H_3O^+(aq)} + \mathrm{HS}^-(\mathrm{aq}) \quad K_{a1} = 8.9 \times 10^{-8}$$

$$\mathrm{HS}^-(\mathrm{aq}) + \mathrm{H_2\ O(l)} \rightleftharpoons \mathrm{H_3O^+(aq)} + \mathrm{S}^{2-}(\mathrm{aq}) \quad K_{a2} = 1.0 \times 10^{-19}$$

Answer available at the end of this section.

A **triprotic acid** is an acid that has three ionizable H atoms. Phosphoric acid is one example:

$$\mathrm{H_3PO_4(aq)} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{H_3O^+(aq)} + \mathrm{H_2\ PO_4}^-(\mathrm{aq}) \quad K_{a1} = 7.5 \times 10^{-3} \qquad \text{(First ionization)}$$

$$\mathrm{H_2PO_4}^-(\mathrm{aq}) + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{H_3O^+(aq)} + \mathrm{HPO_4}^{2-}(\mathrm{aq}) \quad K_{a2} = 6.2 \times 10^{-8} \qquad \text{(Second ionization)}$$

$$\mathrm{HPO_4}^{2-}(\mathrm{aq}) + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{H_3O^+(aq)} + \mathrm{PO_4}^{3-}(\mathrm{aq}) \quad K_{a3} = 4.2 \times 10^{-13} \qquad \text{(Third ionization)}$$

As for the diprotic acid examples, each successive ionization reaction is less extensive than the former, reflected in decreasing values for the stepwise acid ionization constants. 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 $\mathrm{H_3PO_4}$ complicated. However, because the successive ionization constants differ by a factor of 10^5 to 10^6, large differences exist in the small changes in concentration accompanying the ionization reactions. This allows the use of math-simplifying assumptions and processes, as demonstrated in the examples above.

Polyprotic bases are capable of accepting more than one hydrogen ion. The carbonate ion is an example of a **diprotic base**, because it can accept two protons, as shown below. Similar to the case for polyprotic acids, note the ionization constants decrease with ionization step. Likewise, equilibrium calculations involving polyprotic bases follow the same approaches as those for polyprotic acids.

$$\mathrm{H_2\ O(l)} + \mathrm{CO_3}^{2-}(\mathrm{aq}) \rightleftharpoons \mathrm{HCO_3}^-(\mathrm{aq}) + \mathrm{OH}^-(\mathrm{aq}) \quad K_{b1} = 2.1 \times 10^{-4}$$

$$\mathrm{H_2\ O(l)} + \mathrm{HCO_3}^-(\mathrm{aq}) \rightleftharpoons \mathrm{H_2\ CO_3(aq)} + \mathrm{OH}^-(\mathrm{aq}) \quad K_{b2} = 2.3 \times 10^{-8}$$

Learning Objectives

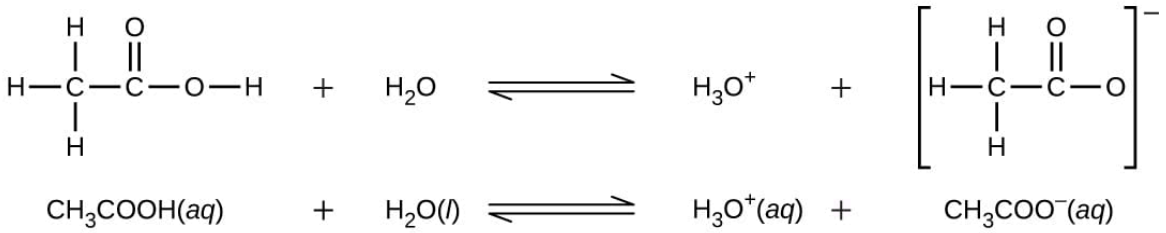
By the end of this section, you will be able to:

- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton

Acids are classified by the number of protons per molecule that they can give up in a reaction. Acids such as HCl, $\mathrm{HNO_3}$, and HCN that contain one ionizable hydrogen atom in each molecule are called **monoprotic acids**. Their reactions with water are:

$$\mathrm{HCl\,(aq) + H_2\ O\,(l) \longrightarrow H_3O^+\,(aq) + Cl^-\,(aq)}$$
$$\mathrm{HNO_3\,(aq) + H_2\ O\,(l) \longrightarrow H_3O^+\,(aq) + NO_3{}^-\,(aq)}$$
$$\mathrm{HCN\,(aq) + H_2\ O\,(l) \rightleftharpoons H_3O^+\,(aq) + CN^-\,(aq)}$$

Even though it contains four hydrogen atoms, acetic acid, $\mathrm{CH_3CO_2H}$, is also monoprotic because only the hydrogen atom from the carboxyl group ($-\mathrm{COOH}$) reacts with bases:



Similarly, monoprotic bases are bases that will accept a single proton.

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:

$$\mathrm{H_2\ SO_4\,(aq) + H_2O\,(l)\ \rightleftharpoons H_3O^+\,(aq) + HSO_4{}^-\,(aq)} \qquad \text{(First ionization)}$$

with $K_{a1} > 10^2$.

$$\mathrm{HSO_4{}^-\,(aq) + H_2\ O\,(l)\ \rightleftharpoons H_3O^+\,(aq) + SO_4{}^{2-}\,(aq)} \qquad \text{(Second ionization)}$$

with $K_{a2} = 1.2 \times 10^{-2}$.

This stepwise ionization process occurs for all polyprotic acids. Carbonic acid, $\mathrm{H_2CO_3}$, is an example of a weak diprotic acid. The first ionization of carbonic acid yields hydronium ions and bicarbonate ions in small amounts.

$$\mathrm{H_2\ CO_3\,(aq) + H_2\ O\,(l)\ \rightleftharpoons H_3O^+\,(aq) + HCO_3{}^-\,(aq)} \qquad \text{(First ionization)}$$

with

$$K_{H_2CO_3} = \frac{[\mathrm{H_3O^+}]\,[\mathrm{HCO_3{}^-}]}{[\mathrm{H_2CO_3}]} = 4.3 \times 10^{-7}$$

The bicarbonate ion can also act as an acid. It ionizes and forms hydronium ions and carbonate ions in even smaller quantities.

$$\mathrm{HCO_3{}^-\,(aq) + H_2\ O\,(l)\ \rightleftharpoons H_3O^+\,(aq) + CO_3{}^{2-}\,(aq)} \qquad \text{(Second ionization)}$$

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 $\mathrm{H_2CO_3}$ is the dominant producer of hydronium ion in the solution. This means that little of the formed by the ionization of $\mathrm{H_2CO_3}$ ionizes to give hydronium ions (and carbonate ions), and the concentrations of $\mathrm{H_3O^+}$ and are practically equal in a pure aqueous solution of $\mathrm{H_2CO_3}$.

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 approach is demonstrated in the following example and exercise.

Example 8.6.1: Ionization of a Diprotic Acid

"Carbonated water" contains a palatable amount of dissolved carbon dioxide. The solution is acidic because CO_2 reacts with water to form carbonic acid, H_2CO_3. What are and in a saturated solution of CO_2 with an initial $[H_2CO_3] = 0.033\,M$?

$$H_2\ CO_3\,(aq) + H_2\ O\,(l) \rightleftharpoons H_3O^+\,(aq) + HCO_3^-\,(aq) \quad K_{a1} = 4.3 \times 10^{-7}$$

$$HCO_3^-\,(aq) + H_2\ O\,(l) \rightleftharpoons H_3O^+\,(aq) + CO_3^{2-}\,(aq) \quad K_{a2} = 4.7 \times 10^{-11}$$

Solution

As indicated by the ionization constants, H_2CO_3 is a much stronger acid than so the stepwise ionization reactions may be treated separately.

The first ionization reaction is

$$H_2\ CO_3\,(aq) + H_2\ O\,(l) \rightleftharpoons H_3O^+\,(aq) + HCO_3^-\,(aq) \quad K_{a1} = 4.3 \times 10^{-7}$$

Using provided information, an ICE table for this first step is prepared:

	H_2CO_3 + H_2O $\rightleftharpoons$	H_3O^+	+ HCO_3^-
Initial concentration (*M*)	0.033	~0	0
Change (*M*)	−*x*	+*x*	+*x*
Equilibrium concentration (*M*)	0.033 − *x*	*x*	*x*

Substituting the equilibrium concentrations into the equilibrium equation gives

$$K_{H_2CO_3} = \frac{[H3O^+]\,[HCO_3^-]}{[H_2CO_3]} = \frac{(x)(x)}{0.033 - x} = 4.3 \times 10^{-7}$$

Assuming $x \ll 0.033$ and solving the simplified equation yields

$$x = 1.2 \times 10^{-4}$$

The ICE table defined *x* as equal to the bicarbonate ion molarity and the hydronium ion molarity:

$$[H_2CO_3] = 0.033M$$

$$[H3O^+] = [HCO_3^-] = 1.2 \times 10^{-4}M$$

Using the bicarbonate ion concentration computed above, the second ionization is subjected to a similar equilibrium calculation:

$$HCO_3^-\,(aq) + H_2\ O\,(l) \rightleftharpoons H_3O^+\,(aq) + CO_3^{2-}\,(aq)$$

$$K_{HCO_{3^-}} = \frac{[H3O^+]\,[CO_3^{2-}]}{[HCO_3^-]} = \frac{\left(1.2 \times 10^{-4}\right)\,[CO_3^{2-}]}{1.2 \times 10^{-4}}$$

$$[CO_3^{2-}] = \frac{\left(4.7 \times 10^{-11}\right)\left(1.2 \times 10^{-4}\right)}{1.2 \times 10^{-4}} = 4.7 \times 10^{-11}M$$

To summarize: at equilibrium $[H_2CO_3] = 0.033M$; $[H_3O^+] = 1.2 \times 10^{-4}$; $[HCO_3^-] = 1.2 \times 10^{-4}\ M$; $[CO_{32}^-] = 4.7 \times 10^{-11}\ M$.

Exercise 8.6.1

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 available at the end of this section.

A **triprotic acid** is an acid that has three ionizable H atoms. Phosphoric acid is one example:

$$H_3PO_4\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + H_2PO_4^-\,(aq) \quad K_{a1} = 7.5 \times 10^{-3} \qquad \text{(First ionization)}$$

$$H_2PO_4^-\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + HPO_4^{2-}\,(aq) \quad K_{a2} = 6.2 \times 10^{-8} \qquad \text{(Second ionization)}$$

$$HPO_4^{2-}\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + PO_4^{3-}\,(aq) \quad K_{a3} = 4.2 \times 10^{-13} \qquad \text{(Third ionization)}$$

As for the diprotic acid examples, each successive ionization reaction is less extensive than the former, reflected in decreasing values for the stepwise acid ionization constants. 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, large differences exist in the small changes in concentration accompanying the ionization reactions. This allows the use of math-simplifying assumptions and processes, as demonstrated in the examples above.

Polyprotic bases are capable of accepting more than one hydrogen ion. The carbonate ion is an example of a **diprotic base**, because it can accept two protons, as shown below. Similar to the case for polyprotic acids, note the ionization constants decrease with ionization step. Likewise, equilibrium calculations involving polyprotic bases follow the same approaches as those for polyprotic acids.

$$H_2O\,(l) + CO_3^{2-}\,(aq) \rightleftharpoons HCO_3^-\,(aq) + OH^-\,(aq) \quad K_{b1} = 2.1 \times 10^{-4}$$

$$H_2O\,(l) + HCO_3^-\,(aq) \rightleftharpoons H_2CO_3\,(aq) + OH^-\,(aq) \quad K_{b2} = 2.3 \times 10^{-8}$$

Answers

Exercise 8.6.1

$[H_2S] = 0.1\ M$

$[H_3O^+] = [HS^-] = 0.000094\ M$

$[\blacksquare] = 1 \times 10^{-19}\ M$

Exercise 8.6.1

$[H_2S] = 0.1\ M$

$[H_3O^+] = [HS^-] = 0.000094\ M$

$[\blacksquare] = 1 \times 10^{-19}\ M$

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8.7: Buffers

Learning Objectives

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

- 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

A solution containing appreciable amounts of a weak conjugate acid-base pair is called a buffer solution, or a **buffer**. Buffer solutions resist a change in pH when small amounts of a strong acid or a strong base are added (Figure 8.7.1). A solution of acetic acid and sodium acetate (CH_3COOH + CH_3COONa) is an example of a buffer that consists of a weak acid and its salt. An example of a buffer that consists of a weak base and its salt is a solution of ammonia and ammonium chloride ($NH_3(aq)$ + $NH_4Cl(aq)$).

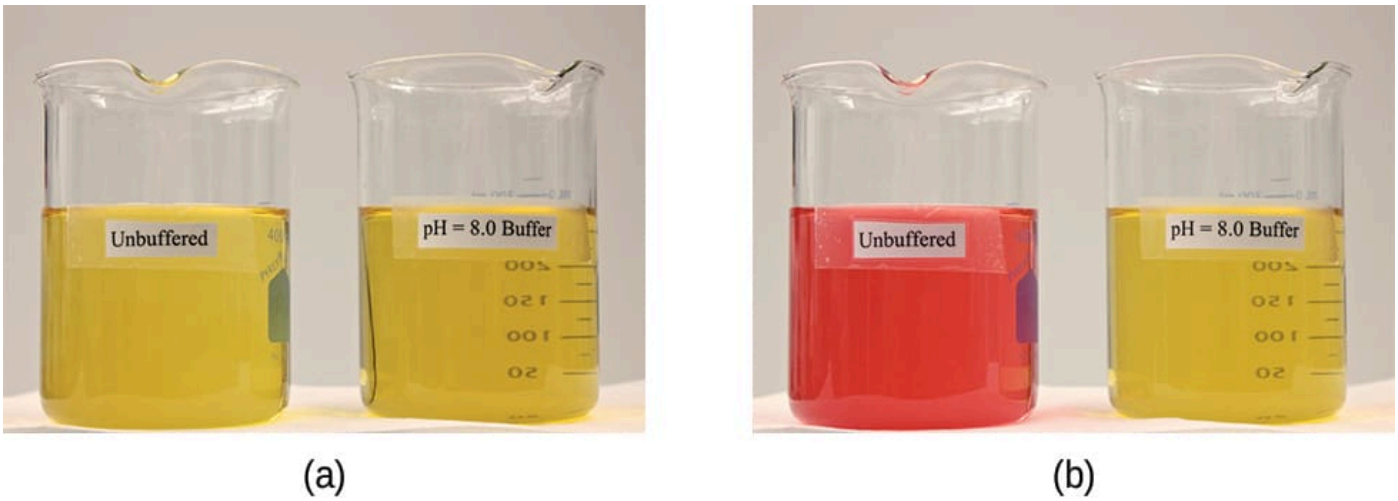


Figure 8.7.1: (a) The unbuffered solution on the left and the buffered solution on the right have the same pH (pH 8); they are basic, showing the yellow color of the indicator methyl orange at this pH. (b) After the addition of 1 mL of a 0.01-*M* HCl solution, the buffered solution has not detectably 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

To illustrate the function of a buffer solution, consider a mixture of roughly equal amounts of acetic acid and sodium acetate. The presence of a weak conjugate acid-base pair in the solution imparts the ability to neutralize modest amounts of added strong acid or base. For example, strong base added to this solution will neutralize hydronium ion, causing the acetic acid ionization equilibrium to shift to the right and generate additional amounts of the weak conjugate base (acetate ion):

$$\mathrm{CH_3\ CO_2\ H\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + CH_3\ CO_2^-\,(aq)}$$

Likewise, strong acid added to this buffer solution will shift the above ionization equilibrium left, producing additional amounts of the weak conjugate acid (acetic acid). Figure 8.7.2 provides a graphical illustration of the changes in conjugate-partner concentration that occur in this buffer solution when strong acid and base are added. The buffering action of the solution is essentially a result of the added strong acid and base being converted to the weak acid and base that make up the buffer's conjugate pair. The weaker acid and base undergo only slight ionization, as compared with the complete ionization of the strong acid and base, and the solution pH, therefore, changes much less drastically than it would in an unbuffered solution.

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

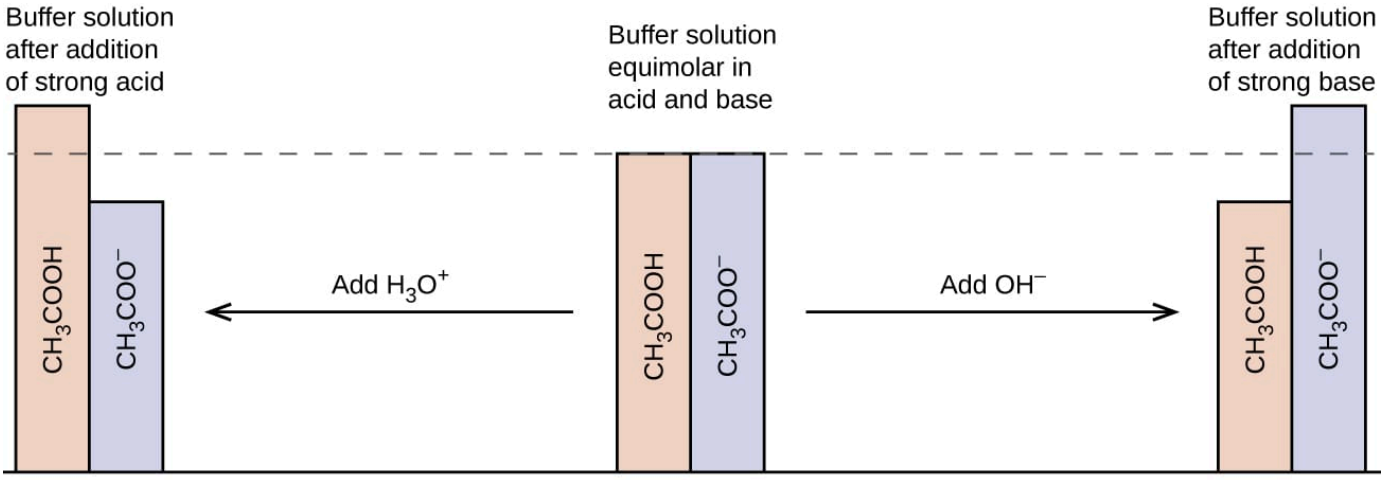


Figure 8.7.2: Buffering action in a mixture of acetic acid and acetate salt.

Example 8.20: 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 affect 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 NaOH is added to 100 mL of this buffer.
c. For comparison, calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of a solution of an unbuffered solution with a pH of 4.74.

Solution

(a) Following the ICE approach to this equilibrium calculation yields the following:

	CH_3CO_2H + H_2O ⇌	H_3O^+ +	$CH_3CO_2^-$
Initial concentration (*M*)	0.10	~0	0.10
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$0.10 - x$	x	$0.10 + x$

Substituting the equilibrium concentration terms into the K_a expression, assuming $x \ll 0.10$, and solving the simplified equation for x yields

$$x = 1.8 \times 10^{-5}\ \text{M}$$

$$[\text{H}_3\text{O}^+] = 0 + x = 1.8 \times 10^{-5}\ \text{M}$$

$$\begin{aligned} pH &= -\log[\text{H}_3\text{O}^+] \\ &= -\log\left(1.8 \times 10^{-5}\right) \\ &= 4.74 \end{aligned}$$

(b) Calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of this buffer.

Adding strong base will neutralize some of the acetic acid, yielding the conjugate base acetate ion. Compute the new concentrations of these two buffer components, then repeat the equilibrium calculation of part (a) using these new concentrations.

$$0.0010 \cancel{L} \times \left(\frac{0.10 \text{ mol NaOH}}{1 \text{ L}} \right) = 1.0 \times 10^{-4} \text{ mol NaOH}$$

The initial molar amount of acetic acid is

$$0.100 \cancel{L} \times \left(\frac{0.100 \text{ mol } CH_3CO_2H}{1 \cancel{L}} \right) = 1.00 \times 10^{-2} \text{ mol } CH_3CO_2H$$

The amount of acetic acid remaining after some is neutralized by the added base is

$$\left(1.0 \times 10^{-2}\right) - \left(0.01 \times 10^{-2}\right) = 0.99 \times 10^{-2} \text{ mol } CH_3CO_2H$$

The newly formed acetate ion, along with the initially present acetate, gives a final acetate concentration of

$$\left(1.0 \times 10^{-2}\right) + \left(0.01 \times 10^{-2}\right) = 1.01 \times 10^{-2} \text{ mol } NaCH_3CO_2$$

Compute molar concentrations for the two buffer components:

$$[CH_3CO_2H] = \frac{9.9 \times 10^{-3} \text{ mol}}{0.101 \text{ L}} = 0.098 \text{ M}$$

$$[NaCH_3CO_2] = \frac{1.01 \times 10^{-2} \text{ mol}}{0.101 \text{ L}} = 0.100 \text{ M}$$

Using these concentrations, the pH of the solution may be computed as in part (a) above, yielding pH = 4.75 (only slightly different from that prior to adding the strong base).

(c) For comparison, calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of a solution of an unbuffered solution with a pH of 4.74.

The amount of hydronium ion initially present in the solution is

$$\left[H_3O^+\right] = 10^{-4.74} = 1.8 \times 10^{-5} \text{ M}$$

$$\text{mol } H_3O^+ = (0.100 \text{ L})\left(1.8 \times 10^{-5} \text{ M}\right) = 1.8 \times 10^{-6} \text{ mol } H_3O^+$$

The amount of hydroxide ion added to the solution is

$$molOH^- = (0.0010L)(0.10M) = 1.0 \times 10^{-4} molOH^-$$

The added hydroxide will neutralize hydronium ion via the reaction

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

The 1:1 stoichiometry of this reaction shows that an excess of hydroxide has been added (greater molar amount than the initially present hydronium ion).

The amount of hydroxide ion remaining is

$$1.0 \times 10^{-4} mol - 1.8 \times 10^{-6} mol = 9.8 \times 10^{-5} molOH^-$$

corresponding to a hydroxide molarity of

$$\frac{9.8 \times 10^{-5} \text{ mol } OH^-}{0.101 \text{ L}} = 9.7 \times 10^{-4} M$$

The pH of the solution is then calculated to be

$$pH = 14.00 - pOH = 14.00 - -\log\left(9.7 \times 10^{-4}\right) = 10.99$$

In this unbuffered solution, addition of the base results in a significant rise in pH (from 4.74 to 10.99) compared with the very slight increase observed for the buffer solution in part (b) (from 4.74 to 4.75).

Exercise 8.7.1

Show that adding 1.0 mL of $0.10\ \mathrm{M\ HCl}$ changes the pH of 100 mL of a $1.8 \times 10^{-5}\ \mathrm{M\ HCl}$ solution from 4.74 to 3.00.

Answer available at the end of this section.

Buffer Capacity

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant (Figure 8.7.3). Instead, the ability of a buffer solution to resist changes in pH relies on the presence of appreciable amounts of its conjugate weak acid-base pair. When enough strong acid or base is added to substantially lower the concentration of either member of the buffer pair, the buffering action within the solution is compromised.



Figure 8.7.3: 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. For example, 1 L of a solution that is 1.0 *M* in acetic acid and 1.0 *M* in sodium acetate has a greater buffer capacity than 1 L of a solution that is 0.10 *M* in acetic acid and 0.10 *M* in sodium acetate even though both solutions have the same pH. The first solution has more buffer capacity because it contains more acetic acid and acetate ion.

Selection of Suitable Buffer Mixtures

There are two useful rules of thumb for selecting buffer mixtures:

1. A good buffer mixture should have about equal concentrations of both of its components. A buffer solution has generally lost its usefulness when one component of the buffer pair is less than about 10% of the other. Figure 8.7.4 shows how pH changes for an acetic acid-acetate ion buffer as base is added. The initial pH is 4.74. A change of 1 pH unit occurs when the acetic acid concentration is reduced to 11% of the acetate ion concentration.

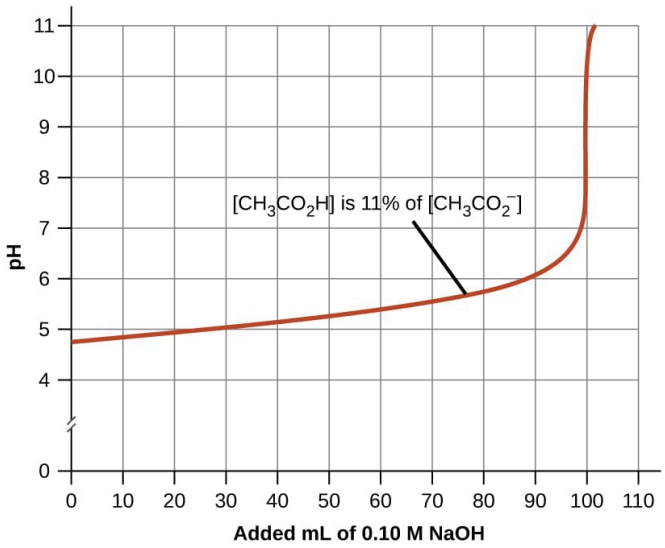


Figure 8.7.4: Change in pH as an increasing amount of a 0.10-*M* NaOH solution is added to 100 mL of a buffer solution in which, initially, $[CH_3CO_2H]$ = 0.10 *M* and Note the greatly diminished buffering action occurring after the buffer capacity has been reached, resulting in drastic rises in pH on adding more strong base.

2. 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.

Blood is an important example of a buffered solution, with the principal acid and ion responsible for the buffering action being carbonic acid, H_2CO_3, and the bicarbonate ion, HCO_3^-. When a hydronium ion is introduced to the blood stream, it is removed primarily by the reaction:

$$H_3O^+(aq) + HCO_3^-(aq) \longrightarrow H_2\ CO_3(aq) + H_2O(l)$$

An added hydroxide ion is removed by the reaction:

$$OH^-(aq) + H_2CO_3(aq) \longrightarrow HCO_3^-(aq) + H_2O(l)$$

The added strong acid or base is thus effectively converted to the much weaker acid or base of the buffer pair (H_3O^+ is converted to H_2CO_3 and OH^- is converted to HCO_3^-). The pH of human blood thus remains very near the value determined by the buffer pairs pKa, in this case, 7.35. Normal variations in blood pH are usually less than 0.1, and pH changes of 0.4 or greater are likely to be fatal.

The Henderson-Hasselbalch Equation

The ionization-constant expression for a solution of a weak acid can be written as:

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

Rearranging to solve for $[H_3O^+]$ yields:

$$[H_3O^+] = K_a \times \frac{[HA]}{[A^-]}$$

Taking the negative logarithm of both sides of this equation gives

$$-\log[H_3O^+] = -\log K_a - \log\frac{[HA]}{[A^-]}$$

which can be written as

$$pH = pK_a + \log \frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$$

where pK_a is the negative of the logarithm of the ionization constant of the weak acid (pK_a = –log K_a). This equation relates the pH, the ionization constant of a weak acid, and the concentrations of the weak conjugate acid-base pair in a buffered solution. Scientists often use this expression, called the Henderson-Hasselbalch equation, to calculate the pH of buffer solutions. It is important to note that the "*x* is small" assumption must be valid to use this equation.

Portrait of a Chemist: Lawrence Joseph Henderson and Karl Albert Hasselbalch

Lawrence Joseph Henderson (1878–1942) was an American physician, biochemist and physiologist, to name only a few of his many pursuits. He obtained a medical degree from Harvard and then spent 2 years studying in Strasbourg, then a part of Germany, before returning to take a lecturer position at Harvard. He eventually became a professor at Harvard and worked there his entire life. He discovered that the acid-base balance in human blood is regulated by a buffer system formed by the dissolved carbon dioxide in blood. He wrote an equation in 1908 to describe the carbonic acid-carbonate buffer system in blood. Henderson was broadly knowledgeable; in addition to his important research on the physiology of blood, he also wrote on the adaptations of organisms and their fit with their environments, on sociology and on university education. He also founded the Fatigue Laboratory, at the Harvard Business School, which examined human physiology with specific focus on work in industry, exercise, and nutrition.

In 1916, Karl Albert Hasselbalch (1874–1962), a Danish physician and chemist, shared authorship in a paper with Christian Bohr in 1904 that described the Bohr effect, which showed that the ability of hemoglobin in the blood to bind with oxygen was inversely related to the acidity of the blood and the concentration of carbon dioxide. The pH scale was introduced in 1909 by another Dane, Sørensen, and in 1912, Hasselbalch published measurements of the pH of blood. In 1916, Hasselbalch expressed Henderson's equation in logarithmic terms, consistent with the logarithmic scale of pH, and thus the Henderson-Hasselbalch equation was born.

How Sciences Interconnect: 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:

$$\mathrm{CO_2\,(g) + 2\,H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq) \rightleftharpoons HCO_3^-\,(aq) + H_3O^+\,(aq)}$$

The concentration of carbonic acid, $\mathrm{H_2CO_3}$ is approximately 0.0012 *M*, and the concentration of the hydrogen carbonate ion, 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:

$$pH = pK_a + \log \frac{[\text{ base }]}{[\text{ acid }]} = 6.4 + \log \frac{0.024}{0.0012} = 7.7$$

The fact that the $\mathrm{H_2CO_3}$ concentration is significantly lower than that of the $\mathrm{HCO_3^-}$ 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 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.

Link to Learning

View information on the buffer system encountered in natural waters.

Answers

Exercise 8.7.1

Initial pH of 1.8×10^{-5} M HCl;

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log[1.8 \times 10^{-5}] = 4.74$$

Moles of H_3O^+ in 100 mL 1.8×10^{-5} M HCl;

$$(1.8 \times 10^{-5} \text{ moles/L}) \times (0.100 \text{ L} = 1.8 \times 10^{-6} \text{ mol}$$

Moles of H_3O^+ added by addition of 1.0 mL of 0.10 *M* HCl:

$$(0.10 \text{ moles/L}) \times (0.0010 \text{ L}) = 1.0 \times 10^{-4} \text{ mol}$$

Final pH after addition of 1.0 mL of 0.10 *M* HCl:

$$pH = -\log\left[\text{H}_3\text{O}^+\right] = -\log\left(\frac{\text{total moles } \text{H}_3\text{O}^+}{\text{total volume}}\right) = -\log\left(\frac{1.0 \times 10^{-4} mol + 1.8 \times 10^{-6} \text{ mol}}{101 \text{ mL}\left(\frac{1 \text{ L}}{1000 \text{ mL}}\right)}\right) = 3.00$$

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8.8: Acid-Base Titrations

Learning Objectives

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

- Interpret titration curves for strong and weak acid-base systems
- Compute sample pH at important stages of a titration
- Explain the function of acid-base indicators

As seen in the chapter on the stoichiometry of chemical reactions, titrations can be used to quantitatively analyze solutions for their acid or base concentrations. In this section, we will explore the underlying chemical equilibria that make acid-base titrimetry a useful analytical technique.

Titration Curves

A titration curve is a plot of some solution property versus the amount of added titrant. For acid-base titrations, solution pH is a useful property to monitor because it varies predictably with the solution composition and, therefore, may be used to monitor the titration's progress and detect its end point. The following example exercise demonstrates the computation of pH for a titration solution after additions of several specified titrant volumes. The first example involves a strong acid titration that requires only stoichiometric calculations to derive the solution pH. The second example addresses a weak acid titration requiring equilibrium calculations.

Example 8.8.1: Calculating pH for Titration Solutions: Strong Acid/Strong Base

A titration is carried out for 25.00 mL of 0.100 *M* HCl (strong acid) with 0.100 *M* of a strong base NaOH (the titration curve is shown in Figure 8.8.1). Calculate the pH at these volumes of added base solution:

a. 0.00 mL
b. 12.50 mL
c. 25.00 mL
d. 37.50 mL

Solution

(a) Titrant volume = 0 mL. The solution pH is due to the acid ionization of HCl. Because this is a strong acid, the ionization is complete and the hydronium ion molarity is 0.100 *M*. The pH of the solution is then

$$\mathrm{pH} = -\log(0.100) = 1.000$$

(b) Titrant volume = 12.50 mL. Since the acid sample and the base titrant are both monoprotic and equally concentrated, this titrant addition involves less than a stoichiometric amount of base, and so it is completely consumed by reaction with the excess acid in the sample. The concentration of acid remaining is computed by subtracting the consumed amount from the initial amount and then dividing by the solution volume:

$$\left[\mathrm{H_3O^+}\right] = \frac{n\left(\mathrm{H^+}\right)}{V} = \frac{0.002500\ \mathrm{mol} \times \left(\frac{1000\ mL}{1\ L}\right) - 0.100\ M \times 12.50\ mL}{25.00\ mL + 12.50\ mL} = 0.0333\ M$$

(c) Titrant volume = 25.00 mL. This titrant addition involves a stoichiometric amount of base (the *equivalence point*), and so only products of the neutralization reaction are in solution (water and NaCl). Neither the cation nor the anion of this salt undergo acid-base ionization; the only process generating hydronium ions is the autoprotolysis of water. The solution is neutral, having a pH = 7.00.

(d) Titrant volume = 37.50 mL. This involves the addition of titrant in excess of the equivalence point. The solution pH is then calculated using the concentration of hydroxide ion:

$$n\left(OH^-\right)_0 > n\left(H^+\right)_0$$

$$[\mathrm{OH^-}] = \frac{n\left(\mathrm{OH^-}\right)}{\mathrm{V}} = \frac{0.100\ \mathrm{M} \times 37.50\ \mathrm{mL} - 0.002500\ \mathrm{mol} \times \left(\frac{1000\ \mathrm{mL}}{1\ \mathrm{L}}\right)}{25.00\ \mathrm{mL} + 37.50\ \mathrm{mL}} = 0.0200\ \mathrm{M}$$

$$\mathrm{pH} = 14 - \mathrm{pOH} = 14 + \log([\mathrm{OH^-}]) = 14 + \log(0.0200) = 12.30$$

Exercise 8.8.1

Calculate the pH for the strong acid/strong base titration between 50.0 mL of 0.100 *M* HNO_3(*aq*) and 0.200 *M* NaOH (titrant) at the listed volumes of added base: 0.00 mL, 15.0 mL, 25.0 mL, and 40.0 mL.

Answer available at the end of this section.

Example 8.8.2: Titration of a Weak Acid with a Strong Base

Consider the titration of 25.00 mL of 0.100 *M* CH_3CO_2H with 0.100 *M* NaOH. The reaction can be represented as:

$$\mathrm{CH_3CO_2H + OH^- \longrightarrow CH_3CO_2^- + H_2O}$$

Calculate the pH of the titration solution after the addition of the following volumes of NaOH titrant:

a. 0.00 mL
b. 25.00 mL
c. 12.50 mL
d. 37.50 mL

Solution

(a) The initial pH is computed for the acetic acid solution in the usual ICE approach:

$$K_a = \frac{[H3O^+]\,[CH_3CO_2^-]}{[CH_3CO_2H]} \approx \frac{[H3O^+]^2}{[CH_3CO_2H]_0}$$

and

$$[H3O^+] = \sqrt{K_a \times [CH_3CO_2H]} = \sqrt{1.8 \times 10^{-5} \times 0.100} = 1.3 \times 10^{-3}$$

$$pH = -\log\left(1.3 \times 10^{-3}\right) = 2.87$$

(b) The acid and titrant are both monoprotic and the sample and titrant solutions are equally concentrated; thus, this volume of titrant represents the equivalence point. Unlike the strong-acid example above, however, the reaction mixture in this case contains a weak conjugate base (acetate ion). The solution pH is computed considering the base ionization of acetate, which is present at a concentration of

$$\frac{0.00250\ \mathrm{mol}}{0.0500\ \mathrm{L}} = 0.0500\ \mathrm{M}\ \mathrm{CH_3CO_2^-}$$

Base ionization of acetate is represented by the equation

$$\mathrm{CH_3CO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons CH_3CO_2H\,(aq) + OH^-\,(aq)}$$

$$K_b = \frac{[H^+]\,[OH^-]}{K_a} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Assuming $x \ll 0.0500$, the pH may be calculated via the usual ICE approach:

$$K_b = \frac{x^2}{0.0500M}$$

$$x = [OH^-] = 5.3 \times 10^{-6}$$

$$\text{pOH} = -\log\left(5.3 \times 10^{-6}\right) = 5.28$$
$$\text{pH} = 14.00 - 5.28 = 8.72$$

Note that the pH at the equivalence point of this titration is significantly greater than 7, as expected when titrating a weak acid with a strong base.

(c) Titrant volume = 12.50 mL. This volume represents one-half of the stoichiometric amount of titrant, and so one-half of the acetic acid has been neutralized to yield an equivalent amount of acetate ion. The concentrations of these conjugate acid-base partners, therefore, are equal. A convenient approach to computing the pH is use of the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\frac{[\text{ Base }]}{[\text{ Acid }]} = -\log\left(K_a\right) + \log\frac{[CH_3CO_2^-]}{[CH_3CO_2H]} = -\log\left(1.8 \times 10^{-5}\right) + \log(1)$$

$$pH = -\log\left(1.8 \times 10^{-5}\right) = 4.74$$

(pH = pK_a at the half-equivalence point in a titration of a weak acid)

(d) Titrant volume = 37.50 mL. This volume represents a stoichiometric excess of titrant, and a reaction solution containing both the titration product, acetate ion, and the excess strong titrant. In such solutions, the solution pH is determined primarily by the amount of excess strong base:

$$[\text{OH}^-] = \frac{(0.003750mol - 0.00250mol)}{0.06250L} = 2.00 \times 10^{-2}M$$

$$\text{pOH} = -\log\left(2.00 \times 10^{-2}\right) = 1.70$$
$$\text{pH} = 14.00 - 1.70 = 12.30$$

Exercise 8.8.1

Calculate the pH for the weak acid/strong base titration between 50.0 mL of 0.100 *M* HCOOH(*aq*) (formic acid) and 0.200 *M* NaOH (titrant) at the listed volumes of added base: 0.00 mL, 15.0 mL, 25.0 mL, and 30.0 mL.

Answer available at the end of this section.

Performing additional calculations similar to those in the preceding example permits a more full assessment of titration curves. A summary of pH/volume data pairs for the strong and weak acid titrations is provided in Table 8.8.1 and plotted as titration curves in Figure 8.8.1. A comparison of these two curves illustrates several important concepts that are best addressed by identifying the four stages of a titration:

- initial state (added titrant volume = 0 mL): pH is determined by the acid being titrated; because the two acid samples are equally concentrated, the weak acid will exhibit a greater initial pH
- pre-equivalence point (0 mL < *V* < 25 mL): solution pH increases gradually and the acid is consumed by reaction with added titrant; composition includes unreacted acid and the reaction product, its conjugate base
- equivalence point (*V* = 25 mL): a drastic rise in pH is observed as the solution composition transitions from acidic to either neutral (for the strong acid sample) or basic (for the weak acid sample), with pH determined by ionization of the conjugate base of the acid
- postequivalence point (*V* > 25 mL): pH is determined by the amount of excess strong base titrant added; since both samples are titrated with the same titrant, both titration curves appear similar at this stage.

Table 8.8.1: pH Values in the Titrations of a Strong Acid and of a Weak Acid

Volume of 0.100 *M* NaOH Added (mL)	Moles of NaOH Added	pH Values 0.100 *M* HCl[1]	pH Values 0.100 *M* CH_3CO_2H[2]
0.0	0.0	1.00	2.87
5.0	0.00050	1.18	4.14
10.0	0.00100	1.37	4.57
15.0	0.00150	1.60	4.92
20.0	0.00200	1.95	5.35
22.0	0.00220	2.20	5.61
24.0	0.00240	2.69	6.13
24.5	0.00245	3.00	6.44
24.9	0.00249	3.70	7.14
25.0	0.00250	7.00	8.72
25.1	0.00251	10.30	10.30
25.5	0.00255	11.00	11.00
26.0	0.00260	11.29	11.29
28.0	0.00280	11.75	11.75
30.0	0.00300	11.96	11.96
35.0	0.00350	12.22	12.22
40.0	0.00400	12.36	12.36
45.0	0.00450	12.46	12.46
50.0	0.00500	12.52	12.52

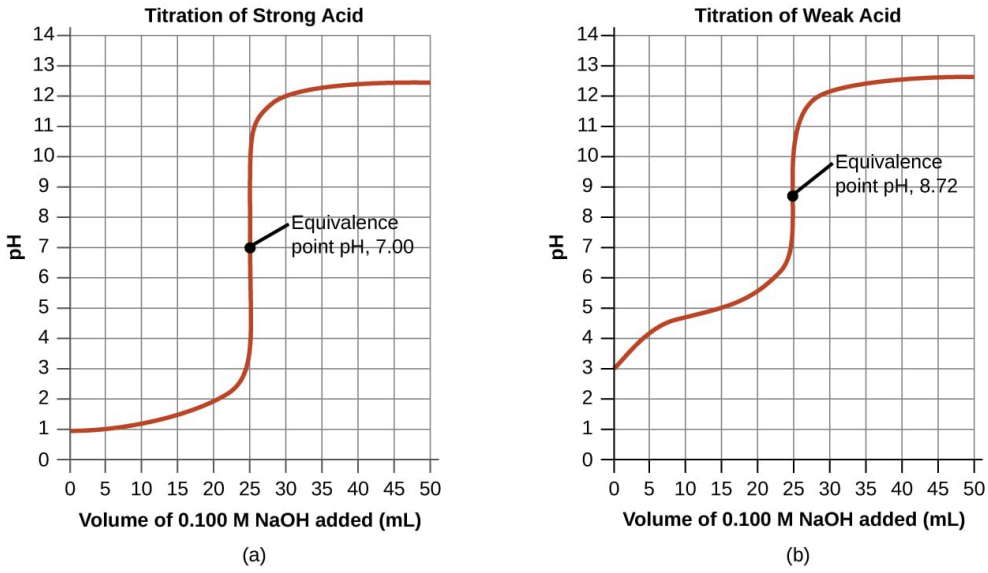


Figure 8.8.1: (a) The titration curve for the titration of 25.00 mL of 0.100 *M* HCl (strong acid) with 0.100 *M* NaOH (strong base) has an equivalence point of 7.00 pH. (b) The titration curve for the titration of 25.00 mL of 0.100 *M* acetic acid (weak acid) with 0.100 *M* NaOH (strong base) has an equivalence point of 8.72 pH.

Acid-Base Indicators

Certain organic substances change color in dilute solution when the hydronium ion concentration reaches a particular value. For example, phenolphthalein is a colorless substance in any aqueous solution with a hydronium ion concentration greater than $5.0 \times 10^{-9}\ \mathrm{M}$ (pH < 8.3). In more basic solutions where the hydronium ion concentration is less than $5.0 \times 10^{-9}\ \mathrm{M}$ (pH > 8.3), it is red or pink. Substances such as phenolphthalein, which can be used to determine the pH of a solution, are called **acid-base indicators**. Acid-base indicators are either weak organic acids or weak organic bases.

The equilibrium in a solution of the acid-base indicator methyl orange, a weak acid, can be represented by an equation in which we use HIn as a simple representation for the complex methyl orange molecule:

$$\underset{\text{red}}{\mathrm{HIn\,(aq)}} + \mathrm{H_2O\,(l)} \rightleftharpoons \underset{\text{yellow}}{\mathrm{H_3O^+\,(aq)}} + In^-(aq)$$

$$K_a = \frac{[\mathrm{H_3O^+}]\,[\mathrm{In^-}]}{[\mathrm{HIn}]} = 4.0 \times 10^{-4}$$

The anion of methyl orange, $\mathrm{In^-}$, is yellow, and the nonionized form, HIn, is red. When we add acid to a solution of methyl orange, the increased hydronium ion concentration shifts the equilibrium toward the nonionized red form, in accordance with Le Chatelier's principle. If we add base, we shift the equilibrium towards the yellow form. This behavior is completely analogous to the action of buffers.

The perceived color of an indicator solution is determined by the ratio of the concentrations of the two species $\mathrm{In^-}$ and HIn. If most of the indicator (typically about 60–90% or more) is present as $\mathrm{In^-}$, the perceived color of the solution is yellow. If most is present as HIn, then the solution color appears red. The Henderson-Hasselbalch equation is useful for understanding the relationship between the pH of an indicator solution and its composition (thus, perceived color):

$$pH = pKa + \log\left(\frac{[\mathrm{In^-}]}{[\mathrm{HIn}]}\right)$$

In solutions where pH > pK_a, the logarithmic term must be positive, indicating an excess of the conjugate base form of the indicator (yellow solution). When pH < pK_a, the log term must be negative, indicating an excess of the conjugate acid (red solution). When the solution pH is close to the indicator pKa, appreciable amounts of both conjugate partners are present, and the solution color is that of an additive combination of each (yellow and red, yielding orange). The **color change interval** (or *pH interval*) for an acid-base indicator is defined as the range of pH values over which a change in color is observed, and for most indicators this range is approximately pK_a ± 1.

There are many different acid-base indicators that cover a wide range of pH values and can be used to determine the approximate pH of an unknown solution by a process of elimination. Universal indicators and pH paper contain a mixture of indicators and exhibit different colors at different pHs. Figure $8.8.2$ presents several indicators, their colors, and their color-change intervals.

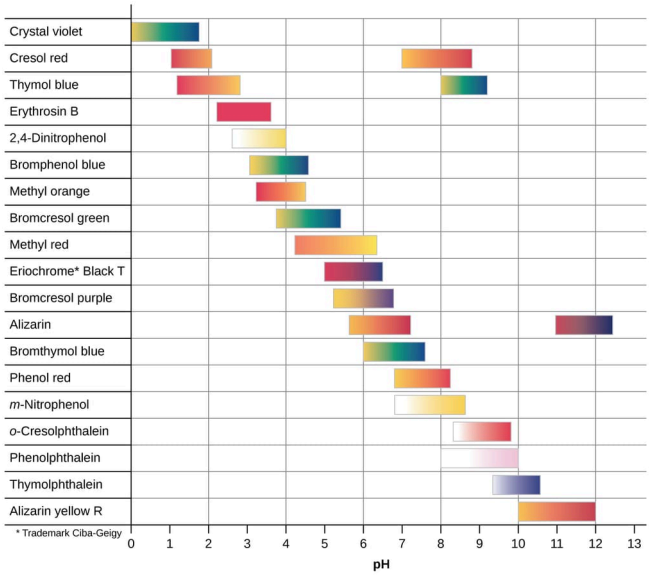


Figure 8.8.2: This chart illustrates the color change intervals for several acid-base indicators.

The titration curves shown in Figure 8.8.3 illustrate the choice of a suitable indicator for specific titrations. In the strong acid titration, use of any of the three indicators should yield reasonably sharp color changes and accurate end point determinations. For this titration, the solution pH reaches the lower limit of the methyl orange color change interval after addition of ~24 mL of titrant, at which point the initially red solution would begin to appear orange. When 25 mL of titrant has been added (the equivalence point), the pH is well above the upper limit and the solution will appear yellow. The titration's end point may then be estimated as the volume of titrant that yields a distinct orange-to-yellow color change. This color change would be challenging for most human eyes to precisely discern. More-accurate estimates of the titration end point are possible using either litmus or phenolphthalein, both of which exhibit color change intervals that are encompassed by the steep rise in pH that occurs around the 25.00 mL equivalence point.

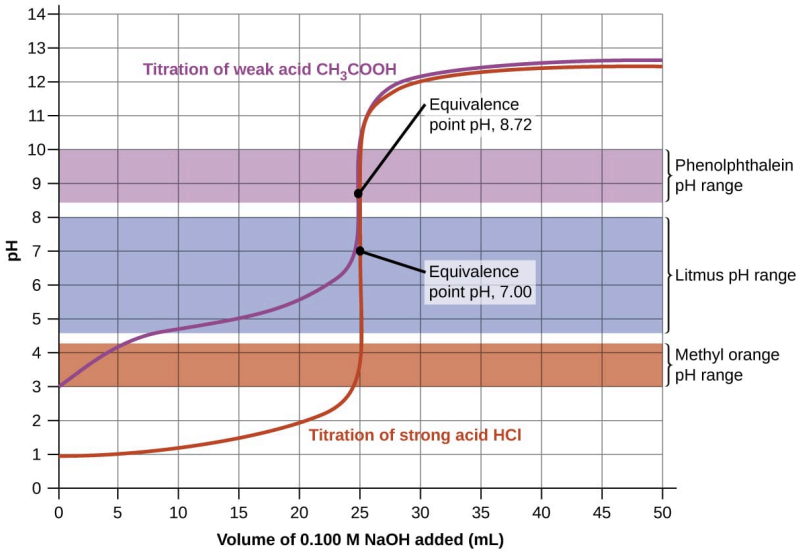


Figure 8.8.3: Titration curves for strong and weak acids illustrating the proper choice of acid-base indicator. Any of the three indicators will exhibit a reasonably sharp color change at the equivalence point of the strong acid titration, but only phenolphthalein is suitable for use in the weak acid titration.

The weak acid titration curve in Figure 8.8.3 shows that only one of the three indicators is suitable for end point detection. If methyl orange is used in this titration, the solution will undergo a gradual red-to-orange-to-yellow color change over a relatively large volume interval (0–6 mL), completing the color change well before the equivalence point (25 mL) has been reached. Use of litmus would show a color change that begins after adding 7–8 mL of titrant and ends just before the equivalence point. Phenolphthalein, on the other hand, exhibits a color change interval that nicely brackets the abrupt change in pH occurring at

the titration's equivalence point. A sharp color change from colorless to pink will be observed within a very small volume interval around the equivalence point.

Footnotes

- 1Titration of 25.00 mL of 0.100 *M* HCl (0.00250 mol of HCI) with 0.100 *M* NaOH.
- 2Titration of 25.00 mL of 0.100 *M* CH_3CO_2H (0.00250 mol of CH_3CO_2H) with 0.100 *M* NaOH.

Answers

Exercise 8.8.1

0.00: 1.000; 15.0: 1.5111; 25.0: 7; 40.0: 12.523

Exercise 8.8.1

0.00 mL: 2.37; 15.0 mL: 3.92; 25.00 mL: 8.29; 30.0 mL: 12.097

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8.9: Key Terms

Example and Directions

Words (or words that have the same definition)	The definition is case sensitive	(Optional) Image to display with the definition [Not displayed in Glossary, only in pop-up on pages]	(Optional) Caption for Image	(Optional) External or Internal Link	(Optional) Source for Definition
(Eg. "Genetic, Hereditary, DNA ...")	(Eg. "Relating to genes or heredity")		The infamous double helix	https://bio.libretexts.org/	CC-BY-SA; Delmar Larsen

Glossary Entries

Word(s)	Definition	Image	Caption	Link	Source
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 an acid ionization reaction				
acid-base indicator	weak acid or base whose conjugate partner imparts a different solution color; used in visual assessments of solution pH				
acidic	a solution in which $[H_3O^+] > [OH^-]$				
amphiprotic	species that may either donate or accept a proton in a Bronsted-Lowry acid-base 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				
base ionization constant (K_b)	equilibrium constant for a base ionization reaction				
basic	a solution in which $[H_3O^+] < [OH^-]$				
Brønsted-Lowry acid	proton donor				
Brønsted-Lowry base	proton acceptor				
buffer	mixture of appreciable amounts of a weak acid-base pair 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)				
color-change interval	range in pH over which the color change of an indicator is observed				
conjugate acid	substance formed when a base gains a proton				

Word(s)	Definition	Image	Caption	Link	Source
conjugate base	substance formed when an acid loses a proton				
diprotic acid	acid containing two ionizable hydrogen atoms per molecule				
diprotic base	base capable of accepting two protons				
Henderson-Hasselbalch equation	logarithmic version of the acid ionization constant expression, conveniently formatted for calculating the pH of buffer solutions				
ion-product constant for water (K_w)	equilibrium constant for the autoionization of water				
leveling effect	observation that acid-base strength of solutes in a given solvent is limited to that of the solvent's characteristic acid and base species (in water, hydronium and hydroxide ions, respectively)				
monoprotic acid	acid containing one ionizable hydrogen atom per molecule				
neutral	describes a solution in which $[H_3O^+] = [OH^-]$				
oxyacid	ternary compound with acidic properties, molecules of which contain a central nonmetallic atom bonded to one or more O atoms, at least one of which is bonded to an ionizable H atom				
percent ionization	ratio of the concentration of ionized acid to initial acid concentration expressed as a percentage				
pH	logarithmic measure of the concentration of hydronium ions in a solution				
pOH	logarithmic measure of the concentration of hydroxide ions in a solution				
stepwise ionization	process in which a polyprotic acid is ionized by losing protons sequentially				
titration curve	plot of some sample property (such as pH) versus volume of added titrant				
triprotic acid	acid that contains three ionizable hydrogen atoms per molecule				

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8.10: Key Equations

$$\mathrm{pH} = -\log\left[\mathrm{H_3O^+}\right]$$

$$\mathrm{pOH} = -\log\left[\mathrm{OH^-}\right]$$

$$\left[\mathrm{H_3O^+}\right] = 10^{-\mathrm{pH}}$$

$$\left[\mathrm{OH^-}\right] = 10^{-\mathrm{pOH}}$$

$$\mathrm{pH} + \mathrm{pOH} = \mathrm{p}K_\mathrm{w} = 14.00 \text{ at } 25^\circ\mathrm{C}$$

$$K_\mathrm{a} = \frac{\left[\mathrm{H_3O^+}\right]\left[\mathrm{A^-}\right]}{\left[\mathrm{HA}\right]}$$

$$K_\mathrm{b} = \frac{\left[\mathrm{HB^+}\right]\left[\mathrm{OH^-}\right]}{\left[\mathrm{B}\right]}$$

$$K_\mathrm{a} \times K_\mathrm{b} = 1.0 \times 10^{-14} = K_\mathrm{w}$$

$$\text{Percent ionization } = \frac{\left[\mathrm{H_3O^+}\right]_\mathrm{eq}}{\left[\mathrm{HA}\right]_0} \times 100$$

$$\mathrm{p}K_\mathrm{a} = -\log K_\mathrm{a}$$

$$\mathrm{p}K_\mathrm{b} = -\log K_\mathrm{b}$$

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{\left[\mathrm{A^-}\right]}{\left[\mathrm{HA}\right]}$$

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8.11: 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:

The ion product of water, K_w is the equilibrium constant for the autoionization reaction:

Concentrations of hydronium and hydroxide ions in aqueous media are often represented as logarithmic pH and pOH values, respectively. At 25 °C, the autoprotolysis equilibrium for water requires the sum of pH and pOH to equal 14 for any aqueous solution. The relative concentrations of hydronium and hydroxide ion in a solution define its status as acidic ($[H_3O^+] > [OH^-]$), basic ($[H_3O^+] < [OH^-]$), or neutral ($[H_3O^+] = [OH^-]$). At 25 °C, a pH < 7 indicates an acidic solution, a pH > 7 a basic solution, and a pH = 7 a neutral solution.

The relative strengths of acids and bases are reflected in the magnitudes of their ionization constants; the stronger the acid or base, the larger its ionization constant. A reciprocal relation exists between the strengths of a conjugate acid-base pair: the stronger the acid, the weaker its conjugate base. Water exerts a leveling effect on dissolved acids or bases, reacting completely to generate its characteristic hydronium and hydroxide ions (the strongest acid and base that may exist in water). The strengths of the binary acids increase from left to right across a period of the periodic table ($CH_4 < NH_3 < H_2O < HF$), and they increase down a group ($HF < HCl < HBr < HI$). The strengths of oxyacids that contain the same central element increase as the oxidation number of the element increases ($H_2SO_3 < H_2SO_4$). The strengths of oxyacids also increase as the electronegativity of the central element increases [$H_2SeO_4 < H_2SO_4$].

The ions composing salts may possess acidic or basic character, ionizing when dissolved in water to yield acidic or basic solutions. Acidic cations are typically the conjugate partners of weak bases, and basic anions are the conjugate partners of weak acids. Many metal ions bond to water molecules when dissolved to yield complex ions that may function as acids.

An acid that contains more than one ionizable proton is a polyprotic acid. These acids undergo stepwise ionization reactions involving the transfer of single protons. The ionization constants for polyprotic acids decrease with each subsequent step; these decreases typically are large enough to permit simple equilibrium calculations that treat each step separately.

Solutions that contain appreciable amounts of a weak conjugate acid-base pair are called buffers. A buffered solution will experience only slight changes in pH when small amounts of acid or base are added. Addition of large amounts of acid or base can exceed the buffer capacity, consuming most of one conjugate partner and preventing further buffering action.

The titration curve for an acid-base titration is typically a plot of pH versus volume of added titrant. These curves are useful in selecting appropriate acid-base indicators that will permit accurate determinations of titration end points.

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8.12: Exercises

1.

Write equations that show NH_3 as both a conjugate acid and a conjugate base.

2.

Write equations that show $\mathrm{H_2PO_4^-}$ acting both as an acid and as a base.

3.

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

(a) H_3O^+

(b) HCl

(c) NH_3

(d) CH_3CO_2H

(e) $\mathrm{NH_4^+}$

(f) $\mathrm{HSO_4^-}$

4.

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry acid:

(a) HNO_3

(b) $\mathrm{PH_4^+}$

(c) $\mathrm{H_2\ S}$

(d) CH_3CH_2COOH

(e) $\mathrm{H_2PO_4^-}$

(f) $\mathrm{HS^-}$

5.

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:

(a) H_2O

(b) OH^-

(c) NH_3

(d) CN^-

(e) $\mathrm{S^{2-}}$

(f) $\mathrm{H_2PO_4^-}$

6.

Show by suitable net ionic equations that each of the following species can act as a Brønsted-Lowry base:

(a) HS^-

(b) PO_4^{3+}

(c) NH_2^-

(d) C_2H_5OH

(e) O^{2-}

(f) $H_2PO_4^-$

7.

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)]$H_5\ N_2^+$

8.

What is the conjugate acid of each of the following? What is the conjugate base of each?

(a) $H_2\ S$

(b) $H_2PO_4^-$

(c) PH_3

(d) HS^-

(e) HSO_3^-

(f) $H_3O_2^+$

(g) $H_4\ N_2$

(h) CH_3OH

9.

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) $\mathrm{HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3^-}$

(b) $\mathrm{CN^- + H_2O \rightarrow HCN + OH^-}$

(c) $\mathrm{H_2SO_4 + Cl^- \rightarrow HCl + HSO_4^-}$

(d) $\mathrm{HSO_4{}^- + OH^- \longrightarrow SO_4{}^{2-} + H_2O}$

(e) $\mathrm{O^{2-} + H_2O \longrightarrow 2OH^-}$

(f) $\mathrm{[Cu\,(H_2O)_3\,(OH)]^+ + [Al\,(H_2O)_6]^{3+} \longrightarrow [Cu\,(H_2O)_4]^{2+} + [Al\,(H_2O)_5\,(OH)]^{2+}}$

(g) $\mathrm{H_2\ S + NH_2{}^- \rightarrow HS^- + NH_3}$

10.

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) $\mathrm{NO_2{}^- + H_2O \longrightarrow HNO_2 + OH^-}$

(b) $\mathrm{HBr + H_2O \longrightarrow H_3O^+ + Br^-}$

(c) $\mathrm{HS^- + H_2O \longrightarrow H_2\ S + OH^-}$

(d) $\mathrm{H_2PO_4{}^- + OH^- \longrightarrow HPO_4{}^{2-} + H_2O}$

(e) $\mathrm{H_2PO_4^- + HCl \longrightarrow H_3PO_4 + Cl^-}$

(f) $\mathrm{[Fe\,(H_2O)_5\,(OH)]^{2+} + [Al\,(H_2O)_6]^{3+} \longrightarrow [Fe\,(H_2O)_6]^{3+} + [Al\,(H_2O)_5\,(OH)]^{2+}}$

(g) $\mathrm{CH_3OH + H^- \longrightarrow CH_3O^- + H_2}$

11.

What are amphiprotic species? Illustrate with suitable equations.

12.

State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species:

(a) $\mathrm{H_2O}$

(b) $\mathrm{HPO_4{}^{2-}}$

(c) $\mathrm{S^{2-}}$

(d) $\mathrm{CO_3{}^{2-}}$

(e) $\mathrm{HSO_4{}^-}$

13.

State which of the following species are amphiprotic and write chemical equations illustrating the amphiprotic character of these species.

(a) $\mathrm{NH_3}$

(b) HPO_4^{2-}

(c) Br^-

(d) NH_4^+

(e) AsO_4^{3-}

14.

Is the self-ionization of water endothermic or exothermic? The ionization constant for water (K_w) is 2.9×10^{-14} at 40 °C and 9.3×10^{-14} at 60 °C.

15.

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.

16.

The ionization constant for water (K_w) is 2.9×10^{-14} at 40 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 40 °C.

17.

The ionization constant for water (K_w) is 9.311×10^{-14} at 60 °C. Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH for pure water at 60 °C.

18.

Calculate the pH and the pOH of each of the following solutions at 25 °C for which the substances ionize completely:

(a) 0.200 *M* HCl

(b) 0.0143 *M* NaOH

(c) 3.0 *M* HNO_3

(d) 0.0031 *M* $Ca(OH)_2$

19.

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

20.

What are the pH and pOH of a solution of 2.0 M HCl, which ionizes completely?

21.

What are the hydronium and hydroxide ion concentrations in a solution whose pH is 6.52?

22.

Calculate the hydrogen ion concentration and the hydroxide ion concentration in wine from its pH. See Figure 14.2 for useful information.

23.

Calculate the hydronium ion concentration and the hydroxide ion concentration in lime juice from its pH. See Figure 14.2 for useful information.

24.

The hydronium ion concentration in a sample of rainwater is found to be 1.7×10^{-6} *M* at 25 °C. What is the concentration of hydroxide ions in the rainwater?

25.

The hydroxide ion concentration in household ammonia is 3.2×10^{-3} *M* at 25 °C. What is the concentration of hydronium ions in the solution?

26.

Explain why the neutralization reaction of a strong acid and a weak base gives a weakly acidic solution.

27.

Explain why the neutralization reaction of a weak acid and a strong base gives a weakly basic solution.

28.

Use this list of important industrial compounds (and Figure 14.8) to answer the following questions regarding: $Ca(OH)_2$, CH_3CO_2H, HCl, H_2CO_3, HF, HNO_2, HNO_3, H_3PO_4, H_2SO_4, NH_3, NaOH, Na_2CO_3.

(a) Identify the strong Brønsted-Lowry acids and strong Brønsted-Lowry bases.

(b) Identify the compounds that can behave as Brønsted-Lowry acids with strengths lying between those of H_3O^+ and H_2O.

(c) Identify the compounds that can behave as Brønsted-Lowry bases with strengths lying between those of H_2O and OH^-.

29.

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.

30.

Household ammonia is a solution of the weak base NH_3 in water. List, in order of descending concentration, all of the ionic and molecular species present in a 1-*M* aqueous solution of this base.

31.

Explain why the ionization constant, K_a, for H_2SO_4 is larger than the ionization constant for H_2SO_3.

32.

Explain why the ionization constant, K_a, for HI is larger than the ionization constant for HF.

33.

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.

34.

Nitric acid reacts with insoluble copper(II) oxide to form soluble copper(II) nitrate, $Cu(NO_3)_2$, a compound that has been used to prevent the growth of algae in swimming pools. Write the balanced chemical equation for the reaction of an aqueous solution of HNO_3 with CuO.

35. What is the ionization constant at 25 °C for the weak acid $\mathrm{CH_3NH_3^+}$, the conjugate acid of the weak base $\mathrm{CH_3NH_2}$, $K_\mathrm{b} = 4.4 \times 10^{-4}$.

36. What is the ionization constant at 25 °C for the weak acid $\mathrm{(CH_3)_2\,NH_2^+}$, the conjugate acid of the weak base $\mathrm{(CH_3)_2\,NH}$, $K_\mathrm{b} = 5.9 \times 10^{-4}$?

37. Which base, $\mathrm{CH_3NH_2}$ or $\mathrm{(CH_3)_2\,NH}$, is the stronger base? Which conjugate acid, $\mathrm{(CH_3)_2\,NH_2^+}$or $\mathrm{CH_3NH_3^+}$, is the stronger acid?

38. Which is the stronger acid, $\mathrm{NH_4^+}$or HBrO ?

39. Which is the stronger base, $\mathrm{(CH_3)_3\ N}$ or $\mathrm{H_2BO_3^-}$?

40. Predict which acid in each of the following pairs is the stronger and explain your reasoning for each.

(a) $\mathrm{H_2O}$ or HF

(b) $\mathrm{B(OH)_3}$ or $\mathrm{Al(OH)_3}$

(c) $\mathrm{HSO_3^-}$or $\mathrm{HSO_4^-}$

(d) $\mathrm{NH_3}$ or $\mathrm{H_2\ S}$

(e) $\mathrm{H_2O}$ or $\mathrm{H_2Te}$

41.

Predict which compound in each of the following pairs of compounds is more acidic and explain your reasoning for each.

(a) $\mathrm{HSO_4^-}$or $\mathrm{HSeO_4^-}$

(b) $\mathrm{NH_3}$ or $\mathrm{H_2O}$

(c) PH_3 or HI

(d) NH_3 or PH_3

(e) H_2 S or HBr

42.

Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.

(a) acidity: HCl, HBr, HI

(b) basicity: H_2O, OH^-, H^-, Cl^-

(c) basicity: $Mg(OH)_2, Si(OH)_4, ClO_3(OH)$ (Hint: Formula could also be written as $HClO_4$.)

(d) acidity: HF, H_2O, NH_3, CH_4

43.

Rank the compounds in each of the following groups in order of increasing acidity or basicity, as indicated, and explain the order you assign.

(a) acidity: $NaHSO_3, NaHSeO_3, NaHSO_4$

(b) basicity: $BrO2-, BrO2-, ClO2-, ClO2- IO2- IO2-$

(c) acidity: $HOCl, HOClO, HOClO_2, HOClO_3$

(d) acidity: $HOCI, HOCIO, HOCIO_2, HOClO_3$

(e) basicity: $NH_2{}^-, HS^-, HTe^-, PH_2{}^-$

(f) basicity: $BrO^-, BrO_2{}^-, BrO_3{}^-, BrO_4{}^-$

44.

Both HF and HCN ionize in water to a limited extent. Which of the conjugate bases, F^- or CN^-, is the stronger base?

45.

The active ingredient formed by aspirin in the body is salicylic acid, $C_6H_4OH(CO_2H)$. The carboxyl group ($–CO_2H$) acts as a weak acid. The phenol group (an OH group bonded to an aromatic ring) also acts as an acid but a much weaker acid. List, in order of descending concentration, all of the ionic and molecular species present in a 0.001-*M* aqueous solution of $C_6H_4OH(CO_2H)$.

46.

Are the concentrations of hydronium ion and hydroxide ion in a solution of an acid or a base in water directly proportional or inversely proportional? Explain your answer.

47.

What two common assumptions can simplify calculation of equilibrium concentrations in a solution of a weak acid or base?

48.

Which of the following will increase the percent of NH_3 that is converted to the ammonium ion in water?

(a) addition of NaOH

(b) addition of HCl

(c) addition of NH_4Cl

49.

Which of the following will increase the percentage of HF that is converted to the fluoride ion in water?

(a) addition of NaOH

(b) addition of HCl

(c) addition of NaF

50.

What is the effect on the concentrations of $\mathrm{msubNO2-,NO2-,HNO_2}$, and $\mathrm{OH^-}$ when the following are added to a solution of KNO_2 in water:

(a) HCl

(b) HNO_2

(c) NaOH

(d) NaCl

(e) KNO

51.

What is the effect on the concentration of hydrofluoric acid, hydronium ion, and fluoride ion when the following are added to separate solutions of hydrofluoric acid?

(a) HCl

(b) KF

(c) NaCl

(d) KOH

(e) HF

52.

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?

53.

From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.

(a)

$\mathrm{CH_3CO_2H}: [\mathrm{H_3O^+}] = 1.34 \times 10^{-3}\mathrm{M};$
$[\mathrm{CH_3CO_2-}] = 1.34 \times 10^{-3}\mathrm{M};$
$[\mathrm{CH_3CO_2H}] = 9.866 \times 10^{-2}\mathrm{M};$

(b)

$\mathrm{ClO^-}: [\mathrm{OH^-}] = 4.0 \times 10^{-4}\mathrm{M};$
$[\mathrm{HClO}] = 2.38 \times 10^{-4}\mathrm{M};$
$[\mathrm{ClO^-}] = 0.273\mathrm{M};$

(c)

$\mathrm{HCO_2H}: [\mathrm{HCO_2H}] = 0.524\mathrm{M};$
$[\mathrm{H_3O^+}] = 9.8 \times 10^{-3}\mathrm{M};$
$[\mathrm{HCO_2^-}] = 9.8 \times 10^{-3}\mathrm{M};$

(d)

$\mathrm{(d)\ C_6H_5NH_3^+}: [\mathrm{C_6H_5NH_3^+}] = 0.233\mathrm{M};$
$[\mathrm{C_6H_5NH_2}] = 2.3 \times 10^{-3} M;$
$[\mathrm{H_3O^+}] = 2.3 \times 10^{-3} M$

54.

From the equilibrium concentrations given, calculate K_a for each of the weak acids and K_b for each of the weak bases.

(a)

$\mathrm{NH_3}: [\mathrm{OH^-}] = 3.1 \times 10^{-3}\mathrm{M};$
$[\mathrm{NH_4^+}] = 3.1 \times 10^{-3}\mathrm{M};$
$[\mathrm{NH_3}] = 0.533\mathrm{M};$

(b)

$\mathrm{HNO_2}: [\mathrm{H_3O^+}] = 0.011\mathrm{M};$
$[\mathrm{NO_2^-}] = 0.0438\mathrm{M};$
$[\mathrm{HNO_2}] = 1.07\mathrm{M};$

(c)

$\mathrm{(CH_3)_3\ N}: [\mathrm{(CH_3)_3\ N}] = 0.25\mathrm{M};$
$[\mathrm{(CH_3)_3NH^+}] = 4.3 \times 10^{-3}\mathrm{M};$
$[\mathrm{OH^-}] = 3.7 \times 10^{-3}\mathrm{M};$

(d)

$\mathrm{NH_4^+}: [\mathrm{NH_4^+}] = 0.100\mathrm{M};$
$[\mathrm{NH_3}] = 7.5 \times 10^{-6}\mathrm{M};$
$[\mathrm{H_3O^+}] = 7.5 \times 10^{-6}\mathrm{M}$

55. Determine K_b for the nitrite ion, $\mathrm{NO_2^-}$. In a $0.10 - \mathrm{M}$ solution this base is 0.0015% ionized.

56. Determine K_a for hydrogen sulfate ion, $\mathrm{HSO_4^-}$. In a $0.10 - M$ solution the acid is 29\% ionized.

57. Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:

(a) $\mathrm{F^-}$

(b) $\mathrm{NH_4^+}$

(c) $\mathrm{AsO_4^{3-}}$

(d) $\mathrm{(CH_3)_2NH_2^+}$

(e) NO_2^-

(f) $HC_2O_4^-$(as a base)

58. Calculate the ionization constant for each of the following acids or bases from the ionization constant of its conjugate base or conjugate acid:

(a) HTe^-(as a base)

(b) $(CH_3)_3NH^+$

(c) $HAsO_4^{2-}$ (as a base)

(d) HO_2^-(as a base)

(e) $C_6H_5NH_3^+$

(f) HSO_3^-(as a base)

59.

Using the K_a value of 1.4×10^{-5}, place $Al(H_2O)_6^{3+}$ in the correct location in this section about the relative strengths of conjugate acids and bases.

60.

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.

(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) $0.120 MFe(H_2O)_6^{2+}$ a weak acid, $K_a = 1.6 \times 10^{-7}$

61.

Propionic acid, $C_2H_5CO_2H$ (K_a = 1.34 × 10^{-5}), is used in the manufacture of calcium propionate, a food preservative. What is the pH of a 0.698-*M* solution of $C_2H_5CO_2H$?

62.

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?

63.

The ionization constant of lactic acid, $CH_3CH(OH)CO_2H$, an acid found in the blood after strenuous exercise, is 1.36 × 10^{-4}. If 20.0 g of lactic acid is used to make a solution with a volume of 1.00 L, what is the concentration of hydronium ion in the solution?

64.

Nicotine, $C_{10}H_{14}N_2$, is a base that will accept two protons (K_{b1} = 7 × 10^{-7}, K_{b2} = 1.4 × 10^{-11}). What is the concentration of each species present in a 0.050-*M* solution of nicotine?

65.

The pH of a 0.23-*M* solution of HF is 1.92. Determine K_a for HF from these data.

66. The pH of a $0.15 - \mathrm{M}$ solution of $\mathrm{HSO_4}^-$is 1.43. Determine K_a for $\mathrm{HSO_4}^-$from these data.

67. The pH of a $0.10 - M$ solution of caffeine is 11.70 . Determine K_b for caffeine from these data:

$\mathrm{C_8H_{10}\ N_4O_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{C_8H_{10}\ N_4O_2H^+}(aq) + \mathrm{OH^-}(aq)$

68.

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.

69.

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

(a) $Al(NO_3)_3$

(b) RbI

(c) $KHCO_2$

(d) CH_3NH_3Br

70.

Determine whether aqueous solutions of the following salts are acidic, basic, or neutral:

(a) $FeCl_3$

(b) K_2CO_3

(c) NH_4Br

(d) $KClO_4$

71.

Novocaine, $C_{13}H_{21}O_2N_2Cl$, is the salt of the base procaine and hydrochloric acid. The ionization constant for procaine is 7×10^{-6}. Is a solution of novocaine acidic or basic? What are $[H_3O^+]$, $[OH^-]$, and pH of a 2.0% solution by mass of novocaine, assuming that the density of the solution is 1.0 g/mL.

72. Which of the following concentrations would be practically equal in a calculation of the equilibrium concentrations in a $0.134 - M$ solution of $\mathrm{H_2CO_3}$, a diprotic acid: $\left[\mathrm{H_3O^+}\right], \left[\mathrm{OH^-}\right], \left[\mathrm{H_2CO_3}\right], \left[\mathrm{HCO_3}^-\right], \left[\mathrm{CO_3}^{2-}\right]$? No calculations are needed to answer this question.

73. Calculate the concentration of each species present in a $0.050 - M$ solution of $\mathrm{H_2\ S}$.

74. Calculate the concentration of each species present in a $0.010 - M$ solution of phthalic acid, $\mathrm{C_6H_4\left(CO_2H\right)_2}$.

$$\mathrm{C_6H_4\left(CO_2H\right)_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{C_6H_4\left(CO_2H\right)\left(CO_2\right)^-}(aq) \quad K_a = 1.1 \times 10^{-3}$$
$$\mathrm{C_6H_4\left(CO_2H\right)\left(CO_2\right)^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{C_6H_4\left(CO_2\right)_2^{2-}}(aq) \quad K_a = 3.9 \times 10^{-6}$$

75. Salicylic acid, $HOC_6H_4CO_2H$, and its derivatives have been used as pain relievers for a long time. Salicylic acid occurs in small amounts in the leaves, bark, and roots of some vegetation (most notably historically in the bark of the willow tree). Extracts of these plants have been used as medications for centuries. The acid was first isolated in the laboratory in 1838.

(a) Both functional groups of salicylic acid ionize in water, with $K_a = 1.0 \times 10^{-3}$ for the—CO_2H group and 4.2×10^{-13} for the –OH group. What is the pH of a saturated solution of the acid (solubility = 1.8 g/L).

(b) Aspirin was discovered as a result of efforts to produce a derivative of salicylic acid that would not be irritating to the stomach lining. Aspirin is acetylsalicylic acid, $CH_3CO_2C_6H_4CO_2H$. The $–CO_2H$ functional group is still present, but its acidity is reduced, $K_a = 3.0 \times 10^{-4}$. What is the pH of a solution of aspirin with the same concentration as a saturated solution of salicylic acid (See Part a).

76.

The ion HTe^- is an amphiprotic species; it can act as either an acid or a base.

(a) What is K_a for the acid reaction of HTe^- with H_2O?

(b) What is K_b for the reaction in which HTe^- functions as a base in water?

(c) 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.

77.

Explain why a buffer can be prepared from a mixture of NH_4Cl and NaOH but not from NH_3 and NaOH.

78.

Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the acid H_3PO_4 and a salt of its conjugate base NaH_2PO_4.

79.

Explain why the pH does not change significantly when a small amount of an acid or a base is added to a solution that contains equal amounts of the base NH_3 and a salt of its conjugate acid NH_4Cl.

80.

What is $[H_3O^+]$in a solution of $0.25 M CH_3CO_2H$ and $0.030 M NaCH_3CO_2$?

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq) \quad K_a = 1.8 \times 10^{-5}$$

81.

What is $[H_3O^+]$in a solution of $0.075 M HNO_2$ and $0.030 M NaNO_2$?

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq) \quad K_a = 4.5 \times 10^{-5}$$

82.

What is $[OH^-]$in a solution of $0.125 M CH_3NH_2$ and $0.130 M CH_3NH_3Cl$?

$$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq) \quad K_b = 4.4 \times 10^{-4}$$

83.

What is $[OH^-]$in a solution of $1.25 M NH_3$ and $0.78 M NH_4NO_3$?

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \quad K_b = 1.8 \times 10^{-5}$$

84.

What is the effect on the concentration of acetic acid, hydronium ion, and acetate ion when the following are added to an acidic buffer solution of equal concentrations of acetic acid and sodium acetate:

(a) HCl

(b) KCH_3CO_2

(c) NaCl

(d) KOH

(e) CH_3CO_2H

85.

What is the effect on the concentration of ammonia, hydroxide ion, and ammonium ion when the following are added to a basic buffer solution of equal concentrations of ammonia and ammonium nitrate:

(a) KI

(b) NH_3

(c) HI

(d) NaOH

(e) NH_4Cl

86.

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?

87.

Calculate the pH of a buffer solution prepared from 0.155 mol of phosphoric acid, 0.250 mole of KH_2PO_4, and enough water to make 0.500 L of solution.

88.

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.)

89.

What mass of NH_4Cl must be added to 0.750 L of a 0.100-*M* solution of NH_3 to give a buffer solution with a pH of 9.26? (Hint: Assume a negligible change in volume as the solid is added.)

90.

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?

91.

A 5.36-g sample of NH_4Cl was added to 25.0 mL of 1.00 *M* NaOH and the resulting solution

diluted to 0.100 L.

(a) What is the pH of this buffer 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 the solution?

92.

Explain how to choose the appropriate acid-base indicator for the titration of a weak base with a strong acid.

93.

Explain why an acid-base indicator changes color over a range of pH values rather than at a specific pH.

94.

Calculate the pH at the following points in a titration of 40 mL (0.040 L) of 0.100 *M* barbituric acid ($K_a = 9.8 \times 10^{-5}$) 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

95.

The indicator dinitrophenol is an acid with a K_a of 1.1×10^{-4}. In a 1.0×10^{-4}-*M* solution, it is colorless in acid and yellow in base. Calculate the pH range over which it goes from 10% ionized (colorless) to 90% ionized (yellow).

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9: ELECTROCHEMISTRY

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9.1: Introduction

Another chapter in this text introduced the chemistry of reduction-oxidation (redox) reactions. This important reaction class is defined by changes in oxidation states for one or more reactant elements, and it includes a subset of reactions involving the transfer of electrons between reactant species. Around the turn of the nineteenth century, chemists began exploring ways these electrons could be transferred *indirectly* via an external circuit rather than directly via intimate contact of redox reactants. In the two centuries since, the field of *electrochemistry* has evolved to yield significant insights on the fundamental aspects of redox chemistry as well as a wealth of technologies ranging from industrial-scale metallurgical processes to robust, rechargeable batteries for electric vehicles (Figure 9.1.1). In this chapter, the essential concepts of electrochemistry will be addressed.



Figure 9.1.1: Electric vehicles are powered by batteries, devices that harness the energy of spontaneous redox reactions. (credit: modification of work by Robert Couse-Baker)

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9.2: Review of Redox Chemistry

Learning Objectives

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

- Describe defining traits of redox chemistry
- Identify the oxidant and reductant of a redox reaction
- Balance chemical equations for redox reactions using the half-reaction method

Since reactions involving electron transfer are essential to the topic of electrochemistry, a brief review of redox chemistry is provided here that summarizes and extends the content of an earlier text chapter (see chapter on reaction stoichiometry). Readers wishing additional review are referred to the text chapter on reaction stoichiometry.

Oxidation Numbers

By definition, a redox reaction is one that entails changes in *oxidation number* (or *oxidation state*) for one or more of the elements involved. The oxidation number of an element in a compound is essentially an assessment of how the electronic environment of its atoms is different in comparison to atoms of the pure element. By this description, *the oxidation number of an atom in an element is equal to zero*. For an atom in a compound, *the oxidation number is equal to the charge the atom would have in the compound if the compound were ionic*. Consequential to these rules, *the sum of oxidation numbers for all atoms in a molecule is equal to the charge on the molecule*. To illustrate this formalism, examples from the two compound classes, ionic and covalent, will be considered.

Simple ionic compounds present the simplest examples to illustrate this formalism, since by definition the elements' oxidation numbers are numerically equivalent to ionic charges. Sodium chloride, NaCl, is comprised of Na^+ cations and Cl^- anions, and so oxidation numbers for sodium and chlorine are, +1 and –1, respectively. Calcium fluoride, CaF_2, is comprised of Ca^{2+} cations and F^- anions, and so oxidation numbers for calcium and fluorine are, +2 and –1, respectively.

Covalent compounds require a more challenging use of the formalism. Water is a covalent compound whose molecules consist of two H atoms bonded separately to a central O atom via polar covalent O–H bonds. The shared electrons comprising an O–H bond are more strongly attracted to the more electronegative O atom, and so it acquires a partial negative charge in the water molecule (relative to an O atom in elemental oxygen). Consequently, H atoms in a water molecule exhibit partial positive charges compared to H atoms in elemental hydrogen. The sum of the partial negative and partial positive charges for each water molecule is zero, and the water molecule is neutral.

Imagine that the polarization of shared electrons within the O–H bonds of water were 100% complete—the result would be *transfer* of electrons from H to O, and water would be an ionic compound comprised of O^{2-} anions and H^+ cations. And so, the oxidations numbers for oxygen and hydrogen in water are –2 and +1, respectively. Applying this same logic to carbon tetrachloride, CCl_4, yields oxidation numbers of +4 for carbon and –1 for chlorine. In the nitrate ion, NO_3^-, the oxidation number for nitrogen is +5 and that for oxygen is –2, summing to equal the 1– charge on the molecule:

$$(1N \text{ atom}) \left(\frac{+5}{N \text{ atom}} \right) + (3O \text{ atoms}) \left(\frac{-2}{O \text{ atom}} \right) = +5 + -6 = -1$$

Balancing Redox Equations

The unbalanced equation below describes the decomposition of molten sodium chloride:

$$\mathrm{NaCl\,(l)} \longrightarrow \mathrm{Na\,(l)} + \mathrm{Cl_2\,(g)} \qquad \text{(unbalanced)}$$

This reaction satisfies the criterion for redox classification, since the oxidation number for Na is decreased from +1 to 0 (it undergoes *reduction*) and that for Cl is increased from –1 to 0 (it undergoes *oxidation*). The equation in this case is easily

balanced by inspection, requiring stoichiometric coefficients of 2 for the NaCl and Na:

$$2\,\mathrm{NaCl}\,(\mathrm{l}) \longrightarrow 2\,\mathrm{Na}\,(\mathrm{l}) + \mathrm{Cl_2}\,(\mathrm{g}) \qquad (\text{balanced})$$

Redox reactions that take place in aqueous solutions are commonly encountered in electrochemistry, and many involve water or its characteristic ions, $H^+(aq)$ and $OH^-(aq)$, as reactants or products. In these cases, equations representing the redox reaction can be very challenging to balance by inspection, and the use of a systematic approach called the *half-reaction method* is helpful.

Balancing REDOX reactions via the half-reaction Method

This approach involves the following steps:

1. Write skeletal equations for the oxidation and reduction half-reactions.
2. Balance each half-reaction for all elements except H and O.
3. Balance each half-reaction for O by adding H_2O.
4. Balance each half-reaction for H by adding H^+.
5. Balance each half-reaction for charge by adding electrons.
6. If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other.
7. Add the two half-reactions and simplify.
8. If the reaction takes place in a basic medium, add OH^- ions the equation obtained in step 7 to neutralize the H^+ ions (add in equal numbers to both sides of the equation) and simplify.

The examples below demonstrate the application of this method to balancing equations for aqueous redox reactions.

Example 9.2.1: Balancing Equations for Redox Reactions in Acidic Solutions

Write the balanced equation representing reaction between solid copper and nitric acid to yield aqueous copper(II) ions and nitrogen monoxide gas.

Solution

Following the steps of the half-reaction method:

Step 1: Write skeletal equations for the oxidation and reduction half-reactions.

$$\begin{aligned} &\text{oxidation:} && \mathrm{Cu}\,(\mathrm{s}) \longrightarrow \mathrm{Cu^{2+}}\,(\mathrm{aq}) \\ &\text{reduction:} && \mathrm{HNO_3}\,(\mathrm{aq}) \longrightarrow \mathrm{NO}\,(\mathrm{g}) \end{aligned}$$

Step 2: Balance each half-reaction for all elements except H and O.

$$\begin{aligned} &\text{oxidation:} && \mathrm{Cu}\,(\mathrm{s}) \longrightarrow \mathrm{Cu^{2+}}\,(\mathrm{aq}) \\ &\text{reduction:} && \mathrm{HNO_3}\,(\mathrm{aq}) \longrightarrow \mathrm{NO}\,(\mathrm{g}) \end{aligned}$$

Step 3: Balance each half-reaction for O by adding $\mathrm{H_2O}$.

$$\begin{aligned} &\text{oxidation:} && \mathrm{Cu}\,(\mathrm{s}) \longrightarrow \mathrm{Cu^{2+}}\,(\mathrm{aq}) \\ &\text{reduction:} && \mathrm{HNO_3}\,(\mathrm{aq}) \longrightarrow \mathrm{NO}\,(\mathrm{g}) + \mathbf{2H2O(l)} \end{aligned}$$

Step 4: Balance each half-reaction for H by adding $\mathrm{H^+}$.

$$\begin{aligned} &\text{oxidation:} && \mathrm{Cu}\,(\mathrm{s}) \longrightarrow \mathrm{Cu^{2+}}\,(\mathrm{aq}) \\ &\text{reduction:} && \mathbf{3H^+(aq)} + \mathrm{HNO_3}\,(\mathrm{aq}) \longrightarrow \mathrm{NO}\,(\mathrm{g}) + 2\,\mathrm{H_2O}\,(\mathrm{l}) \end{aligned}$$

Step 5: Balance each half-reaction for charge by adding electrons.

$$\text{oxidation:} \quad \mathrm{Cu\,(s) \longrightarrow Cu^{2+}\,(aq) + \mathbf{2e^-}}$$
$$\text{reduction:} \quad \mathrm{\mathbf{3e^-} + 3\,H^+\,(aq) + HNO_3\,(aq) \longrightarrow NO\,(g) + 2\,H_2O\,(l)}$$

Step 6: If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other.

$$\text{oxidation } (\times 3): \quad \mathrm{\mathbf{3}\ Cu\,(s) \longrightarrow \mathbf{3}\ Cu^{2+}\,(aq) + \mathbf{6}\ \cancel{2}\ e^-}$$
$$\text{reduction } (\times 2): \quad \mathrm{\mathbf{6}\ \cancel{3}\ e^- + \mathbf{6}\ \cancel{3}\ H^+\,(aq) + \mathbf{2}\ HNO_3\,(aq) \longrightarrow \mathbf{2}\ NO\,(g) + \mathbf{4}\ \cancel{2}\ H_2O\,(l)}$$

Step 7: Add the two half-reactions and simplify.

$$\mathrm{3\,Cu\,(s) + \cancel{6e^-} + 6\,H^+\,(aq) + 2\,HNO_3\,(aq) \longrightarrow 3\,Cu^{2+}\,(aq) + \cancel{6e^-} + 2\,NO\,(g) + 4\,H_2O\,(l)}$$
$$\mathrm{3\,Cu\,(s) + 6\,H^+\,(aq) + 2\,HNO_3\,(aq) \longrightarrow 3\,Cu^{2+}\,(aq) + 2\,NO\,(g) + 4\,H_2O\,(l)}$$

Step 8: If the reaction takes place in a basic medium, add $\mathrm{OH^-}$ ions the equation obtained in step 7 to neutralize the $\mathrm{H^+}$ ions (add in equal numbers to both sides of the equation) and simplify.

This step not necessary since the solution is stipulated to be acidic.

The balanced equation for the reaction in an acidic solution is then

$$\mathrm{3\,Cu\,(s) + 6\,H^+\,(aq) + 2\,HNO_3\,(aq) \longrightarrow 3\,Cu^{2+}\,(aq) + 2\,NO\,(g) + 4\,H_2O\,(l)}$$

Exercise 9.2.1

The reaction above results when using relatively diluted nitric acid. If concentrated nitric acid is used, nitrogen dioxide is produced instead of nitrogen monoxide. Write a balanced equation for this reaction.

Answer available at the end of this section.

Example 9.2.2: Balancing Equations for Redox Reactions in Basic Solutions

Write the balanced equation representing reaction between aqueous permanganate ion, , and solid chromium(III) hydroxide, $Cr(OH)_3$, to yield solid manganese(IV) oxide, MnO_2, and aqueous chromate ion, The reaction takes place in a basic solution.

Solution

Step 1: Write skeletal equations for the oxidation and reduction half-reactions.

$$\text{oxidation:} \quad \mathrm{Cr(OH)_3\,(s) \longrightarrow {CrO_4}^{2-}\,(aq)}$$
$$\text{reduction:} \quad \mathrm{{MnO_4}^-\,(aq) \longrightarrow MnO_2\,(s)}$$

Step 2: Balance each half-reaction for all elements except H and O.

$$\text{oxidation:} \quad \mathrm{Cr(OH)_3\,(s) \longrightarrow {CrO_4}^{2-}\,(aq)}$$
$$\text{reduction:} \quad \mathrm{{MnO_4}^-\,(aq) \longrightarrow MnO_2\,(s)}$$

Step 3: Balance each half-reaction for O by adding $\mathrm{H_2O}$.

$$\text{oxidation:} \quad \mathrm{\mathbf{H2O(l)} + Cr(OH)_3\,(s) \longrightarrow {CrO_4}^{2-}\,(aq)}$$
$$\text{reduction:} \quad \mathrm{{MnO_4}^-\,(aq) \longrightarrow MnO_2\,(s) + \mathbf{2H2O(l)}}$$

Step 4: Balance each half-reaction for H by adding $\mathrm{H^+}$.

$$\text{oxidation:} \quad H_2O\,(l) + Cr(OH)_3\,(s) \longrightarrow CrO_4{}^{2-}\,(aq) + \mathbf{5H^+(aq)}$$
$$\text{reduction:} \quad \mathbf{4H^+(aq)} + MnO_4{}^-\,(aq) \longrightarrow MnO_2\,(s) + 2\,H_2O\,(l)$$

Step 5: Balance each half-reaction for charge by adding electrons.

$$\text{oxidation:} \quad H_2O\,(l) + Cr(OH)_3\,(s) \longrightarrow CrO_4{}^{2-}\,(aq) + 5\,H^+\,(aq) + \mathbf{3e^-}$$
$$\text{reduction:} \quad \mathbf{3e^-} + 4\,H^+\,(aq) + MnO_4{}^-\,(aq) \longrightarrow MnO_2\,(s) + 2\,H_2O\,(l)$$

Step 6: If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other.

This step is not necessary since the number of electrons is already in balance.

Step 7: Add the two half-reactions and simplify.

$$\cancel{H2O(l)} + Cr(OH)_3\,(s) \longrightarrow CrO_4{}^{2-}\,(aq) + \cancel{5}^{1}H^+\,(aq) + \cancel{3e^-}$$
$$+ \quad \cancel{3e^-} + \cancel{4H^+(aq)} + MnO_4{}^-\,(aq) \longrightarrow MnO_2\,(s) + \cancel{2}^{1}\,H_2O\,(l)$$
$$Cr(OH)_3\,(s) + MnO_4{}^-\,(aq) \longrightarrow CrO_4{}^{2-}\,(aq) + MnO_2\,(s) + H^+\,(aq) + H_2O\,(l)$$

Step 8: If the reaction takes place in a basic medium, add OH^- ions the equation obtained in step 7 to neutralize the H^+ ions (add in equal numbers to both sides of the equation) and simplify.

$$OH^-\,(aq) + Cr(OH)_3\,(s) + MnO_4{}^-\,(aq) \longrightarrow CrO_4{}^{2-}\,(aq) + MnO_2\,(s) + \cancel{H^+(aq)} + H_2O\,(l) + \cancel{OH^-(aq)}$$

after neutralizing the H^+, we get the balanced equation for the reaction in a basic solution

$$OH^-\,(aq) + Cr(OH)_3\,(s) + MnO_4{}^-\,(aq) \longrightarrow CrO_4{}^{2-}\,(aq) + MnO_2\,(s) + 2\,H_2O\,(l)$$

Exercise 9.2.2

Aqueous permanganate ion may also be reduced using aqueous bromide ion, Br^-, the products of this reaction being solid manganese(IV) oxide and aqueous bromate ion, $BrO_3{}^-$. Write the balanced equation for this reaction occurring in a basic medium.

Answer available at the end of this section.

Answers

Exercise 9.2.1

$$Cu\,(s) + 2\,H^+\,(aq) + 2\,HNO_3\,(aq) \longrightarrow Cu^{2+}\,(aq) + 2\,NO_2\,(g) + 2\,H_2O\,(l)$$

Exercise 9.2.2

$$H_2O\,(l) + 2\,MnO_4{}^-\,(aq) + Br^-\,(aq) \longrightarrow 2\,MnO_2\,(s) + BrO_3{}^-\,(aq) + 2\,OH^-\,(aq)$$

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9.3: Galvanic Cells

Learning Objectives

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

- Describe the function of a galvanic cell and its components
- Use cell notation to symbolize the composition and construction of galvanic cells

As demonstration of spontaneous chemical change, Figure 9.3.1: shows the result of immersing a coiled wire of copper into an aqueous solution of silver nitrate. A gradual but visually impressive change spontaneously occurs as the initially colorless solution becomes increasingly blue, and the initially smooth copper wire becomes covered with a porous gray solid.

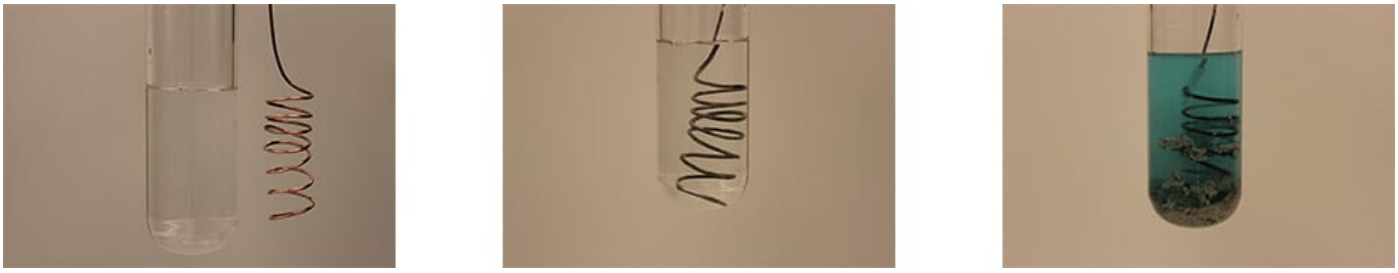


Figure 9.3.1: A copper wire and an aqueous solution of silver nitrate (left) are brought into contact (center) and a spontaneous transfer of electrons occurs, creating blue $Cu^{2+}(aq)$ and gray Ag(s) (right).

These observations are consistent with (i) the oxidation of elemental copper to yield copper(II) ions, $Cu^{2+}(aq)$, which impart a blue color to the solution, and (ii) the reduction of silver(I) ions to yield elemental silver, which deposits as a fluffy solid on the copper wire surface. And so, *the direct transfer of electrons from the copper wire to the aqueous silver ions is spontaneous* under the employed conditions. A summary of this redox system is provided by these equations:

Consider the construction of a device that contains all the reactants and products of a redox system like the one here, but prevents physical contact between the reactants. Direct transfer of electrons is, therefore, prevented; transfer, instead, takes place indirectly through an external circuit that contacts the separated reactants. Devices of this sort are generally referred to as *electrochemical cells*, and those in which a spontaneous redox reaction takes place are called galvanic cells (or voltaic cells).

A galvanic cell based on the spontaneous reaction between copper and silver(I) is depicted in Figure 9.3.2. The cell is comprised of two half-cells, each containing the redox conjugate pair ("couple") of a single reactant. The half-cell shown at the left contains the Cu(0)/Cu(II) couple in the form of a solid copper foil and an aqueous solution of copper nitrate. The right half-cell contains the Ag(I)/Ag(0) couple as solid silver foil and an aqueous silver nitrate solution. An external circuit is connected to each half-cell at its solid foil, meaning the Cu and Ag foil each function as an *electrode*. By definition, the anode of an electrochemical cell is the electrode at which oxidation occurs (in this case, the Cu foil) and the cathode is the electrode where reduction occurs (the Ag foil). The redox reactions in a galvanic cell occur only at the interface between each half-cell's reaction mixture and its electrode. To keep the reactants separate while maintaining charge-balance, the two half-cell solutions are connected by a tube filled with inert electrolyte solution called a salt bridge. The spontaneous reaction in this cell produces Cu^{2+} cations in the anode half-cell and consumes Ag^{+} ions in the cathode half-cell, resulting in a compensatory flow of inert ions from the salt bridge that maintains charge balance. Increasing concentrations of Cu^{2+} in the anode half-cell are balanced by an influx of NO_3^{-} from the salt bridge, while a flow of Na^{+} into the cathode half-cell compensates for the decreasing Ag^{+} concentration.

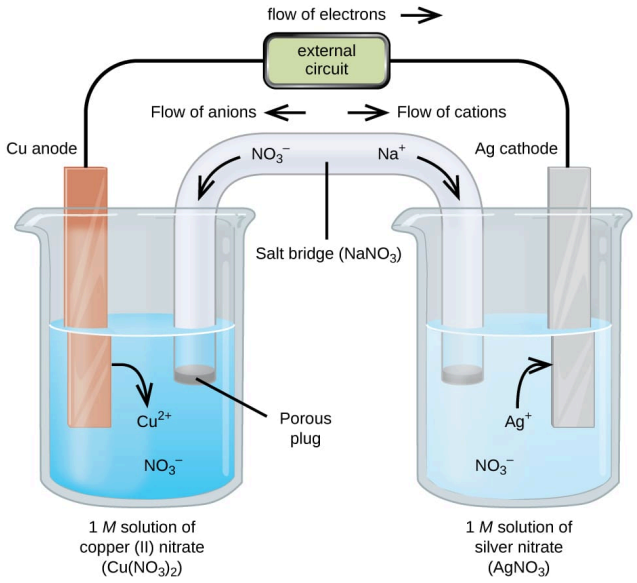


Figure 9.3.2: A galvanic cell based on the spontaneous reaction between copper and silver(I) ions.

Cell Notation

Abbreviated symbolism is commonly used to represent a galvanic cell by providing essential information on its composition and structure. These symbolic representations are called cell notations or cell schematics, and they are written following a few guidelines:

- The relevant components of each half-cell are represented by their chemical formulas or element symbols
- All interfaces between component phases are represented by vertical parallel lines; if two or more components are present in the same phase, their formulas are separated by commas
- By convention, the schematic begins with the anode and proceeds left-to-right identifying phases and interfaces encountered within the cell, ending with the cathode

A verbal description of the cell as viewed from anode-to-cathode is often a useful first-step in writing its schematic. For example, the galvanic cell shown in Figure 9.3.2: consists of a solid copper anode immersed in an aqueous solution of copper(II) nitrate that is connected via a salt bridge to an aqueous silver(I) nitrate solution, immersed in which is a solid silver cathode. Converting this statement to symbolism following the above guidelines results in the cell schematic:

Consider a different galvanic cell (see Figure 9.3.3) based on the spontaneous reaction between solid magnesium and aqueous iron(III) ions:

In this cell, a solid magnesium anode is immersed in an aqueous solution of magnesium chloride that is connected via a salt bridge to an aqueous solution containing a mixture of iron(III) chloride and iron(II) chloride, immersed in which is a platinum cathode. The cell schematic is then written as

Notice the cathode half-cell is different from the others considered thus far in that its electrode is comprised of a substance (Pt) that is neither a reactant nor a product of the cell reaction. This is required when neither member of the half-cell's redox couple can reasonably function as an electrode, which must be electrically conductive and in a phase separate from the half-cell solution. In this case, both members of the redox couple are solute species, and so Pt is used as an inert electrode that can simply provide or accept electrons to redox species in solution. Electrodes constructed from a member of the redox couple, such as the Mg anode in this cell, are called active electrodes.

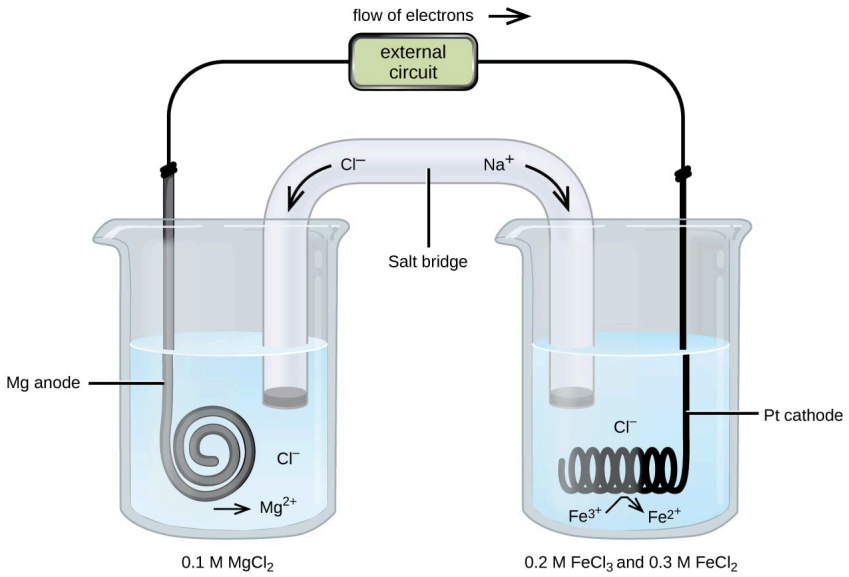


Figure 9.3.3: A galvanic cell based on the spontaneous reaction between magnesium and iron(III) ions.

Example 9.3.1: Writing Galvanic Cell Schematics

A galvanic cell is fabricated by connecting two half-cells with a salt bridge, one in which a chromium wire is immersed in a 1 M $CrCl_3$ solution and another in which a copper wire is immersed in 1 M $CuCl_2$. Assuming the chromium wire functions as an anode, write the schematic for this cell along with equations for the anode half-reaction, the cathode half-reaction, and the overall cell reaction.

Solution

Since the chromium wire is stipulated to be the anode, the schematic begins with it and proceeds left-to-right, symbolizing the other cell components until ending with the copper wire cathode:

The half-reactions for this cell are

Multiplying to make the number of electrons lost by Cr and gained by Cu^{2+} equal yields

Adding the half-reaction equations and simplifying yields an equation for the cell reaction:

Exercise 9.3.1

Omitting solute concentrations and spectator ion identities, write the schematic for a galvanic cell whose net cell reaction is shown below.

Answer available at the end of this section.

Answers

Exercise 9.3.1

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9.4: Electrode and Cell Potentials

Learning Objectives

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

- Describe and relate the definitions of electrode and cell potentials
- Interpret electrode potentials in terms of relative oxidant and reductant strengths
- Calculate cell potentials and predict redox spontaneity using standard electrode potentials

Unlike the spontaneous oxidation of copper by aqueous silver(I) ions described previously, immersing a copper wire in an aqueous solution of lead(II) ions yields no reaction. The two species, $Ag^{+}(aq)$ and $Pb^{2+}(aq)$, thus show a distinct difference in their redox activity towards copper: the silver ion spontaneously oxidized copper, but the lead ion did not. Electrochemical cells permit this relative redox activity to be quantified by an easily measured property, *potential*. This property is more commonly called *voltage* when referenced in regard to electrical applications, and it is a measure of energy accompanying the transfer of charge. Potentials are measured in the volt unit, defined as one joule of energy per one coulomb of charge, V = J/C.

When measured for purposes of electrochemistry, a potential reflects the driving force for a specific type of charge transfer process, namely, the transfer of electrons between redox reactants. Considering the nature of potential in this context, it is clear that the potential of a single half-cell or a single electrode can't be measured; "transfer" of electrons requires both a donor and recipient, in this case a reductant and an oxidant, respectively. Instead, a half-cell potential may only be assessed relative to that of another half-cell. It is only the *difference in potential* between two half-cells that may be measured, and these measured potentials are called cell potentials, E_{cell}, defined as

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

where $E_{cathode}$ and E_{anode} are the potentials of two different half-cells functioning as specified in the subscripts. As for other thermodynamic quantities, the standard cell potential, $E°_{cell}$, is a cell potential measured when both half-cells are under standard-state conditions (1 *M* concentrations, 1 bar pressures, 298 K):

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

To simplify the collection and sharing of potential data for half-reactions, the scientific community has designated one particular half-cell to serve as a universal reference for cell potential measurements, assigning it a potential of exactly 0 V. This half-cell is the **standard hydrogen electrode** (SHE) and it is based on half-reaction below:

$$2\,\mathrm{H^+\,(aq)} + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2\,(g)}$$

A typical SHE contains an inert platinum electrode immersed in precisely 1 *M* aqueous H^+ and a stream of bubbling H_2 gas at 1 bar pressure, all maintained at a temperature of 298 K (see Figure 9.4.1).

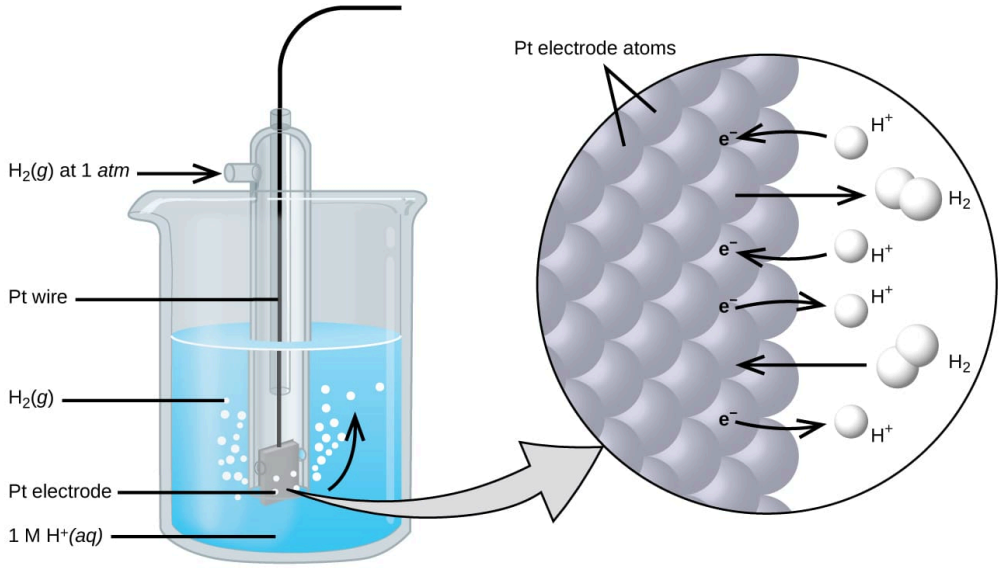


Figure 9.4.1: A standard hydrogen electrode (SHE).

The assigned potential of the SHE permits the definition of a conveniently measured potential for a single half-cell. The electrode potential (E_X) for a half-cell *X* is defined as *the potential measured for a cell comprised of X acting as cathode and the SHE acting as anode*:

$$E_{\text{cell}} = E_X - E_{SHE}$$
$$E_{SHE} = 0V \text{ (defined)}$$
$$E_{\text{cell}} = E_X$$

When the half-cell *X* is under standard-state conditions, its potential is the standard electrode potential, $E°_X$. Since the definition of cell potential requires the half-cells function as cathodes, these potentials are sometimes called *standard reduction potentials*.

This approach to measuring electrode potentials is illustrated in Figure 9.4.2: , which depicts a cell comprised of an SHE connected to a copper(II)/copper(0) half-cell under standard-state conditions. A voltmeter in the external circuit allows measurement of the potential difference between the two half-cells. Since the Cu half-cell is designated as the cathode in the definition of cell potential, it is connected to the red (positive) input of the voltmeter, while the designated SHE anode is connected to the black (negative) input. These connections insure that the sign of the measured potential will be consistent with the sign conventions of electrochemistry per the various definitions discussed above. A cell potential of +0.337 V is measured, and so

$$E°_{\text{cell}} = E°_{\text{Cu}} = +0.337V$$

Tabulations of E° values for other half-cells measured in a similar fashion are available as reference literature to permit calculations of cell potentials and the prediction of the spontaneity of redox processes.

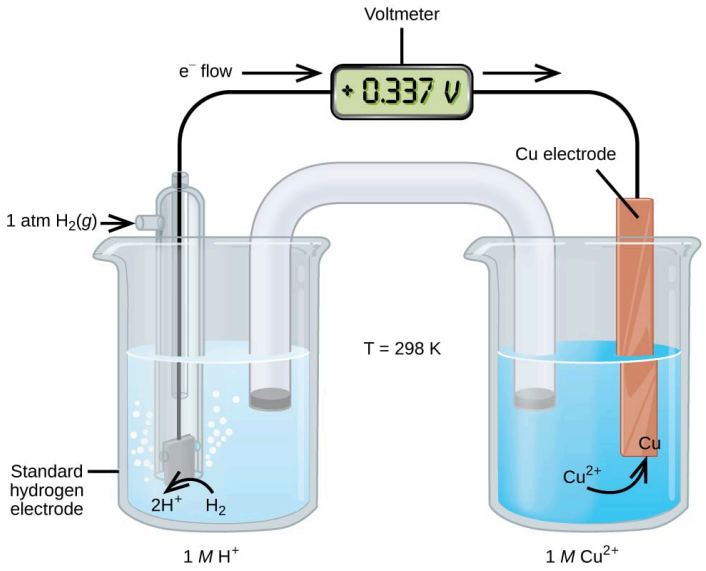


Figure 9.4.2: A cell permitting experimental measurement of the standard electrode potential for the half-reaction

Table 9.4.1 provides a listing of standard electrode potentials for a selection of half-reactions in numerical order, and a more extensive alphabetical listing is given in Appendix 11.12.

Table 9.4.1: 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

Half-Reaction	E° (V)
$\mathrm{Sn^{2+}\,(aq) + 2\,e^- \longrightarrow Sn\,(s)}$	-0.1375
$\mathrm{Ni^{2+}\,(aq) + 2\,e^- \longrightarrow Ni\,(s)}$	-0.257
$\mathrm{Co^{2+}\,(aq) + 2\,e^- \longrightarrow Co\,(s)}$	-0.28
$\mathrm{PbSO_4\,(s) + 2\,e^- \longrightarrow Pb\,(s) + SO_4{}^{2-}\,(aq)}$	-0.3505
$\mathrm{Cd^{2+}\,(aq) + 2\,e^- \longrightarrow Cd\,(s)}$	-0.4030
$\mathrm{Fe^{2+}\,(aq) + 2\,e^- \longrightarrow Fe\,(s)}$	-0.447
$\mathrm{Cr^{3+}\,(aq) + 3\,e^- \longrightarrow Cr\,(s)}$	-0.744
$\mathrm{Mn^{2+}\,(aq) + 2\,e^- \longrightarrow Mn\,(s)}$	-1.185
$\mathrm{Zn(OH)_2\,(s) + 2\,e^- \longrightarrow Zn\,(s) + 2\,OH^-\,(aq)}$	-1.245
$\mathrm{Zn^{2+}\,(aq) + 2\,e^- \longrightarrow Zn\,(s)}$	-0.7618
$\mathrm{Al^{3+}\,(aq) + 3\,e^- \longrightarrow Al\,(s)}$	-1.662
$\mathrm{Mg_2\,(aq) + 2\,e^- \longrightarrow Mg\,(s)}$	-2.372
$\mathrm{Na^+\,(aq) + e^- \longrightarrow Na\,(s)}$	-2.71
$\mathrm{Ca^{2+}\,(aq) + 2\,e^- \longrightarrow Ca\,(s)}$	-2.868
$\mathrm{Ba^{2+}\,(aq) + 2\,e^- \longrightarrow Ba\,(s)}$	-2.912
$\mathrm{K^+\,(aq) + e^- \longrightarrow K\,(s)}$	-2.931
$\mathrm{K^+\,(aq) + e^- \longrightarrow K\,(s)}$	-3.04

Example 9.4.1: Calculating Standard Cell Potentials

What is the standard potential of the galvanic cell shown in Figure 17.3?

Solution

The cell in Figure 17.3 is galvanic, the spontaneous cell reaction involving oxidation of its copper anode and reduction of silver(I) ions at its silver cathode:

$$\begin{aligned}
&\text{anode:} && \mathrm{Cu\,(s) \longrightarrow Cu^{2+} + 2\,e^-} \\
&\text{cathode:} && \mathrm{2\,Ag^+\,(aq) + 2\,e^- \longrightarrow 2\,Ag\,(s)} \\
&\text{cell:} && \mathrm{Cu\,(s) + 2\,Ag^+\,(aq) \longrightarrow Cu^{2+} + 2\,Ag\,(s)} \qquad E^o_{\text{cell}} = 0\,\mathrm{V}
\end{aligned}$$

The standard cell potential computed as

$$\begin{aligned}
E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\
&= E^\circ_{Ag} - E^\circ_{Cu} \\
&= 0.7996V - 0.34V \\
&= +0.46V
\end{aligned}$$

9.4.1Exerc

What is the standard cell potential expected if the silver cathode half-cell in Figure 17.3 is replaced with a lead half-cell:

$$\mathrm{Pb^{2+}\,(aq) + 2\,e^- \longrightarrow Pb\,(s)}$$

Answer available at the end of this section.

Intrepreting Electrode and Cell Potentials

Thinking carefully about the definitions of cell and electrode potentials and the observations of spontaneous redox change presented thus far, a significant relation is noted. The previous section described the spontaneous oxidation of copper by aqueous silver(I) ions, but no observed reaction with aqueous lead(II) ions. Results of the calculations in Example 9.4.1 have just shown *the spontaneous process is described by a positive cell potential* while *the nonspontaneous process exhibits a negative cell potential*. And so, with regard to the relative effectiveness ("strength") with which aqueous Ag^+ and Pb^{2+} ions oxidize Cu under standard conditions, *the stronger oxidant is the one exhibiting the greater standard electrode potential, E°*. Since by convention electrode potentials are for reduction processes, an increased value of E^o corresponds to an increased driving force behind the reduction of the species (hence increased effectiveness of its action as an *oxidizing agent* on some other species). Negative values for electrode potentials are simply a consequence of assigning a value of 0 V to the SHE, indicating the reactant of the half-reaction is a weaker oxidant than aqueous hydrogen ions.

Applying this logic to the numerically ordered listing of standard electrode potentials in Table 9.4.1 shows this listing to be likewise in order of the oxidizing strength of the half-reaction's reactant species, decreasing from strongest oxidant (most positive *E°*) to weakest oxidant (most negative *E°*). Predictions regarding the spontaneity of redox reactions under standard state conditions can then be easily made by simply comparing the relative positions of their table entries. By definition, $E°_{cell}$ is positive when $E^o_{cathode} > E^o_{anode}$, and so any redox reaction in which the oxidant's entry is above the reductant's entry is predicted to be spontaneous.

Reconsideration of the two redox reactions in Example 9.4.1 provides support for this fact. The entry for the silver(I)/silver(0) half-reaction is above that for the copper(II)/copper(0) half-reaction, and so the oxidation of Cu by Ag^+ is predicted to be spontaneous ($E°_{cathode} > E°_{anode}$ and so $E°_{cell} > 0$). Conversely, the entry for the lead(II)/lead(0) half-cell is beneath that for copper(II)/copper(0), and the oxidation of Cu by Pb^{2+} is nonspontaneous ($E°_{cathode} < E°_{anode}$ and so $E°_{cell} < 0$).

Recalling the chapter on thermodynamics, the spontaneities of the forward and reverse reactions of a reversible process show a reciprocal relationship: if a process is spontaneous in one direction, it is non-spontaneous in the opposite direction. As an indicator of spontaneity for redox reactions, the potential of a cell reaction shows a consequential relationship in its arithmetic sign. The spontaneous oxidation of copper by lead(II) ions is *not* observed,

$$\mathrm{Cu\,(s) + Pb^{2+}\,(aq) \longrightarrow Cu^{2+}\,(aq) + Pb\,(s)} \quad E°_{forward} = -0.47\ \mathrm{V(negative, non-spontaneous)}$$

and so the reverse reaction, the oxidation of lead by copper(II) ions, is predicted to occur spontaneously:

$$\mathrm{Pb\,(s) + Cu^{2+}\,(aq) \longrightarrow Pb^{2+}\,(aq) + Cu\,(s)} \quad E°_{forward} = +0.47\ \mathrm{V(positive, spontaneous)}$$

Note that reversing the direction of a redox reaction effectively interchanges the identities of the cathode and anode half-reactions, and so the cell potential is calculated from electrode potentials in the reverse subtraction order than that for the forward reaction. In practice, a voltmeter would report a potential of −0.47 V with its red and black inputs connected to the Pb and Cu electrodes, respectively. If the inputs were swapped, the reported voltage would be +0.47 V.

Example 9.4.2: Predicting Redox Spontaneity

Are aqueous iron(II) ions predicted to spontaneously oxidize elemental chromium under standard state conditions? Assume the half-reactions to be those available in Table 9.4.1.

Solution

Referring to the tabulated half-reactions, the redox reaction in question can be represented by the equations below:

$$\mathrm{Cr\,(s) + Fe^{2+}\,(aq) \longrightarrow Cr^{3+}\,(aq) + Fe\,(s)}$$

The entry for the putative oxidant, Fe^{2+}, appears *above* the entry for the reductant, Cr, and so a spontaneous reaction is predicted per the quick approach described above. Supporting this predication by calculating the standard cell potential for this reaction gives

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= E^\circ_{\text{Fe(II)}} - E^\circ_{\text{Cr}} \\ &= -0.447V - -0.744V = +0.297V \end{aligned}$$

The positive value for the standard cell potential indicates the process is spontaneous under standard state conditions.

9.4.2 Exerc

Use the data in Table 9.4.1 to predict the spontaneity of the oxidation of bromide ion by molecular iodine under standard state conditions, supporting the prediction by calculating the standard cell potential for the reaction. Repeat for the oxidation of iodide ion by molecular bromine.

Answer available at the end of this section.

Answers

−0.47 V

$$\begin{aligned} &\mathrm{I_2\,(s) + 2\,Br^-\,(aq) \longrightarrow 2\,I^-\,(aq) + Br_2\,(l)} \quad && E_{\text{cell}} = -0.5518\,\text{V (nonspontaneous)} \\ &\mathrm{Br_2\,(s) + 2\,I^-\,(aq) \longrightarrow 2\,Br^-\,(aq) + I_2\,(l)} \quad && E^\circ_{\text{cell}} = +0.5518\,\text{V (spontaneous)} \end{aligned}$$

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9.5: Potential, Free Energy, and Equilibrium

Learning Objectives

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

- Explain the relations between potential, free energy change, and equilibrium constants
- Perform calculations involving the relations between cell potentials, free energy changes, and equilibrium
- Use the Nernst equation to determine cell potentials under nonstandard conditions

So far in this chapter, the relationship between the cell potential and reaction *spontaneity* has been described, suggesting a link to the free energy change for the reaction (see chapter on thermodynamics). The interpretation of potentials as measures of oxidant *strength* was presented, bringing to mind similar measures of acid-base strength as reflected in equilibrium constants (see the chapter on acid-base equilibria). This section provides a summary of the relationships between potential and the related thermodynamic properties ΔG and K.

E° and ΔG°

The standard free energy change of a process, ΔG°, was defined in a previous chapter as the maximum work that could be performed by a system, w_{max}. In the case of a redox reaction taking place within a galvanic cell under standard state conditions, essentially all the work is associated with transferring the electrons from reductant-to-oxidant, w_{elec}:

$$\Delta G^\circ = w_{\text{max}} = w_{\text{elec}}$$

The work associated with transferring electrons is determined by the total amount of charge (coulombs) transferred and the cell potential:

$$\Delta G^\circ = w_{\text{elec}} = -nFE^\circ_{\text{cell}}$$

where n is the number of moles of electrons transferred, F is **Faraday's constant**, and E°_{cell} is the standard cell potential. The relation between free energy change and standard cell potential confirms the sign conventions and spontaneity criteria previously discussed for both of these properties: spontaneous redox reactions exhibit positive potentials and negative free energy changes.

E° and K

Combining a previously derived relation between ΔG° and K (see the chapter on thermodynamics) and the equation above relating ΔG° and $E°_{\text{cell}}$ yields the following:

$$\Delta G^\circ = -RT \ln K = -nFE^\circ_{\text{cell}} \tag{9.5.1}$$

with

$$E^\circ_{\text{coll}} = \left(\frac{RT}{nF}\right) \ln K$$

This equation indicates redox reactions with large (positive) standard cell potentials will proceed far towards completion, reaching equilibrium when the majority of reactant has been converted to product. A summary of the relations between $E°$, $\Delta G°$ and K is depicted in Figure $9.5.1$, and a table correlating reaction spontaneity to values of these properties is provided in Table $9.5.1$.

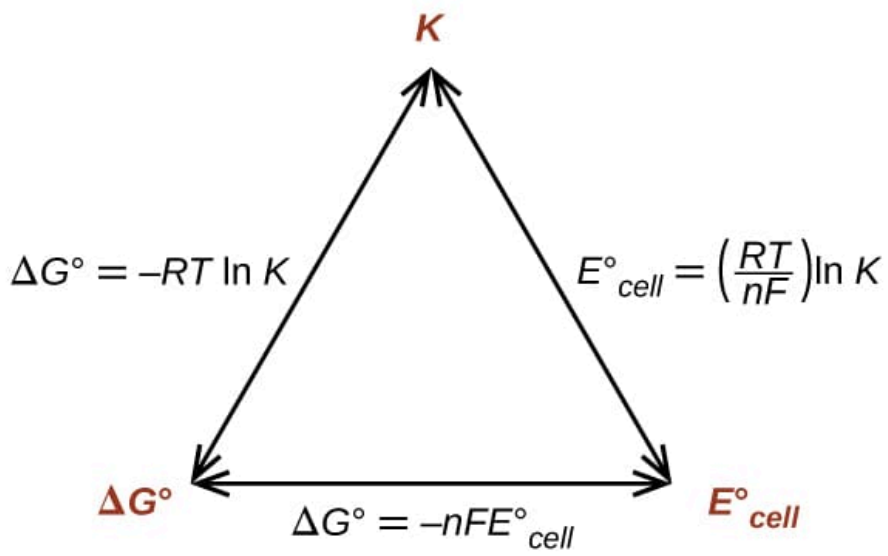


Figure 9.5.1: Graphic depicting the relation between three important thermodynamic properties.

Table 9.5.1

K	Δ*G*°	*E*°cell	Comment
> 1	< 0	> 0	Reaction is spontaneous under standard conditions Products more abundant at equilibrium
< 1	> 0	< 0	Reaction is non-spontaneous under standard conditions Reactants more abundant at equilibrium
= 1	= 0	= 0	Reaction is at equilibrium under standard conditions Reactants and products equally abundant

Example 9.5.1: Equilibrium Constants, Standard Cell Potentials, and Standard Free Energy Changes

Use data from Appendix 11.12 to calculate the standard cell potential, standard free energy change, and equilibrium constant for the following reaction at 25 °C. Comment on the spontaneity of the forward reaction and the composition of an equilibrium mixture of reactants and products.

$$2\,\mathrm{Ag^+(aq)} + \mathrm{Fe(s)} \rightleftharpoons 2\,\mathrm{Ag(s)} + \mathrm{Fe^{2+}(aq)}$$

Solution

The reaction involves an oxidation-reduction reaction, so the standard cell potential can be calculated using the data in Appendix 11.12.

anode:	$\mathrm{Fe(s)} \longrightarrow \mathrm{Fe^{2+}(aq)} + 2\,\mathrm{e^-}$	$E^o_{\mathrm{Fe^{2+}/Fe}} = -0.447\,\mathrm{V}$
cathode:	$2 \times (\mathrm{Ag^+(aq)} + \mathrm{e^-} \longrightarrow \mathrm{Ag(s)})$	$E^o_{\mathrm{Ag^+/Ag}} = +0.7996\,\mathrm{V}$
cell:	$\mathrm{Fe(s)} + 2\,\mathrm{Ag^+(aq)} \longrightarrow \mathrm{Fe^{2+}(aq)} + 2\,\mathrm{Ag(s)}$	$E^o_{\mathrm{cell}} = +1.2247\,\mathrm{V}$

with

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^o_{\text{Fe}^{2+}/\text{Fe}} - E^o_{\text{Ag}^+/\text{Ag}} = +1.2247\,\text{V}$$

With $n = 2$, the equilibrium constant is then

$$\begin{aligned} E^\circ_{\text{cell}} &= \frac{0.0592V}{n}\log K \\ K &= 10^{n\times E^o_{\text{cal}}/0.0592V} \\ &= 10^{2\times 1.247V/0.0592V} \\ &= 10^{42.128} \\ &= 1.3\times 10^{42} \end{aligned}$$

The standard free energy is then Equation 9.5.1

$$\begin{aligned} \Delta G^\circ &= -nFE^\circ_{\text{cell}} \\ &= -2\times 96,485\frac{C}{mol}\times 1.247\frac{J}{C} = -240.6\frac{kJ}{mol} \end{aligned}$$

The reaction is spontaneous, as indicated by a negative free energy change and a positive cell potential. The *K* value is very large, indicating the reaction proceeds to near completion to yield an equilibrium mixture containing mostly products.

Exercise 9.5.1

What is the standard free energy change and the equilibrium constant for the following reaction at room temperature? Is the reaction spontaneous?

$$\text{Sn}\,(\text{s}) + 2\,\text{Cu}^{2+}\,(\text{aq}) \rightleftharpoons \text{Sn}^{2+}\,(\text{aq}) + 2\,\text{Cu}^{+}\,(\text{aq})$$

Answer available at the end of this section.

Potentials at Nonstandard Conditions: The Nernst Equation

Most of the redox processes that interest science and society do not occur under standard state conditions, and so the potentials of these systems under nonstandard conditions are a property worthy of attention. Having established the relationship between potential and free energy change in this section, the previously discussed relation between free energy change and reaction mixture composition can be used for this purpose.

$$\Delta G = \Delta G^\circ + RT\ln Q$$

Notice the reaction quotient, Q, appears in this equation, making the free energy change dependent upon the composition of the reaction mixture. Substituting the equation relating free energy change to cell potential yields the **Nernst equation**:

$$\begin{aligned} -nFE_{\text{cell}} &= -nFE^\circ_{\text{cell}} + RT\ln Q \\ E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{RT}{nF}\ln Q \end{aligned}$$

This equation describes how the potential of a redox system (such as a galvanic cell) varies from its standard state value, specifically, showing it to be a function of the number of electrons transferred, *n*, the temperature, *T*, and the reaction mixture composition as reflected in Q. A convenient form of the Nernst equation for most work is one in which values for the fundamental constants (R and F) and standard temperature (298) K), along with a factor converting from natural to base-10 logarithms, have been included:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592V}{n}\log Q \tag{9.5.2}$$

Example 9.5.2: Predicting Redox Spontaneity Under Nonstandard Conditions

Use the Nernst equation to predict the spontaneity of the redox reaction shown below at room temperature.

$$\mathrm{Co\,(s) + Fe^{2+}(aq,\ 1.94\ M) \longrightarrow Co^{2+}(aq,\ 0.15\ M) + Fe\,(s)}$$

Solution

Collecting information from Appendix 11.12 and the problem,

anode:	$\mathrm{Co\,(s) \longrightarrow Co^{2+}\,(aq) + 2\,e^-}$	$E^o_{\mathrm{Co^{2+}/Co}} = -0.28\,\mathrm{V}$
cathode:	$\mathrm{Fe^{2+}\,(aq) + 2\,e^- \longrightarrow Fe\,(s)}$	$E^o_{\mathrm{Fe^{+}/Fe}} = -0.447\,\mathrm{V}$
cell:	$\mathrm{Co\,(s) + Fe^{2+}(Aq) \longrightarrow Fe\,(s) + Co^{2+}\,(aq)}$	$E^o_{\mathrm{cell}} = -0.17\,\mathrm{V}$

with

$$E^\circ_{\mathrm{cell}} = E^\circ_{\mathrm{cathode}} - E^\circ_{\mathrm{anode}} = -0.447V - (-0.28V) = -0.17V$$

Notice the negative value of the standard cell potential indicates the process is not spontaneous under standard conditions. Substitution of the Nernst equation terms for the nonstandard conditions requires calculating the reaction quotient Q

$$Q = \frac{[\blacksquare]}{[\blacksquare]} = \frac{0.15M}{1.94M} = 0.077$$

them Q and n are substituted into Equation \red{Nernst at room temperature}

$$\begin{aligned} E_{\mathrm{cell}} &= E^\circ_{\mathrm{cell}} - \frac{0.0592\,\mathrm{V}}{n}\log Q \\ &= -0.17\,\mathrm{V} - \frac{0.0592\,\mathrm{V}}{2}\log 0.077 \\ &= -0.17\,\mathrm{V} + 0.033\,\mathrm{V} \\ &= -0.14\,\mathrm{V} \end{aligned}$$

The cell potential remains negative (slightly) under the specified conditions, and so the reaction remains nonspontaneous.

Exercise 9.5.2

For the cell schematic below at room temperature, identify values for *n* and Q, and calculate the cell potential, E_{cell}.

$$\mathrm{Al\,(s)|Al^{3+}(aq,\ 0.15\ M)|Cu^{2+}(aq,\ 0.025\ M)|Cu\,(s)}$$

Answer available at the end of this section.

A **concentration cell** is constructed by connecting two nearly identical half-cells, each based on the same half-reaction and using the same electrode, varying only in the concentration of one redox species. The potential of a concentration cell, therefore, is determined only by the difference in concentration of the chosen redox species. The example problem below illustrates the use of the Nernst equation in calculations involving concentration cells.

Example 9.5.3: Concentration Cells

What is the cell potential of the concentration cell operating at room temperature described by

$$\mathrm{Zn\,(s)|Zn^{2+}(aq,\ 0.10\ M)|Zn^{2+}(aq,\ 0.50\ M)|Zn\,(s)}$$

Solution

From the information given:

$$\begin{array}{lll} \text{anode:} & \mathrm{Zn\,(s) \longrightarrow Zn^{2+}(aq,\ 0.10\ M) + 2\,e^-} & E^o_{\mathrm{Co^{2+}/Co}} = -0.7618\,\mathrm{V} \\ \text{cathode:} & \mathrm{Zn^{2+}(aq,\ 0.50\ M) + 2\,e^- \longrightarrow Zn\,(s)} & E^o_{\mathrm{Fe^{+}/Fe}} = -0,7618\,\mathrm{V} \\ \text{cell:} & \cancel{\mathrm{Zn(s)}} + \mathrm{Zn^{2+}(aq,\ 0.50\ M) \longrightarrow Zn^{2+}(aq,\ 0.10\ M)} + \cancel{\mathrm{Zn(s)}} & E^o_{\text{cell}} = 0\,\mathrm{V} \end{array}$$

Substituting into the Nernst equation (Equation 9.5.2),

$$E_{\text{cell}} = 0.000\,\mathrm{V} - \frac{0.0592\,\mathrm{V}}{2}\log\frac{0.10}{0.50} = +0.021\,\mathrm{V}$$

The positive value for cell potential indicates the overall cell reaction (see above) is spontaneous. This spontaneous reaction is one in which the zinc ion concentration in the cathode falls (it is reduced to elemental zinc) while that in the anode rises (it is produced by oxidation of the zinc anode). A greater driving force for zinc reduction is present in the cathode, where the zinc(II) ion concentration is greater ($E_{\text{cathode}} > E_{\text{anode}}$).

Exercise 9.5.1

The concentration cell above was allowed to operate until the cell reaction reached equilibrium at room temperature. What are the cell potential and the concentrations of zinc(II) in each half-cell for the cell now?

Answer available at the end of this section.

Answers

Exercise 9.5.1

Spontaneous

$n = 2$

$E^\circ_{\text{cell}} = +0.291V$

$[\Delta G^\circ = -56.2\frac{kJ}{mol}$

K = 6.8 10^9.

Exercise 9.5.2

n = 6; Q = 1440; E_{cell} = +1.97 V, spontaneous.

Exercise 9.5.1

E_{cell} = 0.000 V; $[Zn^{2+}]_{\text{cathode}} = [Zn^{2+}]_{\text{anode}}$ = 0.30 M

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9.6: Batteries and Fuel Cells

Learning Objectives

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

- Describe the electrochemistry associated with several common batteries
- Distinguish the operation of a fuel cell from that of a battery

There are many technological products associated with the past two centuries of electrochemistry research, none more immediately obvious than the battery. A **battery** is a galvanic cell that has been specially designed and constructed in a way that best suits its intended use a source of electrical power for specific applications. Among the first successful batteries was the *Daniell cell*, which relied on the spontaneous oxidation of zinc by copper(II) ions (Figure 9.6.1):

$$\mathrm{Zn\,(s) + Cu^{2+}\,(aq) \longrightarrow Zn^{2+}\,(aq) + Cu\,(s)}$$

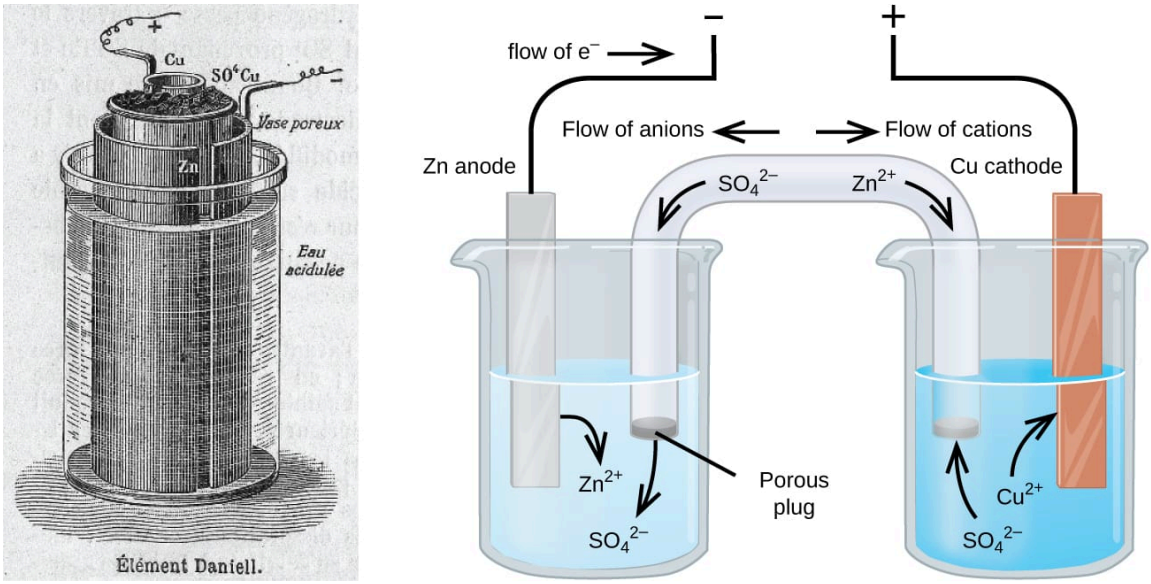


Figure 9.6.1: Illustration of a Daniell cell taken from a 1904 journal publication (left) along with a simplified illustration depicting the electrochemistry of the cell (right). The 1904 design used a porous clay pot to both contain one of the half-cell's content and to serve as a salt bridge to the other half-cell.

Modern batteries exist in a multitude of forms to accommodate various applications, from tiny button batteries that provide the modest power needs of a wristwatch to the very large batteries used to supply backup energy to municipal power grids. Some batteries are designed for single-use applications and cannot be recharged (primary cells), while others are based on conveniently reversible cell reactions that allow recharging by an external power source (secondary cells). This section will provide a summary of the basic electrochemical aspects of several batteries familiar to most consumers, and will introduce a related electrochemical device called a *fuel cell* that can offer improved performance in certain applications.

Link to Learning

Visit this site to learn more about batteries.

Single-Use Batteries

A common primary battery is the dry cell, which uses a zinc can as both container and anode ("–" terminal) and a graphite rod

as the cathode (“+” terminal). The Zn can is filled with an electrolyte paste containing manganese(IV) oxide, zinc(II) chloride, ammonium chloride, and water. A graphite rod is immersed in the electrolyte paste to complete the cell. The spontaneous cell reaction involves the oxidation of zinc:

$$\mathrm{Zn\,(s)} \longrightarrow \mathrm{Zn^{2+}\,(aq)} + 2\,\mathrm{e^-} \qquad \text{(anode)}$$

and the reduction of manganese(IV)

$$2\,\mathrm{MnO_2\,(s)} + 2\,\mathrm{NH_4Cl\,(aq)} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Mn_2O_3\,(s)} + 2\,\mathrm{NH_3\,(aq)} + \mathrm{H_2O\,(l)} + 2\,\mathrm{Cl^-} \qquad \text{(cathode)}$$

which together yield the cell reaction:

$$2\,\mathrm{MnO_2\,(s)} + 2\,\mathrm{NH_4Cl\,(aq)} + \mathrm{Zn\,(s)} \longrightarrow \mathrm{Zn^{2+}\,(aq)} + \mathrm{Mn_2O_3\,(s)} + 2\,\mathrm{NH_3\,(aq)} + \mathrm{H_2O\,(l)} + 2\,\mathrm{Cl^-} \qquad \text{(cell)}$$

The voltage (*cell potential*) of a dry cell is approximately 1.5 V. Dry cells are available in various sizes (e.g., D, C, AA, AAA). All sizes of dry cells comprise the same components, and so they exhibit the same voltage, but larger cells contain greater amounts of the redox reactants and therefore are capable of transferring correspondingly greater amounts of charge. Like other galvanic cells, dry cells may be connected in series to yield batteries with greater voltage outputs, if needed.

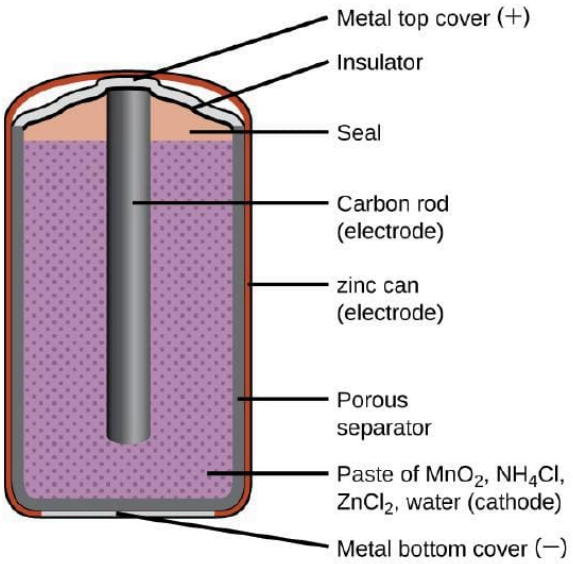


Figure 9.6.2: A schematic diagram shows a typical dry cell.

Link to Learning

Visit this site to learn more about zinc-carbon batteries.

Alkaline batteries (Figure 9.6.3) were developed in the 1950s to improve on the performance of the dry cell, and they were designed around the same redox couples. As their name suggests, these types of batteries use alkaline electrolytes, often potassium hydroxide. The reactions are

$$\begin{aligned}
&\text{anode:} && \mathrm{Zn\,(s)} + 2\,\mathrm{OH^-\,(aq)} \longrightarrow \mathrm{ZnO\,(s)} + \mathrm{H_2O\,(l)} + 2\,\mathrm{e^-} \\
&\text{cathode:} && 2\,\mathrm{MnO_2\,(s)} + \mathrm{H_2O\,(l)} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Mn_2O_3\,(s)} + 2\,\mathrm{OH^-\,(aq)} \\
&\text{cell:} && \mathrm{Zn\,(s)} + 2\,\mathrm{MnO_2\,(s)} \longrightarrow \mathrm{ZnO\,(s)} + \mathrm{Mn_2O_3\,(s)} \qquad E_{\text{cell}} = +1.43\,\mathrm{V}
\end{aligned}$$

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 they should 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.

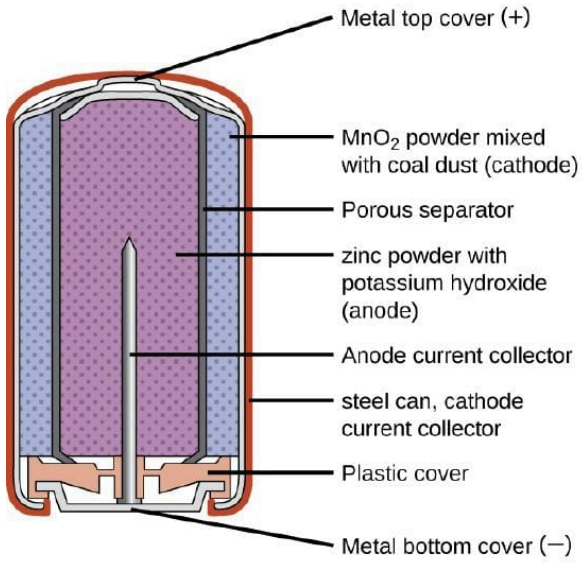


Figure 9.6.3: Alkaline batteries were designed as improved replacements for zinc-carbon (dry cell) batteries.

Link to Learning

Visit this site to learn more about alkaline batteries.

Rechargeable (Secondary) Batteries

Nickel-cadmium, or NiCd, batteries (Figure 9.6.4) 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

$$\begin{aligned}
&\text{anode:} && \mathrm{Cd\,(s) + 2\,OH^-\,(aq) \longrightarrow Cd(OH)_2\,(s) + 2\,e^-} \\
&\text{cathode:} && \mathrm{NiO_2\,(s) + 2\,H_2O\,(l) + 2\,e^- \longrightarrow Ni(OH)_2\,(s) + 2\,OH^-\,(aq)} \\
&\text{cell:} && \mathrm{Cd\,(s) + NiO_2\,(s) + 2\,H_2O\,(l) \longrightarrow Cd(OH)_2\,(s) + Ni(OH)_2\,(s)} \qquad E_{\text{cell}} \approx +1.2\,\text{V}
\end{aligned}$$

When properly treated, a NiCd battery can be recharged about 1000 times. Cadmium is a toxic heavy metal so NiCd batteries should never be ruptured or incinerated, and they should be disposed of in accordance with relevant toxic waste guidelines.

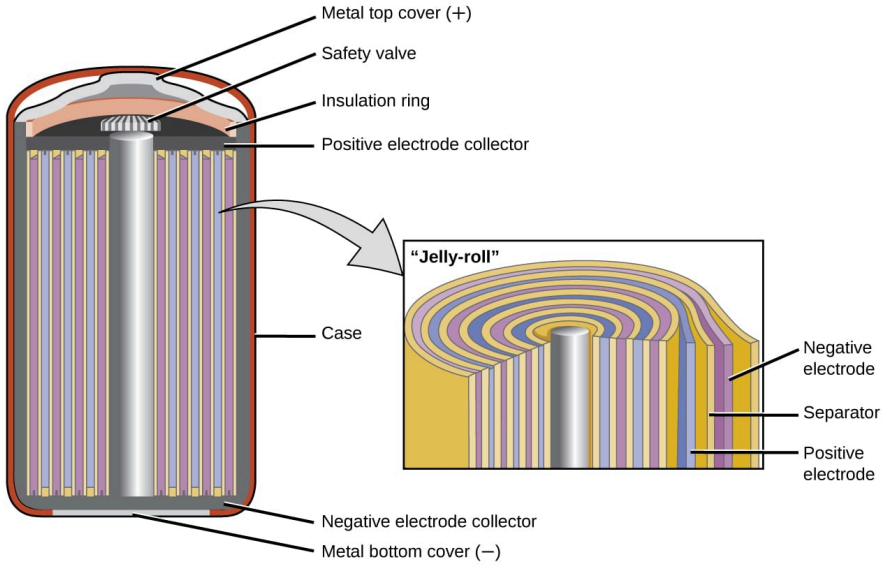


Figure 9.6.4: NiCd batteries use a "jelly-roll" design that significantly increases the amount of current the battery can deliver as compared to a similar-sized alkaline battery.

Link to Learning

Visit this site for more information about nickel cadmium rechargeable batteries.

Lithium ion batteries (Figure 9.6.5) are among the most popular rechargeable batteries and are used in many portable electronic devices. The reactions are

$$\begin{aligned}
&\text{anode:} && \mathrm{LiCoO_2 \longrightarrow Li_{1-x}CoO_2 + x\ Li^+ + x\ e^-} \\
&\text{cathode:} && \mathrm{x\ Li^+ + x\ e^- + x\ C_6 \longrightarrow x\ LiC_6} \\
&\text{cell:} && \mathrm{LiCoO_2 + x\ C_6 \longrightarrow Li_{1-x}CoO_2 + x\ LiC_6} \qquad E_{\text{cell}} \approx +3.7\,\text{V}
\end{aligned}$$

The variable stoichiometry of the cell reaction leads to variation in cell voltages, but for typical conditions, *x* is usually no more than 0.5 and the cell voltage is approximately 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.

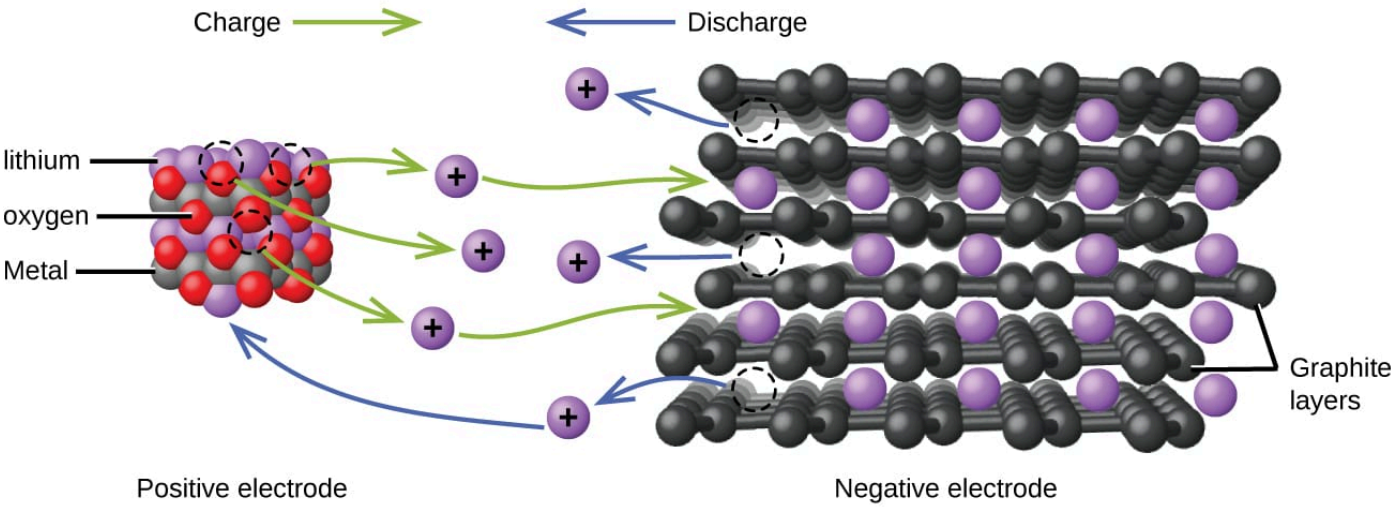


Figure 9.6.5: In a lithium ion battery, charge flows as the lithium ions are transferred between the anode and cathode.

Link to Learning

Visit this site for more information about lithium ion batteries.

The lead acid battery (Figure 9.6.6) is the type of secondary battery commonly used in automobiles. It is inexpensive and capable of producing the high current required by automobile starter motors. The reactions for a lead acid battery are

$$\text{anode:} \quad \mathrm{Pb\,(s) + HSO_4^-\,(aq) \longrightarrow PbSO_4\,(s) + H^+\,(aq) + 2\,e^-}$$

$$\text{cathode:} \quad \mathrm{PbO_2\,(s) + HSO_4^-\,(aq) + 3\,H^+\,(aq) + 2\,e^- \longrightarrow PbSO_4\,(s) + 2\,H_2O\,(l)}$$

$$\text{cell:} \quad \mathrm{Pb\,(s) + PbO_2\,(s) + 2\,H_2SO_4\,(aq) \longrightarrow 2\,PbSO_4\,(s) + 2\,H_2O\,(l)} \qquad E_{\text{cell}} \approx +2\,\text{V}$$

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, $H_2SO_4(aq)$, 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.

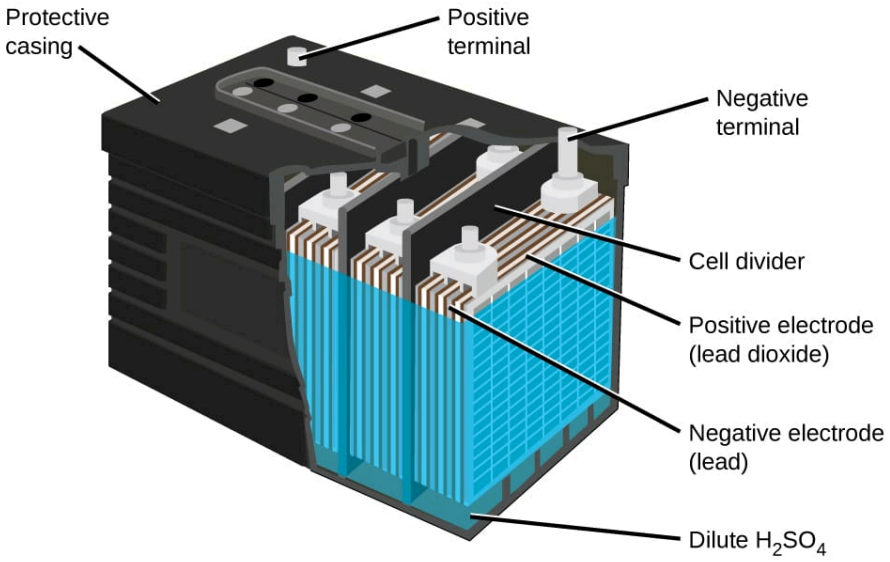


Figure 9.6.6: The lead acid battery in your automobile consists of six cells connected in series to give 12 V.

Link to Learning

Visit this site for more information about lead acid batteries.

Fuel Cells

A fuel cell is a galvanic cell that uses traditional combustive fuels, most often hydrogen or methane, that are continuously fed into the cell along with an oxidant. (An alternative, but not very popular, name for a fuel cell is a *flow battery*.) Within the cell, fuel and oxidant undergo the same redox chemistry as when they are combusted, but via a catalyzed electrochemical that is significantly more efficient. For example, a typical hydrogen fuel cell uses graphite electrodes embedded with platinum-based catalysts to accelerate the two half-cell reactions:

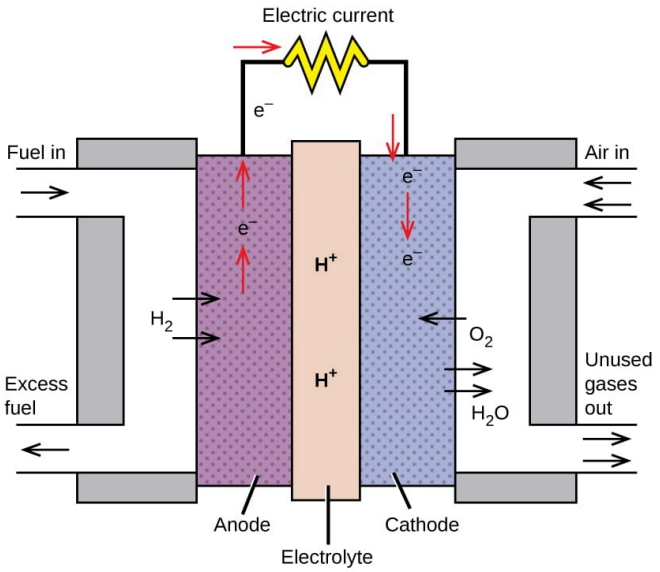


Figure 9.6.7: In this hydrogen fuel cell, oxygen from the air reacts with hydrogen, producing water and electricity.

$$\begin{aligned}
&\text{anode:} && 2\,H_2\,(g) \longrightarrow 4\,H^+\,(aq) + 4\,e^- \\
&\text{cathode:} && O_2\,(g) + 4\,H^+\,(aq) + 4\,e^- \longrightarrow 2\,H_2O\,(g) \\
&\text{cell:} && 2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O\,(g) \qquad E_{\text{cell}} \approx +1.2\,V
\end{aligned}$$

These types of fuel cells generally produce voltages of approximately 1.2 V. Compared to an internal combustion engine, the energy efficiency of a fuel cell using the same redox reaction is typically more than double (~20%–25% for an engine versus ~50%–75% for a fuel cell). Hydrogen fuel cells are commonly used on extended space missions, and prototypes for personal vehicles have been developed, though the technology remains relatively immature.

Link to Learning

Check out this link to learn more about fuel cells.

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9.7: Corrosion

Learning Objectives

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

- Define corrosion
- List some of the methods used to prevent or slow corrosion

Corrosion is usually defined as the degradation of metals by a naturally occurring electrochemical process. The formation of rust on iron, tarnish on silver, and the blue-green patina that develops on copper are all examples of corrosion. The total cost of corrosion remediation in the United States is significant, with estimates in excess of half a trillion dollars a year.

Chemistry in Everyday Life: Statue of Liberty: Changing Colors

The Statue of Liberty is a landmark every American recognizes. The Statue of Liberty is easily identified by its height, stance, and unique blue-green color (Figure $9.7.1$). When this statue was first delivered from France, its appearance was not green. It was brown, the color of its copper "skin." So how did the Statue of Liberty change colors? The change in appearance was a direct result of corrosion. The copper that is the primary component of the statue slowly underwent oxidation from the air. The oxidation-reduction reactions of copper metal in the environment occur in several steps. Copper metal is oxidized to copper(I) oxide (Cu_2O), which is red, and then to copper(II) oxide, which is black

$$2\,\mathrm{Cu}\,(\mathrm{s}) + \tfrac{1}{2}\,\mathrm{O_2}\,(\mathrm{g}) \longrightarrow \mathrm{Cu_2\ O}\,(\mathrm{s}) \qquad (\mathrm{red})$$

$$2\,\mathrm{Cu_2O}\,(\mathrm{s}) + \tfrac{1}{2}\,\mathrm{O_2}\,(\mathrm{g}) \longrightarrow 2\,\mathrm{CuO}\,(\mathrm{s}) \qquad (\mathrm{black})$$

Coal, which was often high in sulfur, was burned extensively in the early part of the last century. As a result, atmospheric sulfur trioxide, carbon dioxide, and water all reacted with the CuO:

$$2\,\mathrm{CuO}\,(\mathrm{s}) + \mathrm{CO_2}\,(\mathrm{g}) + \mathrm{H_2O}\,(\mathrm{l}) \longrightarrow \mathrm{Cu_2CO_3(OH)_2}\,(\mathrm{s}) \qquad (\mathrm{green})$$

$$3\,\mathrm{CuO}\,(\mathrm{s}) + 2\,\mathrm{CO_2}\,(\mathrm{g}) + \mathrm{H_2O}\,(\mathrm{l}) \longrightarrow \mathrm{Cu_2(CO_3)_2(OH)_2}\,(\mathrm{s}) \qquad (\mathrm{blue})$$

$$4\,\mathrm{CuO}\,(\mathrm{s}) + \mathrm{SO_3}\,(\mathrm{g}) + 3\,\mathrm{H_2O}\,(\mathrm{l}) \longrightarrow \mathrm{Cu_4SO_4(OH)_6}\,(\mathrm{s}) \qquad (\mathrm{green})$$

These three compounds are responsible for the characteristic blue-green patina seen on the Statue of Liberty (and other outdoor copper structures). Fortunately, formation of patina creates a protective layer on the copper surface, preventing further corrosion of the underlying copper. The formation of the protective layer is called *passivation*, a phenomenon discussed further in another chapter of this text.



(a) (b)

Figure 9.7.1: (a) The Statue of Liberty is covered with a copper skin, and was originally brown, as shown in this painting. (b) Exposure to the elements has resulted in the formation of the blue-green patina seen today.

Perhaps the most familiar example of corrosion is the formation of rust on iron. Iron will rust when it is exposed to oxygen and water. Rust formation involves the creation of a galvanic cell at an iron surface, as illustrated in Figure 9.7.1. The relevant redox reactions are described by the following equations:

$$\begin{aligned}
&\text{anode:} && \mathrm{Fe(s)} \longrightarrow \mathrm{Fe^{2+}(aq)} + 2\,\mathrm{e^-} && E^\circ_{\mathrm{Fe^{2+}\,/\,Fe}} = -0.44\,\mathrm{V}\\
&\text{cathode:} && \mathrm{O_2(g)} + 4\,\mathrm{H^+(aq)} + 4\,\mathrm{e^-} \longrightarrow 2\,\mathrm{H_2O(l)} && E^\circ_{\mathrm{O_2\,/O^{2-}}} = +1.23\,\mathrm{V}\\
&\text{overall:} && 2\,\mathrm{Fe(s)} + \mathrm{O_2(g)} + 4\,\mathrm{H^+(aq)} \longrightarrow 2\,\mathrm{Fe^{2+}(aq)} + 2\,\mathrm{H_2O(l)} && E^\circ_{\mathrm{cell}} = +1.67\,\mathrm{V}
\end{aligned}$$

Further reaction of the iron(II) product in humid air results in the production of an iron(III) oxide hydrate known as rust:

$$4\,\mathrm{Fe^{2+}(aq)} + \mathrm{O_2(g)} + (4+2\,\mathrm{x})\ \ \mathrm{H_2O(l)} \longrightarrow 2\,\mathrm{Fe_2O_3}\ \cdot \mathrm{x}\ \ \mathrm{H_2O(s)} + 8\,\mathrm{H^+(aq)}$$

The stoichiometry of the hydrate varies, as indicated by the use of *x* in the compound formula. Unlike the patina on copper, the formation of rust does not create a protective layer and so corrosion of the iron continues as the rust flakes off and exposes fresh iron to the atmosphere.

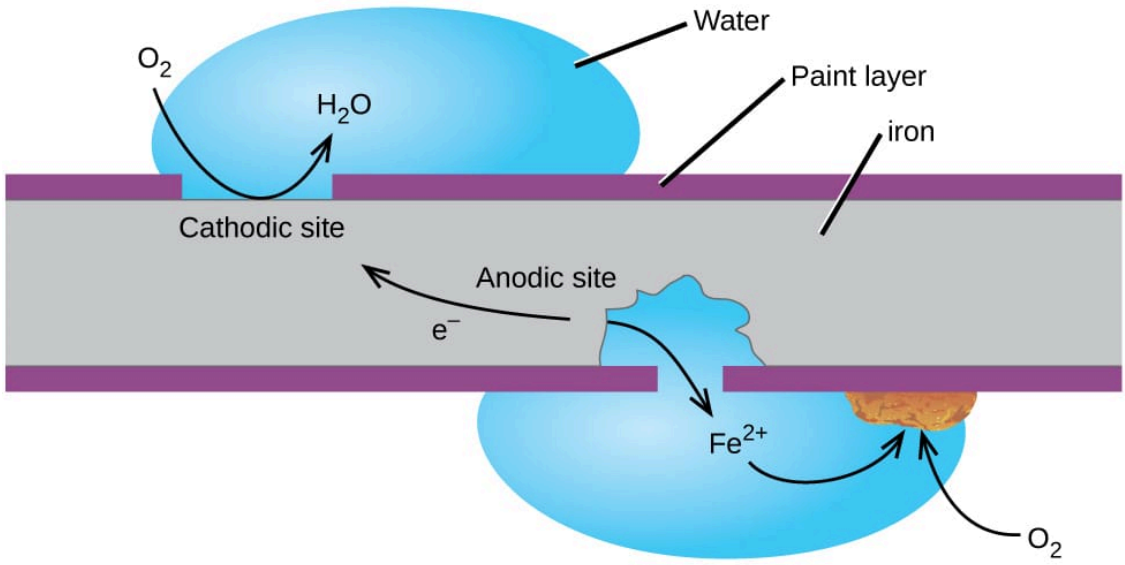


Figure 9.7.2: Corrosion can occur when a painted iron or steel surface is exposed to the environment by a scratch through the paint. A galvanic cell results that may be approximated by the simplified cell schematic Fe(s) | $Fe^{2+}(aq)$ ||$O_2(aq)$, $H_2O(l)$ | Fe(s).

One way to keep iron from corroding is to keep it painted. The layer of paint prevents the water and oxygen necessary for rust formation from coming into contact with the iron. As long as the paint remains intact, the iron is protected from corrosion.

Other strategies include alloying the iron with other metals. For example, stainless steel is an alloy of iron containing a small amount of chromium. The chromium tends to collect near the surface, where it corrodes and forms a passivating an oxide layer that protects the iron.

Iron and other metals may also be protected from corrosion by **galvanization**, a process in which the metal to be protected is coated with a layer of a more readily oxidized metal, usually zinc. When the zinc layer is intact, it prevents air from contacting the underlying iron and thus prevents corrosion. If the zinc layer is breached by either corrosion or mechanical abrasion, the iron may still be protected from corrosion by a *cathodic protection* process, which is described in the next paragraph.

Another important way to protect metal is to make it the cathode in a galvanic cell. This is **cathodic protection** and can be used for metals other than just iron. For example, the rusting of underground iron storage tanks and pipes can be prevented or greatly reduced by connecting them to a more active metal such as zinc or magnesium (Figure 9.7.3). This is also used to protect the metal parts in water heaters. The more active metals (lower reduction potential) are called **sacrificial anodes** because as they get used up as they corrode (oxidize) at the anode. The metal being protected serves as the cathode for the reduction of oxygen in air, and so it simply serves to conduct (not react with) the electrons being transferred. When the anodes are properly monitored and periodically replaced, the useful lifetime of the iron storage tank can be greatly extended.

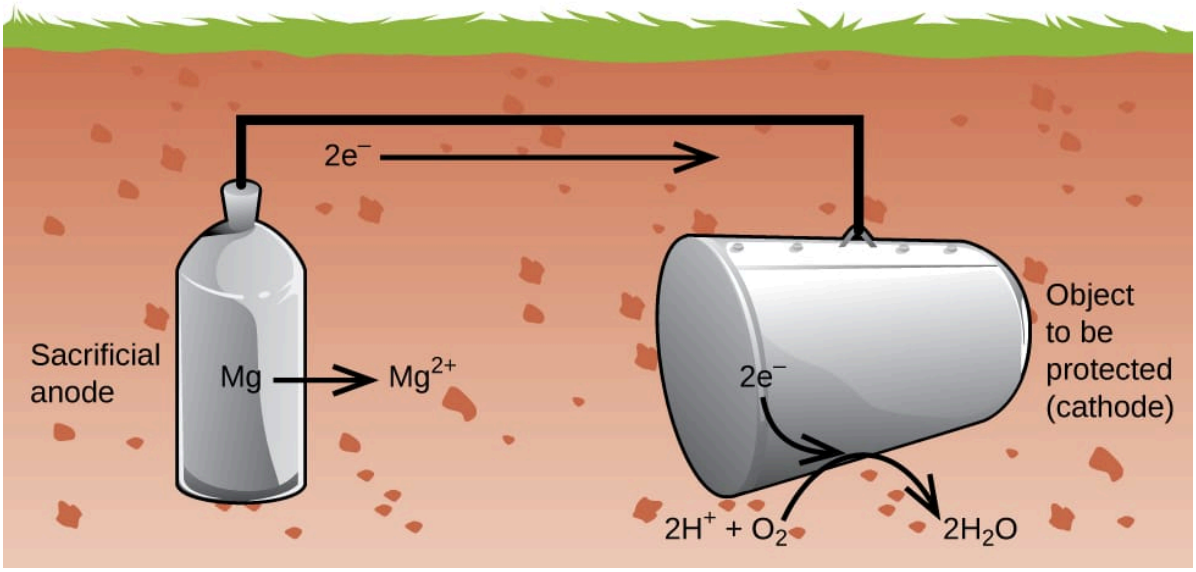


Figure 9.7.3: Cathodic protection is a useful approach to electrochemically preventing corrosion of underground storage tanks.

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9.8: Electrolysis

Learning Objectives

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

- Describe the process of electrolysis
- Compare the operation of electrolytic cells with that of galvanic cells
- Perform stoichiometric calculations for electrolytic processes

Electrochemical cells in which spontaneous redox reactions take place (*galvanic cells*) have been the topic of discussion so far in this chapter. In these cells, *electrical work is done by a redox system on its surroundings* as electrons produced by the redox reaction are transferred through an external circuit. This final section of the chapter will address an alternative scenario in which *an external circuit does work on a redox system* by imposing a voltage sufficient to drive an otherwise nonspontaneous reaction, a process known as **electrolysis**. A familiar example of electrolysis is recharging a battery, which involves use of an external power source to drive the spontaneous (discharge) cell reaction in the reverse direction, restoring to some extent the composition of the half-cells and the voltage of the battery. Perhaps less familiar is the use of electrolysis in the refinement of metallic ores, the manufacture of commodity chemicals, and the *electroplating* of metallic coatings on various products (e.g., jewelry, utensils, auto parts). To illustrate the essential concepts of electrolysis, a few specific processes will be considered.

The Electrolysis of Molten Sodium Chloride

Metallic sodium, Na, and chlorine gas, Cl_2, are used in numerous applications, and their industrial production relies on the large-scale electrolysis of molten sodium chloride, NaCl(*l*). The industrial process typically uses a *Downs cell* similar to the simplified illustration shown in Figure 9.8.1. The reactions associated with this process are:

$$\begin{aligned} \text{oxidation:} \quad & 2\,\mathrm{Cl^-(l)} \longrightarrow \mathrm{Cl_2}(g) + 2\mathrm{e^-} \\ \text{reduction:} \quad & \mathrm{Na^+(l)} + \mathrm{e^-} \longrightarrow \mathrm{Na}(l) \\ \text{cell:} \quad & 2\,\mathrm{Cl^-(l)} + 2\,\mathrm{Na^+(l)} \longrightarrow \mathrm{Cl_2}(g) \end{aligned}$$

The cell potential for the above process is negative, indicating the reaction as written (decomposition of liquid NaCl) is not spontaneous. To force this reaction, *a positive potential of magnitude greater than the negative cell potential* must be applied to the cell.

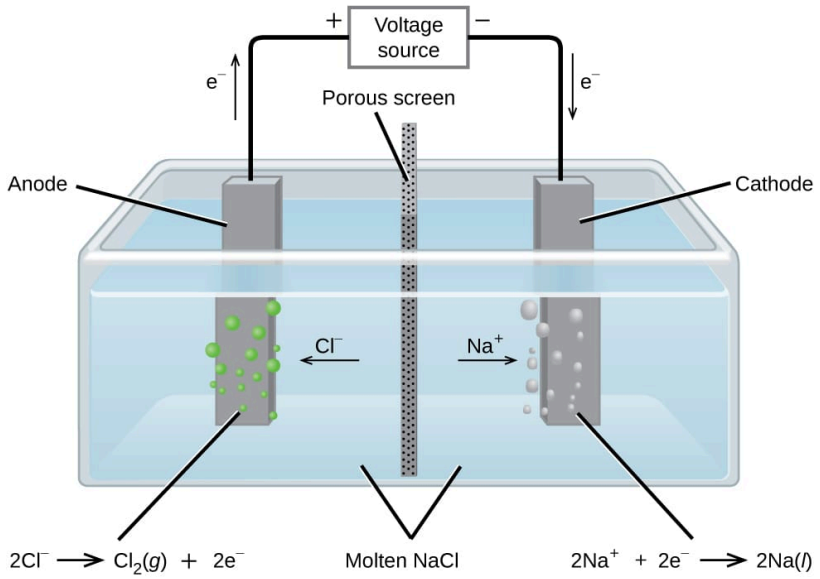


Figure 9.8.1: Cells of this sort (a cell for the electrolysis of molten sodium chloride) are used in the *Downs process* for production of sodium and chlorine, and they typically use iron cathodes and carbon anodes.

The Electrolysis of Water

Water may be electrolytically decomposed in a cell similar to the one illustrated in Figure 9.8.2. To improve electrical conductivity without introducing a different redox species, the hydrogen ion concentration of the water is typically increased by addition of a strong acid. The redox processes associated with this cell are

$$\begin{array}{lrcll} \text{oxidation:} & 2\,\mathrm{H_2O\,(l)} & \longrightarrow & \mathrm{O_2}(g) + 4\mathrm{H^+}(aq) + 4\mathrm{e^-} & E^o_{anode} = +1.299\,\mathrm{V} \\ \text{reduction:} & 2\mathrm{H^+\,(aq)} + 2\mathrm{e^-} & \longrightarrow & \mathrm{H_2}(g) & E^o_{anode} = 0\,\mathrm{V} \\ \text{cell:} & 2\,\mathrm{H_2O\,(l)} & \longrightarrow & 2\mathrm{H_2}(g) + \mathrm{O_2}(g) & E^o_{cell} = -1.299\,\mathrm{V} \end{array}$$

Again, the cell potential as written is negative, indicating a nonspontaneous cell reaction that must be driven by imposing a cell voltage greater than +1.229 V. Keep in mind that *standard* electrode potentials are used to inform thermodynamic predictions here, though the cell is *not* operating under standard state conditions. Therefore, at best, calculated cell potentials should be considered ballpark estimates.

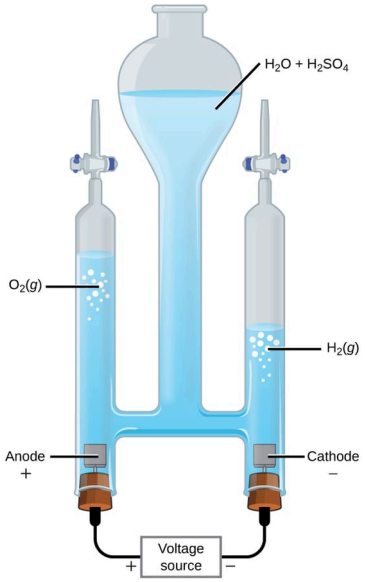


Figure 9.8.2: The electrolysis of water produces stoichiometric amounts of oxygen gas at the anode and hydrogen at the anode.

The Electrolysis of Aqueous Sodium Chloride

When aqueous solutions of ionic compounds are electrolyzed, the anode and cathode half-reactions may involve the electrolysis of either water species (H_2O, H^+, OH^-) or solute species (the cations and anions of the compound). As an example, the electrolysis of aqueous sodium chloride could involve either of these two anode reactions:

$$2\,\mathrm{Cl^-\,(aq)} \longrightarrow \mathrm{Cl_2\,(g)} + 2\,\mathrm{e^-} \quad E^\circ_{\text{anode}} = +1.35827\,\mathrm{V} \tag{i}$$

or

$$2\,\mathrm{H_2O\,(l)} \longrightarrow \mathrm{O_2\,(g)} + 4\,\mathrm{H^+\,(aq)} + 4\,\mathrm{e^-} \quad E^\circ_{\text{anode}} = +1.229\,\mathrm{V} \tag{ii}$$

The standard electrode (*reduction*) potentials of these two half-reactions indicate water may be *oxidized* at a less negative/more positive potential (–1.229 V) than chloride ion (–1.358 V). Thermodynamics thus predicts that water would be more readily oxidized, though in practice it is observed that both water and chloride ion are oxidized under typical conditions, producing a mixture of oxygen and chlorine gas.

Turning attention to the cathode, the possibilities for reduction are:

$$2\,\mathrm{H^+\,(aq)} + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2\,(g)} \quad E^\circ_{\text{anode}} = 0\,\mathrm{V} \tag{iii}$$

or

$$2\,\mathrm{H_2O\,(l)} + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2\,(g)} + 4\,\mathrm{OH^-\,(aq)} \quad E^\circ_{\text{anode}} = -0.8277\,\mathrm{V} \tag{iv}$$

or

$$\mathrm{Na^+\,(aq)} + \mathrm{e^-} \longrightarrow \mathrm{Na\,(s)} \quad E^\circ_{\text{anode}} = -2.71\,\mathrm{V} \tag{v}$$

Comparison of these *standard* half-reaction potentials suggests the reduction of hydrogen ion is thermodynamically favored. However, in a neutral aqueous sodium chloride solution, the concentration of hydrogen ion is far below the standard state value of 1 *M* (approximately 10^{-7} *M*), and so the observed cathode reaction is actually reduction of water. The net cell reaction in this case is then

$$2\,\mathrm{H_2O\,(l)} + 2\,\mathrm{Cl^-\,(aq)} \longrightarrow \mathrm{H_2\,(g)} + \mathrm{Cl_2\,(g)} + 2\,\mathrm{OH^-\,(aq)} \quad E^\circ_{\text{cell}} = -2.186\,\mathrm{V}$$

This electrolysis reaction is part of the *chlor-alkali process* used by industry to produce chlorine and sodium hydroxide (lye).

Chemistry in Everyday Life: 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. The silver plating of eating utensils is used here to illustrate the process. (Figure 9.8.3).

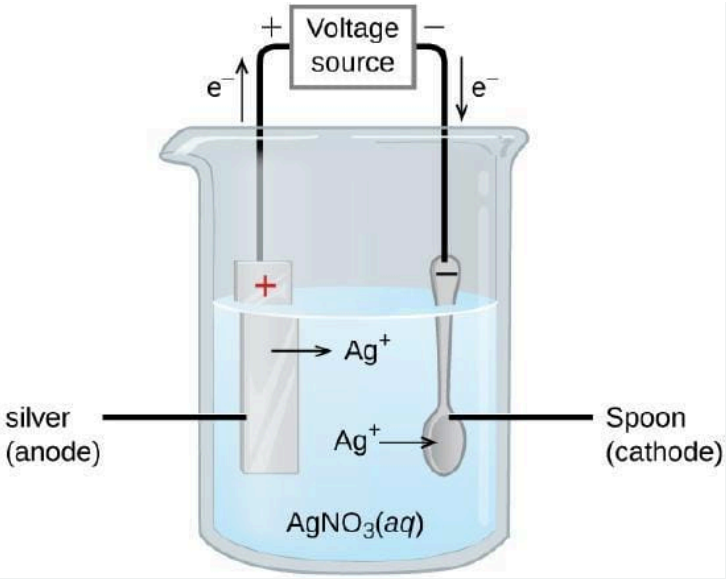


Figure 9.8.3: This schematic shows an electrolytic cell for silver plating eating utensils.

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. Applying a sufficient potential results in the oxidation of the silver anode

$$\mathrm{Ag\,(s)} \longrightarrow \mathrm{Ag^{+}\,(aq)} + \mathrm{e^{-}} \qquad \text{(anode)}$$

and reduction of silver ion at the (spoon) cathode:

$$\mathrm{Ag^{+}\,(aq)} + \mathrm{e^{-}} \longrightarrow \mathrm{Ag\,(s)} \qquad \text{(cathode)}$$

The net result is the transfer of silver metal from the anode to the cathode. Several experimental factors must be carefully controlled to obtain high-quality silver coatings, including the exact composition of the electrolyte solution, the cell voltage applied, and the rate of the electrolysis reaction (electrical current).

Quantitative Aspects of Electrolysis

Electrical current is defined as the rate of flow for any charged species. Most relevant to this discussion is the flow of electrons. Current is measured in a composite unit called an ampere, defined as one coulomb per second (A = 1 C/s). The charge transferred, *Q*, by passage of a constant current, *I*, over a specified time interval, *t*, is then given by the simple mathematical product

$$Q = It$$

When electrons are transferred during a redox process, the stoichiometry of the reaction may be used to derive the total amount of (electronic) charge involved. For example, the generic reduction process

$$\mathrm{M^{\mathit{n}+}\,(aq)} + \mathrm{n\,e^{-}} \longrightarrow \mathrm{M\,(s)}$$

involves the transfer of n mole of electrons. The total charge transferred is, therefore,

$$Q = nF$$

where F is Faraday's constant, the charge in coulombs for one mole of electrons. If the reaction takes place in an electrochemical cell, the current flow is conveniently measured, and it may be used to assist in stoichiometric calculations related to the cell reaction.

Example 9.8.1: 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

$$n = \frac{Q}{F} = \frac{\frac{10.23C}{s} \times 1hr \times \frac{60min}{hr} \times \frac{60s}{\text{min}}}{96,485C/mole^-} = \frac{36,830C}{96,485C/mole^-} = 0.3817mole^-$$

From the problem, the solution contains $AgNO_3$, so the reaction at the cathode involves 1 mole of electrons for each mole of silver

$$\mathrm{Ag^+(aq) + e^- \longrightarrow Ag(s)} \qquad \text{(cathode)}$$

The atomic mass of silver is 107.9 g/mol, so

$$\text{mass } Ag = 0.3817\,\text{mol e}^- \times \frac{1\,\text{mol Ag}}{1\,\text{mol e}^-} \times \frac{107.9\,\text{g Ag}}{1\,\text{mol Ag}} = 41.19\,\text{g Ag}$$

Exercise 9.8.1

Aluminum metal can be made from aluminum(III) ions by electrolysis. What is the half-reaction at the cathode? What mass of aluminum metal would be recovered if a current of 25.0 A passed through the solution for 15.0 minutes?

Answer available at the end of this section.

Example 9.8.2: 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

First, compute the volume of chromium that must be produced (equal to the product of surface area and thickness):

$$\text{volume } = \left(0.010mm \times \frac{1cm}{10mm}\right) \times \left(3.3m^2 \times \left(\frac{10,000cm^2}{1m^2}\right)\right) = 33cm^3$$

Use the computed volume and the provided density to calculate the molar amount of chromium required:

$$\text{mass } = \text{ volume } \times \text{ density } = 33cm^3 \times \frac{7.19g}{cm^3} = 237gCr$$

$$molCr = 237gCr \times \frac{1molCr}{52.00gCr} = 4.56molCr$$

The stoichiometry of the chromium(III) reduction process requires three moles of electrons for each mole of chromium(0) produced, and so the total charge required is:

$$Q = 4.56 molCr \times \frac{3 mole^-}{1 molCr} \times \frac{96485 C}{mole^-} = 1.32 \times 10^6 C$$

Finally, if this charge is passed at a rate of 33.46 C/s, the required time is:

$$t = \frac{Q}{I} = \frac{1.32 \times 10^6 C}{33.46 C/s} = 3.95 \times 10^4 s = 11.0 hr$$

Exercise 9.8.2

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 available at the end of this section.

Answers

Exercise 9.8.1

$$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$$

0.0777 mol Al = 2.10 g Al.

Exercise 9.8.2

11.8 kg Zn requires 382 hours.

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9.9: Key Terms

Example and Directions

Words (or words that have the same definition)	The definition is case sensitive	(Optional) Image to display with the definition [Not displayed in Glossary, only in pop-up on pages]	(Optional) Caption for Image	(Optional) External or Internal Link	(Optional) Source for Definition
(Eg. "Genetic, Hereditary, DNA ...")	(Eg. "Relating to genes or heredity")		The infamous double helix	https://bio.libretexts.org/	CC-BY-SA; Delmar Larsen

Glossary Entries

Word(s)	Definition	Image	Caption	Link	Source
active electrode	electrode that participates as a reactant or product in the oxidation-reduction reaction of an electrochemical cell; the mass of an active electrode changes during the oxidation-reduction reaction				
alkaline battery	primary battery similar to a *dry cell* that uses an alkaline (often potassium hydroxide) electrolyte; designed to be an improved replacement for the dry cell, but with more energy storage and less electrolyte leakage than typical dry cell				
anode	electrode in an electrochemical cell at which oxidation occurs				
battery	single or series of galvanic cells designed for use as a source of electrical power				
cathode	electrode in an electrochemical cell at which reduction occurs				
cathodic protection	approach to preventing corrosion of a metal object by connecting it to a *sacrificial anode* composed of a more readily oxidized metal				
cell notation (schematic)	symbolic representation of the components and reactions in an electrochemical cell				
cell potential (E_{cell})	difference in potential of the cathode and anode half-cells				
concentration cell	galvanic cell comprising half-cells of identical composition but for the concentration of one redox reactant or product				
corrosion	degradation of metal via a natural electrochemical process				
dry cell	primary battery, also called a zinc-carbon battery, based on the spontaneous oxidation of zinc by manganese(IV)				
electrode potential (E_X)	the potential of a cell in which the half-cell of interest acts as a cathode when connected to the standard hydrogen electrode				
electrolysis	process using electrical energy to cause a nonspontaneous process to occur				
electrolytic cell	electrochemical cell in which an external source of electrical power is used to drive an otherwise nonspontaneous process				
Faraday's constant (F)	charge on 1 mol of electrons; F = 96,485 C/mol e^-				
fuel cell	devices similar to galvanic cells that require a continuous feed of redox reactants; also called a *flow battery*				

Word(s)	Definition	Image	Caption	Link	Source
galvanic (voltaic) cell	electrochemical cell in which a spontaneous redox reaction takes place; also called a *voltaic cell*				
galvanization	method of protecting iron or similar metals from corrosion by coating with a thin layer of more easily oxidized zinc.				
half cell	component of a cell that contains the redox conjugate pair (“couple”) of a single reactant				
inert electrode	electrode that conducts electrons to and from the reactants in a half-cell but that is not itself oxidized or reduced				
lead acid battery	rechargeable battery commonly used in automobiles; it typically comprises six galvanic cells based on Pb half-reactions in acidic solution				
lithium ion battery	widely used rechargeable battery commonly used in portable electronic devices, based on lithium ion transfer between the anode and cathode				
Nernst equation	relating the potential of a redox system to its composition				
nickel-cadmium battery	rechargeable battery based on Ni/Cd half-cells with applications similar to those of lithium ion batteries				
primary cell	nonrechargeable battery, suitable for single use only				
sacrificial anode	electrode constructed from an easily oxidized metal, often magnesium or zinc, used to prevent corrosion of metal objects via cathodic protection				
salt bridge	tube filled with inert electrolyte solution				
secondary cell	battery designed to allow recharging				
standard cell potential	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				
standard electrode potential ()	electrode potential measured under standard conditions (1 bar or 1 atm for gases; 1 *M* for solutes) usually at 298.15 K				
standard hydrogen electrode (SHE)	half-cell based on hydrogen ion production, assigned a potential of exactly 0 V under standard state conditions, used as the universal reference for measuring electrode potential				

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9.10: Key Equations

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$E^\circ_{\text{cell}} = \frac{RT}{nF}\ln K$$

$$E^\circ_{\text{cell}} = \frac{0.0257\ \text{V}}{n}\ln K = \frac{0.0592\ \text{V}}{n}\log K \quad (\text{ at } 298.15K)$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF}\ln Q \quad (\text{ Nernst equation })$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592\ \text{V}}{n}\log Q \quad (\text{ at } 298.15K)$$

$$\Delta G = -nFE_{\text{cell}}$$

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

$$w_{\text{ele}} = w_{\text{max}} = -nFE_{\text{cell}}$$

$$Q = I \times t = n \times F$$

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9.11: Summary

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.

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).

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).

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.

Galvanic cells designed specifically to function as electrical power supplies are called batteries. A variety of both single-use batteries (primary cells) and rechargeable batteries (secondary cells) are commercially available to serve a variety of applications, with important specifications including voltage, size, and lifetime. Fuel cells, sometimes called flow batteries, are devices that harness the energy of spontaneous redox reactions normally associated with combustion processes. Like batteries, fuel cells enable the reaction's electron transfer via an external circuit, but they require continuous input of the redox reactants (fuel and oxidant) from an external reservoir. Fuel cells are typically much more efficient in converting the energy released by the reaction to useful work in comparison to internal combustion engines.

Spontaneous oxidation of metals by natural electrochemical processes is called corrosion, familiar examples including the rusting of iron and the tarnishing of silver. Corrosion process involve the creation of a galvanic cell in which different sites on the metal object function as anode and cathode, with the corrosion taking place at the anodic site. Approaches to preventing corrosion of metals include use of a protective coating of zinc (galvanization) and the use of sacrificial anodes connected to the metal object (cathodic protection).

Nonspontaneous redox processes may be forced to occur in electrochemical cells by the application of an appropriate potential using an external power source—a process known as electrolysis. Electrolysis is the basis for certain ore refining processes, the industrial production of many chemical commodities, and the electroplating of metal coatings on various products. Measurement of the current flow during electrolysis permits stoichiometric calculations.

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9.12: Exercises

Review of Redox Chemistry

1.

Identify each half-reaction below as either oxidation or reduction.

(a) $\mathrm{Fe^{3+} + 3e^- \longrightarrow Fe}$
(b) $\mathrm{Cr \longrightarrow Cr^{3+} + 3e^-}$
(c) $\mathrm{{MnO_4}^{2-} \longrightarrow {MnO_4}^- + e^-}$
(d) $\mathrm{Li^+ + e^- \longrightarrow Li}$

half-reaction below as either oxidation or reduction.

(a) $\mathrm{Cl^- \longrightarrow Cl_2}$
(b) $\mathrm{Mn^{2+} \longrightarrow MnO_2}$
(c) $\mathrm{H_2 \longrightarrow H^+}$
(d) $\mathrm{NO_3^- \longrightarrow NO}$

3.

Assuming each pair of half-reactions below takes place in an acidic solution, write a balanced equation for the overall reaction.

(a) $\mathrm{Ca \longrightarrow Ca^{2+} + 2e^-, F_2 + 2e^- \longrightarrow 2\ F^-}$
(b) $\mathrm{Li \longrightarrow Li^+ + e^-, Cl_2 + 2e^- \longrightarrow 2Cl^-}$
(c) $\mathrm{Fe \longrightarrow Fe^{3+} + 3e^-, Br_2 + 2e^- \longrightarrow 2Br^-}$
(d) $\mathrm{Ag \longrightarrow Ag^+ + e^-, {MnO_4}^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O}$

4.

Balance the equations below assuming they occur in an acidic solution.

(a) $\mathrm{H_2O_2 + Sn^{2+} \longrightarrow H_2O + Sn^{4+}}$
(b) $\mathrm{PbO_2 + Hg \longrightarrow {Hg_2}^{2+} + Pb^{2+}}$
(c) $\mathrm{Al + {Cr_2O_7}^{2-} \longrightarrow Al^{3+} + Cr^{3+}}$

5.

Identify the oxidant and reductant of each reaction of the previous exercise.

6.

Balance the equations below assuming they occur in a basic solution.

(a) $\mathrm{{SO_3}^{2-}(aq) + Cu(OH)_2(s) \longrightarrow {SO_4}^{2-}(aq) + Cu(OH)(s)}$
(b) $\mathrm{O_2(g) + Mn(OH)_2(s) \longrightarrow MnO_2(s)}$
(c) $\mathrm{{NO_3}^-(aq) + H_2(g) \rightarrow NO(g)}$
(d) $\mathrm{Al(s) + {CrO_4}^{2-}(aq) \longrightarrow Al(OH)_3(s) + Cr(OH)_4{}^-(aq)}$

7.

Identify the oxidant and reductant of each reaction of the previous exercise.

8.

Why don't hydroxide ions appear in equations for half-reactions occurring in acidic solution?

9.

Why don't hydrogen ions appear in equations for half-reactions occurring in basic solution?

10.

Why must the charge balance in oxidation-reduction reactions?

Galvanic Cells

11.

Write cell schematics for the following cell reactions, using platinum as an inert electrode as needed

(a) $\mathrm{Mg}(s) + \mathrm{Ni}^{2+}(aq) \longrightarrow \mathrm{Mg}^{2+}(aq) + \mathrm{Ni}(s)$
(b) $2\mathrm{Ag}^{+}(aq) + \mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{2+}(aq) + 2\mathrm{Ag}(s)$
(c) $\mathrm{Mn}(s) + \mathrm{Sn}\left(\mathrm{NO}_3\right)_2(aq) \rightarrow \mathrm{Mn}\left(\mathrm{NO}_3\right)_2(aq) + \mathrm{Sn}(s)$
(d) $3\mathrm{CuNO}_3(aq) + \mathrm{Au}\left(\mathrm{NO}_3\right)_3(aq) \longrightarrow 3\mathrm{Cu}\left(\mathrm{NO}_3\right)_2(aq) + \mathrm{Au}(s)$

12.

Assuming the schematics below represent galvanic cells as written, identify the half-cell reactions occurring in each.

(a) $\mathrm{Mg}(s)\left|\mathrm{Mg}^{2+}(aq)\right\|\mathrm{Cu}^{2+}(aq)\left|\mathrm{Cu}(s)\right.$
(b) $\mathrm{Ni}(s)\left|\mathrm{Ni}^{2+}(aq)\right\|\mathrm{Ag}^{+}(aq)\left|\mathrm{Ag}(s)\right.$

13.

Write a balanced equation for the cell reaction of each cell in the previous exercise.

14.

Balance each reaction below, and write a cell schematic representing the reaction as it would occur in a galvanic cell.

(a) $\mathrm{Al}(s) + \mathrm{Zr}^{4+}(aq) \longrightarrow \mathrm{Al}^{3+}(aq) + \mathrm{Zr}(s)$
(b) $\mathrm{Ag}^{+}(aq) + \mathrm{NO}(g) \longrightarrow \mathrm{Ag}(s) + {\mathrm{NO}_3}^{-}(aq)$ acidic solution
(c) ${\mathrm{SiO}_3}^{2-}(aq) + \mathrm{Mg}(s) \longrightarrow \mathrm{Si}(s) + \mathrm{Mg(OH)}_2(s)$ basic solution
(d) ${\mathrm{ClO}_3}^{-}(aq) + \mathrm{MnO}_2(s) \longrightarrow \mathrm{Cl}^{-}(aq) + {\mathrm{MnO}_4}^{-}(aq)$ basic solution

15.

Identify the oxidant and reductant in each reaction of the previous exercise.

16.

From the information provided, use cell notation to describe the following systems:

a. In one half-cell, a solution of $Pt(NO_3)_2$ forms Pt metal, while in the other half-cell, Cu metal goes into a $Cu(NO_3)_2$ solution with all solute concentrations 1 *M*.
b. The cathode consists of a gold electrode in a 0.55 *M* $Au(NO_3)_3$ solution and the anode is a magnesium electrode in 0.75 *M* $Mg(NO_3)_2$ solution.
c. One half-cell consists of a silver electrode in a 1 *M* $AgNO_3$ solution, and in the other half-cell, a copper electrode in 1 *M* $Cu(NO_3)_2$ is oxidized.

17.

Why is a salt bridge necessary in galvanic cells like the one in Figure 17.3?

18.

An active (metal) electrode was found to gain mass as the oxidation-reduction reaction was allowed to proceed. Was the electrode an anode or a cathode? Explain.

19.

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.

20.

The masses of three electrodes (A, B, and C), each from three different galvanic cells, were measured before and after the cells were allowed to pass current for a while. The mass of electrode A increased, that of electrode B was unchanged, and that of electrode C decreased. Identify each electrode as active or inert, and note (if possible) whether it functioned as anode or cathode.

Electrode and Cell Potentials

21.

Calculate the standard cell potential for each reaction below, and note whether the reaction is spontaneous under standard state conditions.

(a) $\mathrm{Mg}(s) + \mathrm{Ni}^{2+}(aq) \longrightarrow \mathrm{Mg}^{2+}(aq) + \mathrm{Ni}(s)$
(b) $2\mathrm{Ag}^{+}(aq) + \mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{2+}(aq) + 2\mathrm{Ag}(s)$
(c) $\mathrm{Mn}(s) + \mathrm{Sn}\left(\mathrm{NO}_3\right)_2(aq) \longrightarrow \mathrm{Mn}\left(\mathrm{NO}_3\right)_2(aq) + \mathrm{Sn}(s)$
(d) $3\mathrm{Fe}\left(\mathrm{NO}_3\right)_2(aq) + \mathrm{Au}\left(\mathrm{NO}_3\right)_3(aq) \longrightarrow 3\mathrm{Fe}\left(\mathrm{NO}_3\right)_3(aq) + \mathrm{Au}(s)$

22.

Calculate the standard cell potential for each reaction below, and note whether the reaction is spontaneous under standard state conditions.

(a) $\mathrm{Mn}(s) + \mathrm{Ni}^{2+}(aq) \longrightarrow \mathrm{Mn}^{2+}(aq) + \mathrm{Ni}(s)$
(b) $3\mathrm{Cu}^{2+}(aq) + 2\mathrm{Al}(s) \longrightarrow 2\mathrm{Al}^{3+}(aq) + 3\mathrm{Cu}(s)$
(c) $\mathrm{Na}(s) + \mathrm{LiNO}_3(aq) \rightarrow \mathrm{NaNO}_3(aq) + \mathrm{Li}(s)$
(d) $\mathrm{Ca}\left(\mathrm{NO}_3\right)_2(aq) + \mathrm{Ba}(s) \longrightarrow \mathrm{Ba}\left(\mathrm{NO}_3\right)_2(aq) + \mathrm{Ca}(s)$

23.

Write the balanced cell reaction for the cell schematic below, calculate the standard cell potential, and note whether the reaction is spontaneous under standard state conditions.

$\mathrm{Cu}(s)\left|\mathrm{Cu}^{2+}(aq)\right\|\mathrm{Au}^{3+}(aq)\left|\mathrm{Au}(s)\right.$

24.

Determine the cell reaction and standard cell potential at 25 °C for a cell made from a cathode half-cell consisting of a silver electrode in 1 *M* silver nitrate solution and an anode half-cell consisting of a zinc electrode in 1 *M* zinc nitrate. Is the reaction spontaneous at standard conditions?

25.

Determine the cell reaction and standard cell potential at 25 °C for a cell made from an anode half-cell containing a cadmium electrode in 1 *M* cadmium nitrate and a cathode half-cell consisting of an aluminum electrode in 1 *M* aluminum nitrate solution. Is the reaction spontaneous at standard conditions?

26.

Write the balanced cell reaction for the cell schematic below, calculate the standard cell potential, and note whether the reaction is spontaneous under standard state conditions.

$\mathrm{Pt}(s)\,|\mathrm{H_2}(g)|\,\mathrm{H^+}(aq)\|\mathrm{Br_2}(aq),\mathrm{Br^-}(aq)\,|\,\mathrm{Pt}(s)$

27.

For each pair of standard cell potential and electron stoichiometry values below, calculate a corresponding standard free energy change (kJ).

a. 0.000 V, n = 2
b. +0.434 V, n = 2
c. –2.439 V, n = 1

28.

For each pair of standard free energy change and electron stoichiometry values below, calculate a corresponding standard cell potential.

a. 12 kJ/mol, n = 3
b. –45 kJ/mol, n = 1

29.

Determine the standard cell potential and the cell potential under the stated conditions for the electrochemical reactions described here. State whether each is spontaneous or nonspontaneous under each set of conditions at 298.15 K.

a.
b. The cell made from an anode half-cell consisting of an aluminum electrode in 0.015 *M* aluminum nitrate solution and a cathode half-cell consisting of a nickel electrode in 0.25 *M* nickel(II) nitrate solution.
c. The cell comprised of a half-cell in which aqueous bromine (1.0 *M*) is being oxidized to bromide ion (0.11 *M*) and a half-cell in which Al^{3+} (0.023 *M*) is being reduced to aluminum metal.

30.

Determine ΔG and $\Delta G°$ for each of the reactions in the previous problem.

31.

Use the data in Appendix L to calculate equilibrium constants for the following reactions. Assume 298.15 K if no temperature is given.

a. \($\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq)$\)
b. $\mathrm{CdS}(s) \rightleftharpoons \mathrm{Cd^{2+}}(aq) + \mathrm{S^{2-}}(aq)$
c. $\mathrm{Hg^{2+}}(aq) + 4\mathrm{Br^-}(aq) \rightleftharpoons [\mathrm{HgBr_4}]^{2-}(aq)$
d. $\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{OH^-}(aq)$ \end{aligned}\)

32.

Consider a battery made from one half-cell that consists of a copper electrode in 1 *M* $CuSO_4$ solution and another half-cell that consists of a lead electrode in 1 *M* $Pb(NO_3)_2$ solution.

a. What is the standard cell potential for the battery?
b. What are the reactions at the anode, cathode, and the overall reaction?
c. Most devices designed to use dry-cell batteries can operate between 1.0 and 1.5 V. Could this cell be used to make a battery that could replace a dry-cell battery? Why or why not.
d. Suppose sulfuric acid is added to the half-cell with the lead electrode and some $PbSO_4$(s) forms. Would the cell potential increase, decrease, or remain the same?

33.

Consider a battery with the overall reaction:

a. What is the reaction at the anode and cathode?
b. A battery is “dead” when its cell potential is zero. What is the value of Q when this battery is dead?
c. If a particular dead battery was found to have $[Cu^{2+}] = 0.11\ M$, what was the concentration of silver ion?

34.

Why do batteries go dead, but fuel cells do not?

35.

Use the Nernst equation to explain the drop in voltage observed for some batteries as they discharge.

36.

Using the information thus far in this chapter, explain why battery-powered electronics perform poorly in low temperatures.

37.

Which member of each pair of metals is more likely to corrode (oxidize)?

a. Mg or Ca
b. Au or Hg
c. Fe or Zn
d. Ag or Pt

38.

Consider the following metals: Ag, Au, Mg, Ni, and Zn. Which of these metals could be used as a sacrificial anode in the cathodic protection of an underground steel storage tank? Steel is an alloy composed mostly of iron, so use −0.447 V as the standard reduction potential for steel.

39.

Aluminum is more easily oxidized than iron and yet when both are exposed to the environment, untreated aluminum has very good corrosion resistance while the corrosion resistance of untreated iron is poor. What might explain this observation?

40.

If a sample of iron and a sample of zinc come into contact, the zinc corrodes but the iron does not. If a sample of iron comes into contact with a sample of copper, the iron corrodes but the copper does not. Explain this phenomenon.

41.

Suppose you have three different metals, A, B, and C. When metals A and B come into contact, B corrodes and A does not corrode. When metals A and C come into contact, A corrodes and C does not corrode. Based on this information, which metal corrodes and which metal does not corrode when B and C come into contact?

42.

Why would a sacrificial anode made of lithium metal be a bad choice

43.

If a 2.5 A current flows through a circuit for 35 minutes, how many coulombs of charge moved through the circuit?

44.

For the scenario in the previous question, how many electrons moved through the circuit?

45.

Write the half-reactions and cell reaction occurring during electrolysis of each molten salt below.

a. $CaCl_2$
b. LiH
c. $AlCl_3$
d. $CrBr_3$

46.

What mass of each product is produced in each of the electrolytic cells of the previous problem if a total charge of 3.33 10^5 C passes through each cell?

47.

How long would it take to reduce 1 mole of each of the following ions using the current indicated?

a. Al^{3+}, 1.234 A
b. Ca^{2+}, 22.2 A
c. Cr^{5+}, 37.45 A
d. Au^{3+}, 3.57 A

48.

A current of 2.345 A passes through the cell shown in Figure 17.19 for 45 minutes. What is the volume of the hydrogen collected at room temperature if the pressure is exactly 1 atm? (Hint: Is hydrogen the only gas present above the water?)

49.

An irregularly shaped metal part made from a particular alloy was galvanized with zinc using a $Zn(NO_3)_2$ solution. When a current of 2.599 A was used, it took exactly 1 hour to deposit a 0.01123-mm layer of zinc on the part. What was the total surface area of the part? The density of zinc is 7.140 g/cm^3.

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10: KINETICS

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10.1: Introduction

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. A cold lizard is a slower lizard and an easier meal for predators.



Figure 10.1.1: 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. Two questions are typically posed when planning to carry out a chemical reaction. The first is: "Will the reaction produce the desired products in useful quantities?" The second question is: "How rapidly will the reaction occur?" 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. This chapter examines the factors that influence the rates of chemical reactions, the mechanisms by which reactions proceed, and the quantitative techniques used to describe the rates at which reactions occur.

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10.2: Chemical Reaction Rates

Learning Objectives

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

- 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.

For reactants and products in solution, their relative amounts (concentrations) are conveniently used for purposes of expressing reaction rates. For example, the concentration of hydrogen peroxide, H_2O_2, in an aqueous solution changes slowly over time as it decomposes according to the equation:

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

The rate at which the hydrogen peroxide decomposes can be expressed in terms of the rate of change of its concentration, as shown here:

$$\begin{aligned}\text{rate of decomposition of } \mathrm{H_2O_2} &= -\frac{\text{change in concentration of reactant}}{\text{time interval}} \\ &= -\frac{[\mathrm{H_2O_2}]_{t_2} - [\mathrm{H_2O_2}]_{t_1}}{t_2 - t_1} \\ &= -\frac{\Delta\,[\mathrm{H_2O_2}]}{\Delta t}\end{aligned}$$

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, $[\mathrm{H_2O_2}]_{t_1}$ represents the molar concentration of hydrogen peroxide at some time t_1; likewise, $[\mathrm{H_2O_2}]_{t_2}$ represents the molar concentration of hydrogen peroxide at a later time t2; and Δ[H2O2] 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, $\Delta\,[\mathrm{H_2O_2}]$ is a negative quantity. Reaction rates are, by convention, positive quantities, and so this negative change in concentration is multiplied by –1. Figure $10.2.1$ provides an example of data collected during the decomposition of $\mathrm{H_2O_2}$.

Time (h)	$[H_2O_2]$ (mol L^{-1})	$\Delta[H_2O_2]$ (mol L^{-1})	Δt (h)	Rate of Decomposition, (mol L^{-1} h^{-1})
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	0.010
24.00	0.0625			

Figure 10.2.1: 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:

$$\frac{-\Delta\left[H_2O_2\right]}{\Delta t} = \frac{-(0.500mol/L - 1.000mol/L)}{(6.00h - 0.00h)} = 0.0833molL^{-1}h^{-1}$$

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:

$$\frac{-\Delta\left[H_2O_2\right]}{\Delta t} = \frac{-(0.0625mol/L - 0.125mol/L)}{(24.00h - 18.00h)} = 0.010molL^{-1}h^{-1}$$

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. In a plot of 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 10.2.2). These tangent line slopes may be evaluated using calculus, but the procedure for doing so is beyond the scope of this chapter.

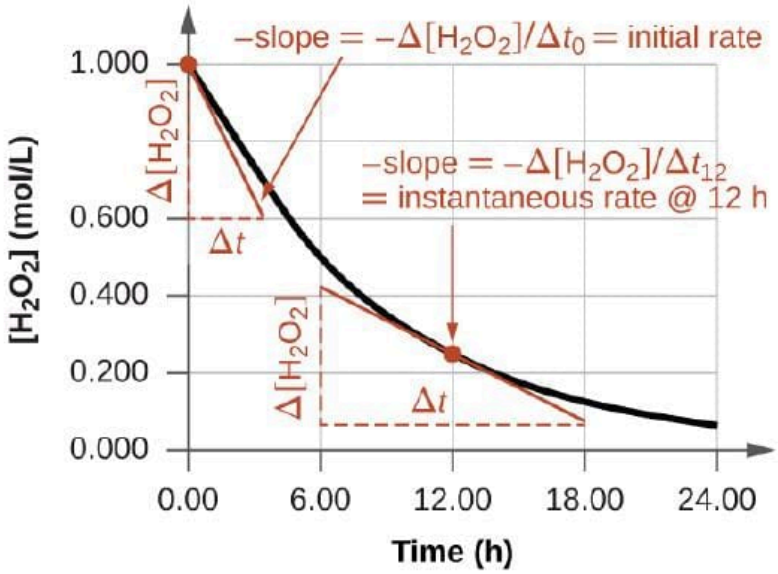


Figure 10.2.2: This graph shows a plot of concentration versus time for a 1.000 *M* solution of H_2O_2. The rate at any time is equal to the negative of the slope of a line tangent to the curve at that time. Tangents are shown at *t* = 0 h ("initial rate") and at *t* = 12 h ("instantaneous rate" at 12 h).

Chemistry in Everyday Life: 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 10.2.3). 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:

$$C_6H_{12}O_6 + O_2 \xrightarrow{\text{catalyst}} C_6H_{10}O_6 + H_2O_2$$

$$2H_2O_2 + 2I^- \xrightarrow{\text{catalyst}} I_2 + 2H_2O + O_2$$

The first equation 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, 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.

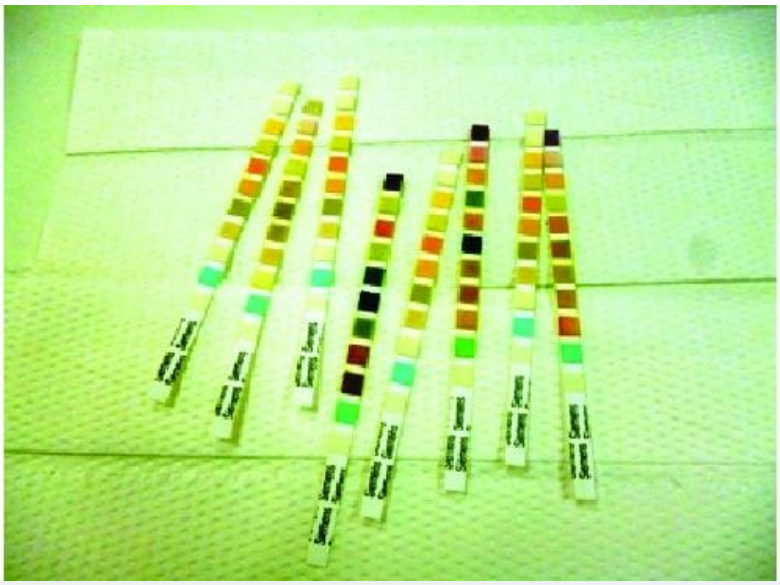


Figure 10.2.3: Test strips are commonly used to detect the presence of specific substances in a person's urine. Many test strips have several pads containing various reagents to permit the detection of multiple substances on a single strip. (credit: Iqbal Osman)

Relative Rates of Reaction

The rate of a reaction may be expressed as the change in concentration of any reactant or product. For any given reaction, these rate expressions are all related simply to one another according to the reaction stoichiometry. The rate of the general reaction

$$A \longrightarrow B \tag{10.2.1}$$

can be expressed in terms of the decrease in the concentration of A or the increase in the concentration of B. These two rate expressions are related by the stoichiometry of the reaction:

$$\text{rate } = -\left(\frac{1}{a}\right)\left(\frac{\Delta A}{\Delta t}\right) = \left(\frac{1}{b}\right)\left(\frac{\Delta B}{\Delta t}\right)$$

Consider the reaction represented by the following equation:

$$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$$

The relation between the reaction rates expressed in terms of nitrogen production and ammonia consumption, for example, is:

$$-\frac{\Delta mol\ NH_3}{\Delta t} \times \frac{1mol\ N_2}{2mol\ NH_3} = \frac{\Delta mol\ N_2}{\Delta t}$$

This may be represented in an abbreviated format by omitting the units of the stoichiometric factor:

$$-\frac{1}{2}\frac{\Delta mol\ NH_3}{\Delta t} = \frac{\Delta mol\ N_2}{\Delta t}$$

Note that a negative sign has been included as a factor to account for the opposite signs of the two amount changes (the reactant amount is decreasing while the product amount is increasing). For homogeneous reactions, both the reactants and products are present in the same solution and thus occupy the same volume, so the molar amounts may be replaced with molar concentrations:

$$-\frac{1}{2}\frac{\Delta\left[NH_3\right]}{\Delta t} = \frac{\Delta\left[N_2\right]}{\Delta t}$$

Similarly, the rate of formation of H_2 is three times the rate of formation of N_2 because three moles of H_2 are produced for each mole of N_2 produced.

$$\frac{1}{3}\frac{\Delta\left[H_2\right]}{\Delta t} = \frac{\Delta\left[N_2\right]}{\Delta t}$$

Figure 10.2.4: illustrates the change in concentrations over time for the decomposition of ammonia into nitrogen and hydrogen at 1100 °C. Slopes of the tangent lines at t = 500 s show that the instantaneous rates derived from all three species involved in the reaction 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:

$$\frac{2.91 \times 10^{-6} M/s}{9.70 \times 10^{-7} M/s} \approx 3$$

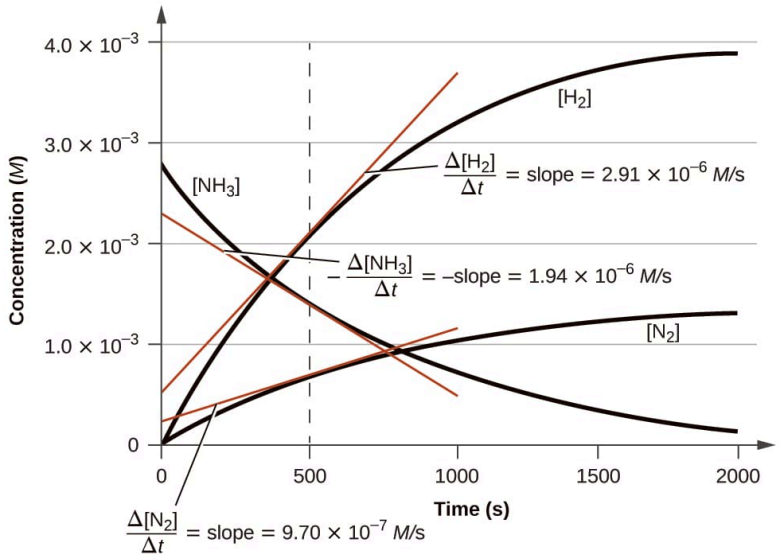


Figure 10.2.4: Changes in concentrations of the reactant and products for the reaction $2\,\mathrm{NH_3} \longrightarrow \mathrm{N_2} + 3\,\mathrm{H_2}$. The rates of change of the three concentrations are related by the reaction stoichiometry, as shown by the different slopes of the tangents at t = 500 s.

Example 10.2.1: Expressions for Relative Reaction Rates

The first step in the production of nitric acid is the combustion of ammonia:

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g) \tag{10.2.2}$$

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:

$$-\frac{1}{4}\frac{\Delta\left[NH_3\right]}{\Delta t} = -\frac{1}{5}\frac{\Delta\left[O_2\right]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO]}{\Delta t} = \frac{1}{6}\frac{\Delta\left[H_2O\right]}{\Delta t}$$

Exercise 10.2.1

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:

$$5Br^- + BrO_3^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

Write the equations that relate the rates of consumption of the reactants and the rates of formation of the products.

Answer available at the end of this section.

Example 10.2.2: Reaction Rate Expressions for Decomposition of H_2O_2

The graph in Figure 10.2.2: shows the rate of the decomposition of H_2O_2 over time:

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

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:

$$-\frac{1}{2}\frac{\Delta\left[\mathrm{H_2O_2}\right]}{\Delta t} = \frac{1}{2}\frac{\Delta\left[\mathrm{H_2O}\right]}{\Delta t} = \frac{\Delta\left[\mathrm{O_2}\right]}{\Delta t} \tag{10.2.3}$$

What is the instantaneous rate of production of $\mathrm{H_2O}$ and $\mathrm{O_2}$?

Solution

The reaction stoichiometry shows that

$$-\frac{1}{2}\frac{\Delta\left[\mathrm{H_2O_2}\right]}{\Delta t} = \frac{1}{2}\frac{\Delta\left[\mathrm{H_2O}\right]}{\Delta t} = \frac{\Delta\left[\mathrm{O_2}\right]}{\Delta t} \tag{10.2.4}$$

Therefore:

$$\frac{1}{2} \times 3.20 \times 10^{-2} molL^{-1}h^{-1} = \frac{\Delta\left[O_2\right]}{\Delta t}$$

and

$$\frac{\Delta\left[O_2\right]}{\Delta t} = 1.60 \times 10^{-2} molL^{-1}h^{-1}$$

Exercise 10.2.2

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 available at the end of this section.

Answers

Exercise 10.2.1

$$-\frac{1}{5}\frac{\Delta\left[Br^-\right]}{\Delta t} = -\frac{\Delta\left[BrO_3^-\right]}{\Delta t} = -\frac{1}{6}\frac{\Delta\left[H^+\right]}{\Delta t} = \frac{1}{3}\frac{\Delta\left[Br_2\right]}{\Delta t} = \frac{1}{3}\frac{\Delta\left[H_2O\right]}{\Delta t}$$

Exercise 10.2.2

1.05 10^{-6} mol/L/s, N_2 and 3.15 10^{-6} mol/L/s, H_2.

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10.3: Factors Affecting Reaction Rates

Learning Objectives

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

- 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. Five factors typically affecting the rates of chemical reactions will be explored in this section: 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.

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.

The Physical States of the Reactants

A chemical reaction between two or more substances requires intimate contact between the reactants. When reactants are in different physical states, or phases (solid, liquid, gaseous, dissolved), the reaction takes place only at the interface between the phases. Consider the heterogeneous reaction between a solid phase and either a liquid or gaseous phase. Compared with the reaction rate for large solid particles, the rate for smaller particles will be greater because the surface area in contact with the other reactant phase is greater. For example, large pieces of iron react more slowly with acids than they do with finely divided iron powder (Figure 10.3.1). Large pieces of wood smolder, smaller pieces burn rapidly, and saw dust burns explosively.

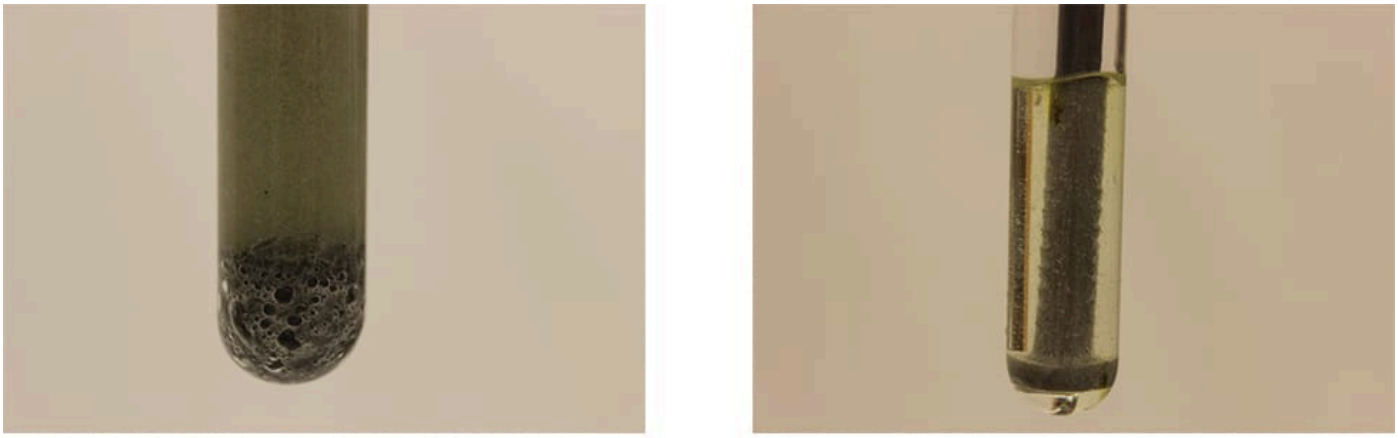


Figure 10.3.1: (a) Iron powder reacts rapidly with dilute hydrochloric acid and produces bubbles of hydrogen gas: $2Fe(s) + 6HCl(aq)\ 2FeCl_3(aq) + 3H_2(g)$. (b) An iron nail reacts more slowly because the surface area exposed to the acid is much less.

Link to Learning

Watch this video to see the reaction of cesium with water in slow motion and a discussion of how the state of reactants and particle size affect reaction rates.

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. Gas burners, hot plates, and ovens are often used in the laboratory to increase the speed of reactions that proceed slowly at ordinary temperatures. For many chemical processes, reaction rates are approximately doubled when the temperature is raised by 10 °C.

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 10.3.2). An acidic oxide, sulfur dioxide combines with water vapor in the air to produce sulfurous acid in the following reaction:

$$\mathrm{SO_2\,(g) + H_2O\,(g) \longrightarrow H_2SO_3\,(aq)}$$

Calcium carbonate reacts with sulfurous acid as follows:

$$\mathrm{CaCO_3\,(s) + H_2SO_3\,(aq) \longrightarrow CaSO_3\,(aq) + CO_2\,(g) + H_2O\,(l)}$$

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.

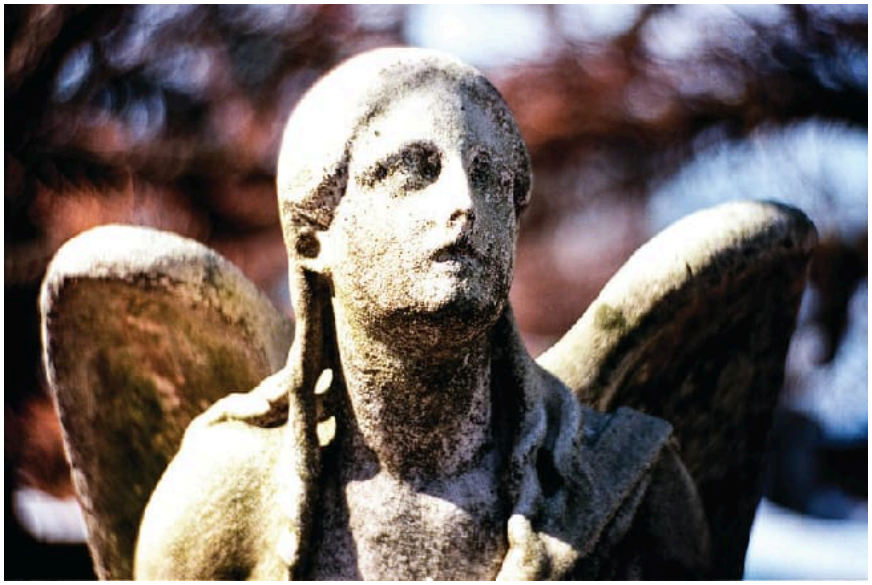


Figure 10.3.2: Statues made from carbonate compounds such as limestone and marble typically weather slowly over time due to the actions of water, and thermal expansion and contraction. However, pollutants like sulfur dioxide can accelerate weathering. As the concentration of air pollutants increases, deterioration of limestone occurs more rapidly. (credit: James P Fisher III)

Link to Learning

Phosphorus burns rapidly in air, but it will burn even more rapidly if the concentration of oxygen is higher. Watch this video to see an example.

The Presence of a Catalyst

Relatively dilute aqueous solutions of hydrogen peroxide, $\mathrm{H_2O_2}$, are commonly used as topical antiseptics. Hydrogen peroxide decomposes to yield water and oxygen gas according to the equation:

$$2\,\mathrm{H_2O_2\,(aq)} \longrightarrow 2\,\mathrm{H_2O\,(l)} + \mathrm{O_2\,(g)}$$

Under typical conditions, this decomposition occurs very slowly. When dilute $\mathrm{H_2O_2\,(aq)}$ is poured onto an open wound, however, the reaction occurs rapidly and the solution foams because of the vigorous production of oxygen gas. This dramatic difference is caused by the presence of substances within the wound's exposed tissues that accelerate the decomposition process. Substances that function to increase the rate of a reaction are called **catalysts**, a topic treated in greater detail later in this chapter.

Link to Learning

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.

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10.4: Rate Laws

Learning Objectives

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

- 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 often affected by the concentrations of reactants. Rate laws (sometimes called *differential 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. As an example, consider the reaction described by the chemical equation

$$aA + bB \longrightarrow \text{ products}$$

where a and b are stoichiometric coefficients. The rate law for this reaction is written as:

$$\text{rate } = k[A]^m[B]^n$$

in which [*A*] and [*B*] 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* and *n* are the **reaction orders** and are typically positive integers, though they can be fractions, negative, or zero. The rate constant *k* and the reaction orders *m* and *n* 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 reactant concentrations, but it does vary with temperature.

The reaction orders in a rate law describe the mathematical dependence of the rate on reactant concentrations. Referring to the generic rate law above, the reaction is *m* order with respect to *A* and *n* order with respect to *B*. For example, if *m* = 1 and *n* = 2, the reaction is first order in *A* and second order in *B*. The overall reaction order is simply the sum of orders for each reactant. For the example rate law here, the reaction is third order overall (1 + 2 = 3). A few specific examples are shown below to further illustrate this concept.

The rate law:

$$\text{rate } = k\left[H_2O_2\right]$$

describes a reaction that is first order in hydrogen peroxide and first order overall. The rate law:

$$\text{rate } = k\left[\mathrm{C_4H_6}\right]^2$$

describes a reaction that is second order in $\mathrm{C_4H_6}$ and second order overall. The rate law:

$$\text{rate } = k\left[\mathrm{H^+}\right]\left[\mathrm{OH^-}\right]$$

describes a reaction that is first order in $\mathrm{H^+}$, first order in $\mathrm{OH^-}$, and second order overall.

Example 10.4.1: Writing Rate Laws from Reaction Orders

An experiment shows that the reaction of nitrogen dioxide with carbon monoxide:

$$\mathrm{NO_2\,(g) + CO\,(g) \longrightarrow NO\,(g) + CO_2\,(g)}$$

is second order in $\mathrm{NO_2}$ and zero order in CO at 100 °C. What is the rate law for the reaction?

Solution

The reaction will have the form:

$$\text{rate } = k\left[\text{NO}_2\right]^m\left[\text{CO}\right]^n$$

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:

$$\text{rate } = k\left[\text{NO}_2\right]^2\left[\text{CO}\right]^0 = k\left[\text{NO}_2\right]^2$$

Remember that a number raised to the zero power is equal to 1, thus $[CO]^0 = 1$, which is why the CO concentration term may be omitted from the rate law: the rate of reaction is solely dependent on the concentration of NO_2. A later chapter section on reaction mechanisms will explain how a reactant's concentration can have no effect on a reaction rate despite being involved in the reaction.

Exercise $10.4.1A$

The rate law for the reaction:

$$\text{H}_2\left(\text{g}\right) + 2\,\text{NO}\left(\text{g}\right) \longrightarrow \text{N}_2\text{O}\left(\text{g}\right) + \text{H}_2\text{O}\left(\text{g}\right)$$

has been 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 available at the end of this section.

Exercise $10.4.1B$

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 ($\text{CH}_3\text{CH}_2\text{OCOCH}_3$) as a sample reaction before studying the chemical reactions that produce biodiesel:

$$\text{CH}_3\text{OH} + \text{CH}_3\text{CH}_2\text{OCOCH}_3 \longrightarrow \text{CH}_3\text{OCOCH}_3 + \text{CH}_3\text{CH}_2\text{OH}$$

The rate law for the reaction between methanol and ethyl acetate is, under certain conditions, determined to be:

$$\text{rate } = k\left[\text{CH}_3\text{OH}\right]$$

What is the order of reaction with respect to methanol and ethyl acetate, and what is the overall order of reaction?

Answer available at the end of this section.

A common experimental approach to the determination of rate laws is the **method of initial rates**. This method involves measuring reaction rates for multiple experimental trials carried out using different initial reactant concentrations. Comparing the measured rates for these trials permits determination of the reaction orders and, subsequently, the rate constant, which together are used to formulate a rate law. This approach is illustrated in the next two example exercises.

Example $10.4.2$: 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 $10.4.1$). One such reaction is the combination of nitric oxide, NO, with ozone, O_3:

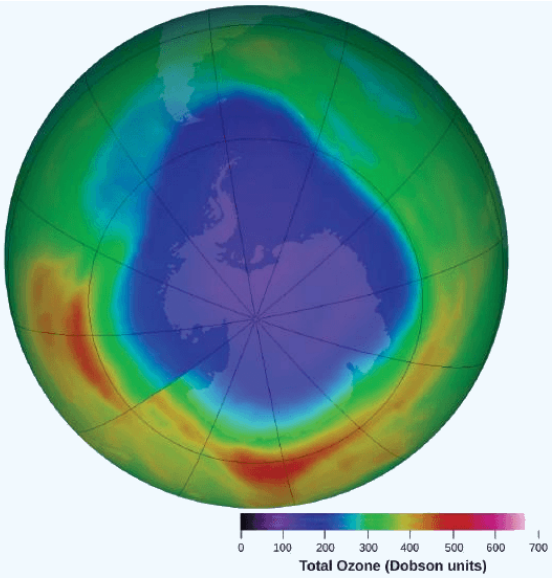


Figure 10.4.1: A contour map showing stratospheric ozone concentration and the “ozone hole” that occurs over Antarctica during its spring months. (credit: modification of work by NASA)

$$\mathrm{NO\,(g) + O_3\,(g) \longrightarrow NO_2\,(g) + O_2\,(g)}$$

This reaction has been studied in the laboratory, and the following rate data were determined at 25 °C.

Trial	[NO] (mol/L)	[O_3] (mol/L)	$\frac{\Delta[NO_2]}{\Delta t}(\mathrm{mol\,L^{-1}\,s^{-1}})$
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:

$$\mathrm{rate} = k[NO]^m\,[O_3]^n$$

Determine the values of *m*, *n*, and *k* from the experimental data using the following three-part process:

Step 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.

Step 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:

$$\text{rate } = k[NO]^1\,[O_3]^1 = k[NO]\,[O_3]$$

Step 3:

Determine the value of k *from one set of concentrations and the corresponding rate*. The data from trial 1 are used below:

$$\begin{aligned} k &= \frac{\text{rate}}{[\text{NO}]\,[\text{O}_3]} \\ &= \frac{6.60 \times 10^{-5}\ \text{mol L}^{-1}\text{s}^{-1}}{\left(1.00 \times 10^{-6}\ \text{mol L}^{-1}\right)\left(3.00 \times 10^{-6}\ \text{mol L}^{-1}\right)} \\ &= 2.20 \times 10^{7}\ \text{L mol}^{-1}\text{s}^{-1} \end{aligned}$$

Exercise 10.4.2

Acetaldehyde decomposes when heated to yield methane and carbon monoxide according to the equation:

$$\text{CH}_3\text{CHO}\,(\text{g}) \longrightarrow \text{CH}_4\,(\text{g}) + \text{CO}\,(\text{g})$$

Determine the rate law and the rate constant for the reaction from the following experimental data:

Trial	[CH_3CHO] (mol/L)	$-\frac{\Delta[\text{CH}_3\text{CHO}]}{\Delta t}(\text{mol L}^{-1}\text{s}^{-1})$
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 available at the end of this section.

Example 10.4.3: 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:

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$$

Trial	[NO] (mol/L)	[Cl_2] (mol/L)	$-\frac{\Delta[\text{CO}]}{\Delta t}(\text{mol } L^{-1}\text{s}^{-1})$
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:

$$\text{rate } = k[NO]^m\,[Cl_2]^n$$

As in Example 10.4.2, 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, an explicit algebraic approach (vs. the implicit approach of the previous example) will be used to determine the values of *m* and *n*:

Step 1

Determine the value of m from the data in which $[\mathrm{NO}]$ varies and $[\mathrm{Cl_2}]$ is constant. Write the ratios with the subscripts x and y to indicate data from two different trials:

$$\frac{\text{rate }_x}{\text{rate }_y} = \frac{k[NO]_x^m\,[Cl_2]_x^n}{k[NO]_y^m\,[Cl_2]_y^n}$$

Using the third trial and the first trial, in which $[\mathrm{Cl_2}]$ does not vary, gives:

$$\frac{\text{rate 3}}{\text{rate 1}} = \frac{0.00675}{0.00300} = \frac{k(0.15)^m(0.10)^n}{k(0.10)^m(0.10)^n}$$

Canceling equivalent terms in the numerator and denominator leaves:

$$\frac{0.00675}{0.00300} = \frac{(0.15)^m}{(0.10)^m}$$

which simplifies to:

$$2.25 = (1.5)^m$$

Use logarithms to determine the value of the exponent *m*:

$$\ln(2.25) = m\ln(1.5)$$
$$\frac{\ln(2.25)}{\ln(1.5)} = m$$
$$2 = m$$

Confirm the result

$$1.5^2 = 2.25$$

Step 2

Determine the value of n from data in which $[\mathrm{Cl_2}]$ varies and $[\mathrm{NO}]$ is constant.

$$\frac{\text{rate 2}}{\text{rate 1}} = \frac{0.00450}{0.00300} = \frac{k0.10)^m(0.15)^n}{k(0.10)^m(0.10)^n}$$

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:

$$\text{rate } = k[NO]^m\,[Cl_2]^n = k[NO]^2\,[Cl_2]$$

Step 3.

Determine the numerical value of the constant with appropriate units. The units for the rate of a reaction are mol/L/s. The units for 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^{-} L/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*:

$$0.00300 \text{ mol } L^{-1}s^{-1} = k\left(0.10 \text{ mol } L^{-1}\right)^2\left(0.10 \text{ mol } L^{-1}\right)^1$$
$$k = 3.0 \text{ mol}^{-2}L^2s^{-1}$$

Exercise 10.4.3

Use the provided initial rate data to derive the rate law for the reaction whose equation is:

$$OCl^-(aq) + I^-(aq) \longrightarrow OI^-(aq) + Cl^-(aq)$$

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 available at the end of this section.

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:

$$\begin{aligned}
NO_2 + CO &\longrightarrow NO + CO_2 & \text{rate} &= k\left[NO_2\right]^2\\
CH_3\ CHO &\longrightarrow CH_4 + CO & \text{rate} &= k\left[CH_3CHO\right]^2\\
2\,N_2\ O_5 &\longrightarrow NO_2 + O_2 & \text{rate} &= k\left[N_2O_5\right]\\
2\,NO_2 + F_2 &\longrightarrow 2\,NO_2\ F & \text{rate} &= k\left[NO_2\right]\left[F_2\right]\\
2\,NO_2\ Cl &\longrightarrow 2\,NO_2 + Cl_2 & \text{rate} &= k\left[NO_2Cl\right]
\end{aligned}$$

Note

It is important to note that *rate laws are determined by experiment only and are not reliably predicted by reaction stoichiometry.*

The units for a rate constant will vary as appropriate to accommodate the overall order of the reaction. The unit of the rate constant for the second-order reaction described in Example 10.4.2 was determined to be k was derived to be $L\ mol^{-1}s^{-1}$. For the third-order reaction, k was derived to be $L^2mol^{-2}s^{-1}$. Dimensional analysis requires the rate constant unit for a reaction whose overall order is x to be $L^{x-1}\ mol^{1-x}s^{-1}$. Table 10.4.1 summarizes the rate constant units for common reaction orders.

Table 10.4.1*: Rate Constant Units for Common Reaction Orders*

Overall Reaction Order (x)	Rate Constant Unit (L^{x-1} mol^{1-x} s^{-1})
0 (zero)	mol L^{-1} s^{-1}
1 (first)	s^{-1}
2 (second)	L mol^{-1} s^{-1}
3 (third)	L^2 mol^{-2} s^{-1}

Note that the units in this table were derived using specific units for concentration (mol/L) and time (s), though any valid units for these two properties may be used.

Answers

Exercise 10.4.1A

order in NO = 2; order in H_2 = 1; overall order = 3

Exercise 10.4.1B

order in CH_3OH = 1; order in $CH_3CH_2OCOCH_3$ = 0; overall order = 1

Exercise 10.4.2

$\text{rate } = k\left[CH_3CHO\right]^2$ with k = 6.7310^{-6} L/mol/s

Exercise 10.4.3

$$\frac{\text{rate 2}}{\text{rate 3}} = \frac{0.00092}{0.00046} = \frac{k(0.0020)^x(0.0040)^y}{k(0.0020)^x(0.0020)^y}$$

$$2.00 = 2.00^y$$

$$y = 1$$

$$\frac{\text{rate 1}}{\text{rate 2}} = \frac{0.00184}{0.00092} = \frac{k(0.0040)^x(0.0020)^y}{k(0.0020)^x(0.0040)^y}$$

$$2.00 = \frac{2^x}{2^y}$$

$$2.00 = \frac{2^x}{2^1}$$

$$4.00 = 2^x$$

$$x = 2$$

Substituting the concentration data from trial 1 and solving for k yields:

$$\text{rate } = k\left[OCl^-\right]^2\left[I^-\right]^1$$

$$0.00184 = k(0.0040)^2(0.0020)^1$$

$$k = 5.75 \times 10^4 mol^{-2}L^2s^{-1}$$

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10.5: Integrated Rate Laws

Learning Objectives

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

- 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 discussed 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.

First-Order Reactions

Integration of the rate law for a simple first-order reaction (rate = $k[A]$) results in an equation describing how the reactant concentration varies with time:

$$[A]_t = [A]_0 e^{-kt}$$

where $[A]t$ is the concentration of A at any time t, $[A]_0$ is the initial concentration of A, and k is the first-order rate constant.

For mathematical convenience, this equation may be rearranged to other formats, including direct and indirect proportionalities:

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$$

or

$$\ln\left(\frac{[A]_0}{[A]_t}\right) = kt$$

and a format showing a linear dependence of concentration in time:

$$\ln [A]_t = \ln [A]_0 - kt$$

Example 10.5.1: The Integrated Rate Law for a First-Order Reaction

The rate constant for the first-order decomposition of cyclobutane, $\mathrm{C_4H_8}$ at 500 °C is 9.2 10^{-3} s^{-1}:

$$\mathrm{C_4H_8} \longrightarrow 2\,\mathrm{C_2H_4}$$

How long will it take for 80.0% of a sample of $\mathrm{C_4H_8}$ to decompose?

Solution

Since the relative change in reactant concentration is provided, a convenient format for the integrated rate law is:

$$\ln\left(\frac{[A]_0}{[A]_t}\right) = kt$$

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 0.200*x*. Rearranging the rate law to isolate *t* and substituting the provided quantities yields:

$$\begin{aligned} t &= \ln\frac{[x]}{[0.200x]} \times \frac{1}{k} \\ &= \ln 5 \times \frac{1}{9.2 \times 10^{-3}\ \text{s}^{-1}} \\ &= 1.609 \times \frac{1}{9.2 \times 10^{-3}\ \text{s}^{-1}} \\ &= 1.7 \times 10^{2}\ \text{s} \end{aligned}$$

Exercise 10.5.1

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}. 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 available at the end of this section.

In the next example exercise, a linear format for the integrated rate law will be convenient:

$$\begin{aligned} \ln[A]_t &= (-k)(t) + \ln[A]_0 \\ y &= mx + b \end{aligned}$$

A plot of $\ln[A]_t$ versus *t* for a first-order reaction is a straight line with a slope of –*k* and a *y*-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*.

Example 10.5.2: Graphical Determination of Reaction Order and Rate Constant

Show that the data in Figure 10.5.1 can be represented by a first-order rate law by graphing $\ln[H_2O_2]$ versus time. Determine the rate constant for the decomposition of H_2O_2 from these data.

Solution

The data from Figure 10.5.1 are tabulated below, and a plot of $\ln[H_2O_2]$ is shown in Figure 10.5.1.

Time (h)	$[H_2O_2]$ (*M*)	$\ln[H_2O_2]$
0.00	1.000	0.000
6.00	0.500	–0.693
12.00	0.250	–1.386
18.00	0.125	–2.079

Time (h)	$[H_2O_2]$ (*M*)	$\ln[H_2O_2]$
24.00	0.0625	−2.772

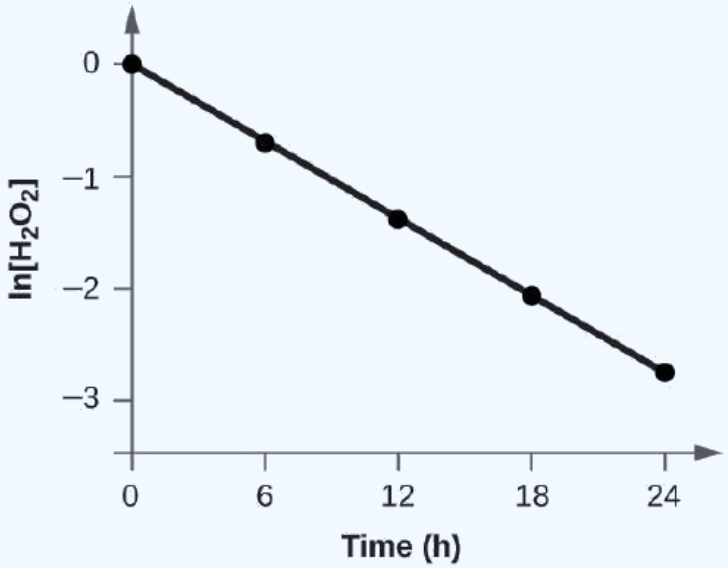


Figure 10.5.1: A linear relationship between $\ln[H_2O_2]$ and time suggests the decomposition of hydrogen peroxide is a first-order reaction.

The plot of $\ln[H_2O_2]$ versus time is linear, indicating that the reaction may be described by a first-order rate law.

According to the linear format of the first-order integrated rate law, the rate constant is given by the negative of this plot's slope.

$$\text{slope} = \frac{\text{change in } y}{\text{change in } x} = \frac{\Delta y}{\Delta x} = \frac{\Delta \ln [H_2O_2]}{\Delta t}$$

The slope of this line may be derived from 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 0.00 h is 0.000; the value when *t* = 24.00 h is −2.772

$$\begin{aligned} \text{slope} &= \frac{-2.772 - 0.000}{24.00 - 0.00h} \\ &= \frac{-2.772}{24.00h} \\ &= -0.116h^{-1} \\ k = -\text{ slope} &= -\left(-0.116h^{-1}\right) = 0.116h^{-1} \end{aligned}$$

Exercise 10.5.2

Graph the following data to determine whether the reaction $A \longrightarrow B + C$ is first order.

Time (s)	[*A*]
4.0	0.220
8.0	0.144
12.0	0.110
16.0	0.088
20.0	0.074

Answer available at the end of this section.

Second-Order Reactions

The equations that relate the concentrations of reactants and the rate constant of second-order reactions can be fairly complicated. To illustrate the point with minimal complexity, only the simplest second-order reactions will be described here, namely, those whose rates depend on the concentration of just one reactant. For these types of reactions, the differential rate law is written as:

$$\text{rate } = k[A]^2$$

For these second-order reactions, the integrated rate law is:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

where the terms in the equation have their usual meanings as defined earlier.

Example 10.5.3: The Integrated Rate Law for a Second-Order Reaction

The reaction of butadiene gas (C_4H_6) to yield C_8H_{12} gas is described by the equation:

$$2C_4H_6(g) \longrightarrow C_8H_{12}(g)$$

This "dimerization" reaction is second order with a rate constant equal to 5.76 10^{-2} L mol^{-1} min^{-1} under certain conditions. If the initial concentration of butadiene is 0.200 *M*, what is the concentration after 10.0 min?

Solution

For a second-order reaction, the integrated rate law is written

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

We know three variables in this equation: $[A]_0$ = 0.200 mol/L, k = 5.76 10^{-2} L/mol/min, and t = 10.0 min. Therefore, we can solve for [*A*], the fourth variable:

$$\begin{aligned}\frac{1}{[A]_t} &= \left(5.76 \times 10^{-2} L mol^{-1} min^{-1}\right)(10 min) + \frac{1}{0.200 mol^{-1}} \\ &= \left(5.76 \times 10^{-1} L mol^{-1}\right) + 5.00 L mol^{-1} \\ &= 5.58 L mol^{-1} \\ [A]_t &= 1.79 \times 10^{-1} mol L^{-1}\end{aligned}$$

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 10.5.3

If the initial concentration of butadiene is 0.0200 *M*, what is the concentration remaining after 20.0 min?

Answer available at the end of this section.

The integrated rate law for second-order reactions has the form of the equation of a straight line:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$y = mx + b$$

A plot of $\frac{1}{[A]_t}$ versus t for a second-order reaction is a straight line with a slope of *k* and a *y*-intercept of $\frac{1}{[A]_0}$. If the plot is not a straight line, then the reaction is not second order.

Example 10.5.4: Graphical Determination of Reaction Order and Rate Constant

The data below are for the same reaction described in Example 10.5.3. Prepare and compare two appropriate data plots to identify the reaction as being either first or second order. After identifying the reaction order, estimate a value for the rate constant.

Solution

Time (s)	$[C_4H_6]$ (*M*)
0	1.00×10^{-2}
1600	5.04×10^{-3}
3200	3.37×10^{-3}
4800	2.53×10^{-3}
6200	2.08×10^{-3}

In order to distinguish a first-order reaction from a second-order reaction, prepare a plot of $\ln[C_4H_6]_t$ versus *t* and compare it to a plot of $\frac{1}{[C_4H_6]_t}$ 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
4800	395	−5.978
6200	481	−6.175

The plots are shown in Figure 10.5.2, which clearly shows the plot of $\ln [C_4H_6]_t$ versus t is not linear, therefore the reaction is not first order. The plot of $\frac{1}{[C_4H_6]_t}$ versus t is linear, indicating that the reaction is second order.

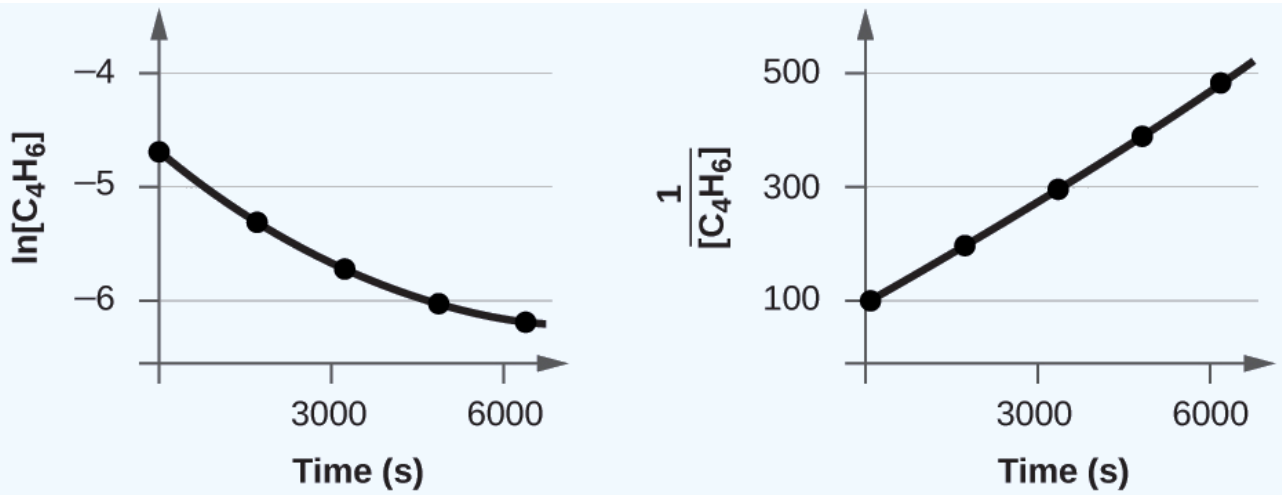


Figure 10.5.2: These two graphs show first- and second-order plots for the dimerization of C_4H_6. The linear trend in the second-order plot (right) indicates that the reaction follows second-order kinetics.

According to the second-order integrated rate law, the rate constant is equal to the slope of the versus *t* plot. Using the data for *t* = 0 s and *t* = 6200 s, the rate constant is estimated as follows:

$$k = \text{ slope } = \frac{(481M^{-1} - 100M^{-1})}{(6200s - 0s)} = 0.0614M^{-1}s^{-1}$$

Exercise 10.5.4

Do the following data fit a second-order rate law?

Time (s)	[*A*] (*M*)
5	0.952
10	0.625
15	0.465
20	0.370
25	0.308
35	0.230

Answer available at the end of this section.

Zero-Order Reactions

For zero-order reactions, the differential rate law is:

$$\text{rate } = k$$

A zero-order reaction thus exhibits a constant reaction rate, regardless of the concentration of its reactant(s). This may seem counterintuitive, since the reaction rate certainly can't be finite when the reactant concentration is zero. For purposes of this introductory text, it will suffice to note that zero-order kinetics are observed for some reactions only under certain specific conditions. These same reactions exhibit different kinetic behaviors when the specific conditions aren't met, and for this reason the more prudent term *pseudo-zero-order* is sometimes used.

The integrated rate law for a zero-order reaction is a linear function:

$$[A]_t = -kt + [A]_0$$
$$y = mx + b$$

A plot of [*A*] versus *t* for a zero-order reaction is a straight line with a slope of –*k* and a *y*-intercept of $[A]_0$. Figure 10.5.3: shows a plot of $[NH_3]$ versus *t* for the thermal decomposition of ammonia at the surface of two different heated solids. The decomposition reaction exhibits first-order behavior at a quartz (SiO_2) surface, as suggested by the exponentially decaying plot of concentration versus time. On a tungsten surface, however, the plot is linear, indicating zero-order kinetics.

Example 10.5.5: Graphical Determination of Zero-Order Rate Constant

Use the data plot in Figure 10.5.3 to graphically estimate the zero-order rate constant for ammonia decomposition at a tungsten surface.

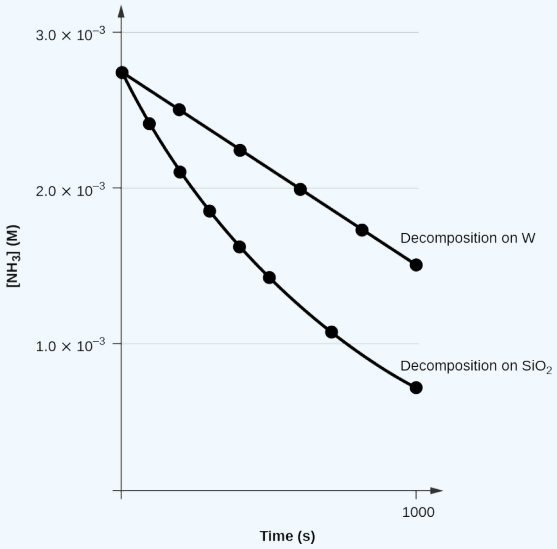


Figure 10.5.3: The decomposition of NH_3 on a tungsten (W) surface is a zero-order reaction, whereas on a quartz (SiO_2) surface, the reaction is first order.

Solution

The integrated rate law for zero-order kinetics describes a linear plot of reactant concentration, $[A]_t$, versus time, *t*, with a slope equal to the negative of the rate constant, –*k*. Following the mathematical approach of previous examples, the slope of the linear data plot (for decomposition on W) is estimated from the graph. Using the ammonia concentrations at *t* = 0 and *t* = 1000 s:

$$k = -\text{ slope } = -\frac{(0.0015 molL^{-1} - 0.0028 molL^{-1})}{(1000s - 0s)} = 1.3 \times 10^{-6} molL^{-1}s^{-1}$$

Exercise 10.5.5

The zero-order plot in Figure 10.5.3 shows an initial ammonia concentration of 0.0028 mol L^{-1} decreasing linearly with time for 1000 s. Assuming no change in this zero-order behavior, at what time (min) will the concentration reach 0.0001 mol L^{-1}?

Answer available at the end of this section.

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. Using the decomposition of hydrogen peroxide (Figure 10.5.1) as an example, 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.

First-Order Reactions

An equation relating the half-life of a first-order reaction to its rate constant may be derived from the integrated rate law as follows:

$$\ln \frac{[A]_0}{[A]_t} = kt$$

$$t = \ln \frac{[A]_0}{[A]_t} \times \frac{1}{k}$$

Invoking the definition of half-life, symbolized requires that the concentration of *A* at this point is one-half its initial concentration: $t = t_{1/2}$, $[A]_t = \frac{1}{2}[A]_0$

Substituting these terms into the rearranged integrated rate law and simplifying yields the equation for half-life:

$$t_{1/2} = \ln \frac{[A]_0}{\frac{1}{2}[A]_0} \times \frac{1}{k}$$

$$= \ln 2 \times \frac{1}{k} = 0.693 \times \frac{1}{k}$$

$$t_{1/2} = \frac{0.693}{k}$$

This equation describes an expected inverse relation between the half-life of the reaction and its rate constant, *k*. Faster reactions exhibit larger rate constants and correspondingly shorter half-lives. Slower reactions exhibit smaller rate constants and longer half-lives.

Example 10.5.6: 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 10.5.4.

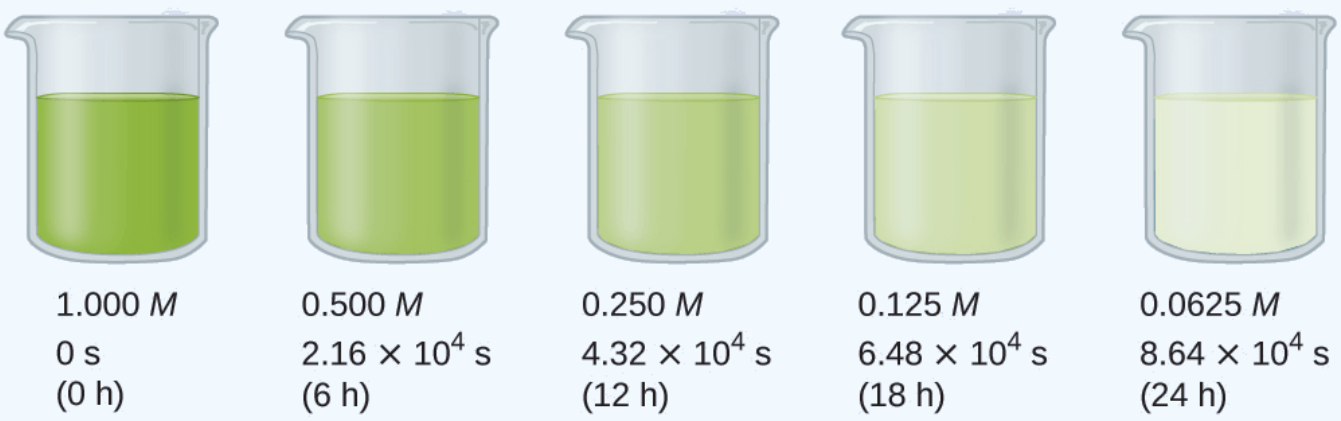


Figure 10.5.4: The decomposition of H_2O_2 at 40 °C is illustrated. The intensity of the color symbolizes the concentration of H_2O_2 at the indicated times; H_2O_2 is actually colorless.

Solution

Inspecting the concentration/time data in Figure 10.5.4 shows the half-life for the decomposition of H_2O_2 is 2.16 × 10^4 s:

$$t_{1/2} = \frac{0.693}{k}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.16 \times 10^4 s} = 3.21 \times 10^{-5} s^{-1}$$

Exercise 10.5.1

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 available at the end of this section.

Second-Order Reactions

Following the same approach as used for first-order reactions, an equation relating the half-life of a second-order reaction to its rate constant and initial concentration may be derived from its integrated rate law:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

or

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

Restrict t to $t_{1/2}$

$$t = t_{1/2}$$

define $[A]_t$ as one-half $[A]_0$

$$[A]_t = \frac{1}{2}[A]_0$$

and then substitute into the integrated rate law and simplify:

$$\frac{1}{\frac{1}{2}[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$

$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$

$$\frac{1}{[A]_0} = kt_{1/2}$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

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. 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.

Zero-Order Reactions

As for other reaction orders, an equation for zero-order half-life may be derived from the integrated rate law:

$$[A] = -kt + [A]_0$$

Restricting the time and concentrations to those defined by half-life: and Substituting these terms into the zero-order integrated rate law yields:

$$\frac{[A]_0}{2} = -kt_{1/2} + [A]_0$$

$$kt_{1/2} = \frac{[A]_0}{2}$$

$$t_{1/2} = \frac{[A]_0}{2k}$$

As for all reaction orders, the half-life for a zero-order reaction is inversely proportional to its rate constant. However, 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 10.5.1.

Table 10.5.1: 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	vs. t
relationship between slope of linear plot and rate constant	k = –slope	k = –slope	k = slope
half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{[A]_0 k}$

Example 10.5.7: Half-Life for Zero-Order and Second-Order Reactions

What is the half-life for the butadiene dimerization reaction described in Example 10.5.3?

Solution

The reaction in question is second order, is initiated with a 0.200 mol L^{-1} reactant solution, and exhibits a rate constant of 0.0576 L mol^{-1} min^{-1}. Substituting these quantities into the second-order half-life equation:

$$t_{1/2} = \frac{1}{[(0.0576 L mol^{-1} min^{-1})\,(0.200 mol L^{-1})]} = 86.8 \text{ min}$$

Exercise 10.5.7

What is the half-life (min) for the thermal decomposition of ammonia on tungsten (see Figure 10.5.3)?

Answer available at the end of this section.

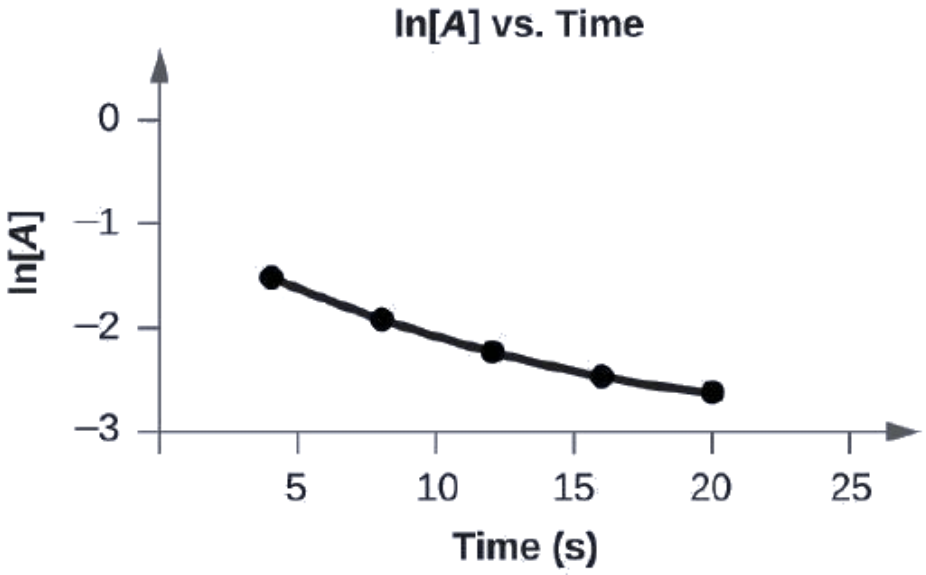
Answers

Exercise 10.5.1

16.7 days

Exercise 10.5.2

The plot of ln$[A]_t$ vs. t is not linear, indicating the reaction is not first order:

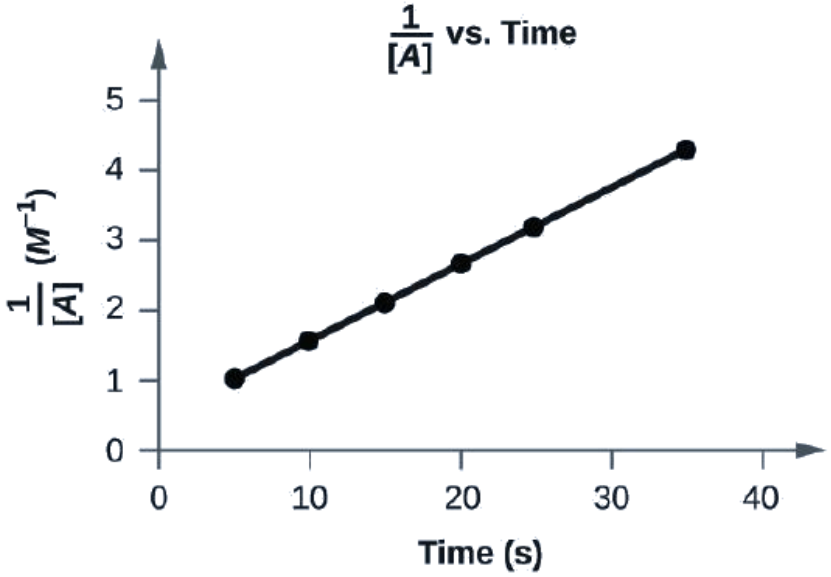


Exercise 10.5.3

0.0195 mol/L

Exercise 10.5.4

Yes. The plot of $\frac{1}{[A]_t}$ vs. t is linear:



Exercise 10.5.5

35 min

Exercise 10.5.1

5.02 d.

Exercise 10.5.7

87 min

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10.6: Collision Theory

Learning Objectives

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

- 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:

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:

$$2\,\mathrm{CO\,(g)} + \mathrm{O_2\,(g)} \longrightarrow 2\,\mathrm{CO_2\,(g)}$$

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 amounts, the reaction will occur 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:

$$\mathrm{CO\,(g)} + \mathrm{O_2\,(g)} \longrightarrow \mathrm{CO_2\,(g)} + \mathrm{O\,(g)}$$

Although there are many different possible orientations the two molecules can have relative to each other, consider the two presented in Figure $10.6.1$. 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 (\ce{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.

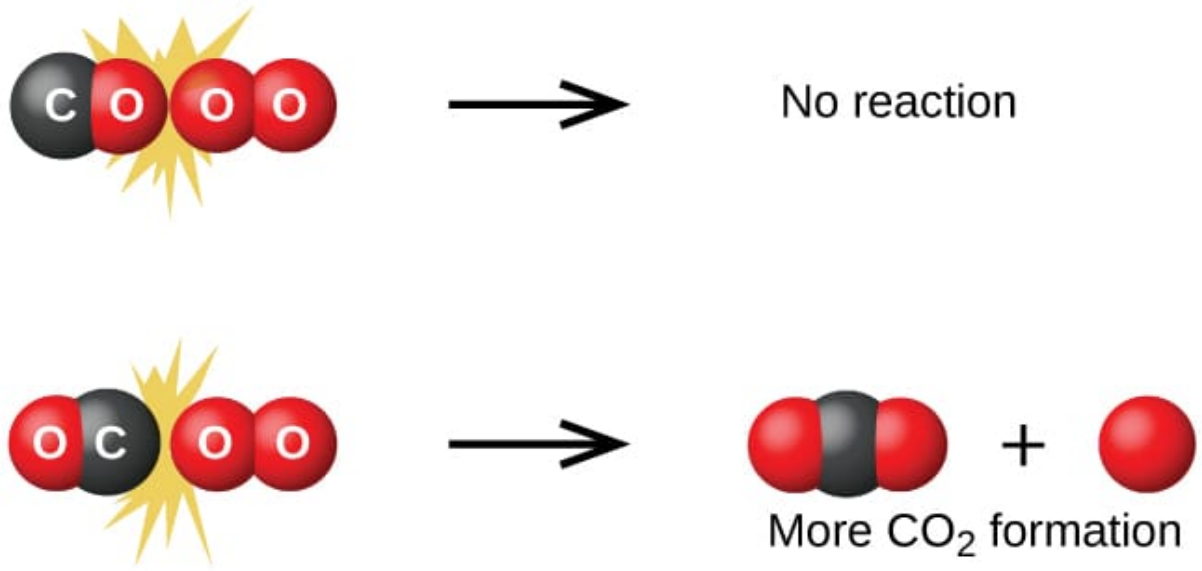


Figure 10.6.1: Illustrated are two collisions that might take place between carbon monoxide and oxygen molecules. The orientation of the colliding molecules partially determines whether a reaction between the two molecules will occur.

If the collision does take place with the correct orientation, there is still no guarantee that the reaction will proceed to form carbon dioxide. In addition to a proper orientation, the collision must also occur with sufficient energy to result in product formation. When reactant species collide with both proper orientation and adequate energy, they combine to form an unstable species called an **activated complex** or a **transition state**. These species are very short lived and usually undetectable by most analytical instruments. In some cases, sophisticated spectral measurements have been used to observe transition states.

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.

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). How this energy compares to the kinetic energy provided by colliding reactant molecules is a primary factor affecting the rate of a chemical reaction. If the activation energy is much larger than the average kinetic energy of the molecules, the reaction will occur slowly since 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, a large fraction of molecules will be adequately energetic and the reaction will proceed rapidly.

Figure 10.6.2 shows how the energy of a chemical system changes as it undergoes a reaction converting reactants to products according to the equation

$$\mathrm{A^{+}B} \longrightarrow \mathrm{C^{+}D}$$

These reaction diagrams are widely used in chemical kinetics to illustrate various properties of the reaction of interest. Viewing the diagram from left to right, the system initially comprises reactants only, $\mathrm{A} + \mathrm{B}$. Reactant molecules with sufficient energy can collide to form a high-energy activated complex or transition state. The unstable transition state can then subsequently decay to yield stable products, *C* + *D*. The diagram depicts the reaction's activation energy, E_a, as the energy difference between the reactants and the transition state. Using a specific energy, the *enthalpy* (see chapter on thermochemistry), the enthalpy change of the reaction, ΔH, is estimated as the energy difference between the reactants and products. In this case, the reaction is exothermic ($\Delta H < 0$) since it yields a decrease in system enthalpy.

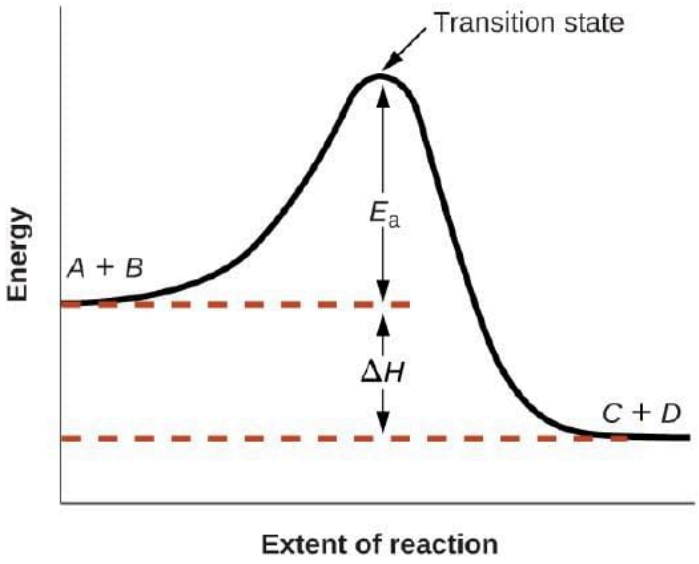


Figure 10.6.2: Reaction diagram for the exothermic reaction

The **Arrhenius equation** relates the activation energy and the rate constant, *k*, for many chemical reactions:

$$k = Ae^{-E_a/RT}$$

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.

Postulates of collision theory are nicely accommodated by the Arrhenius equation. The frequency factor, *A*, reflects how well the reaction conditions favor properly oriented collisions between reactant molecules. An increased probability of effectively oriented collisions results in larger values for *A* and faster reaction rates.

The exponential term, $e^{-Ea/RT}$, describes the effect of activation energy on reaction rate. According to kinetic molecular theory (see chapter on gases), the temperature of matter is a measure of the average kinetic energy of its constituent atoms or molecules. The distribution of energies among the molecules composing a sample of matter at any given temperature is described by the plot shown in Figure $10.6.3a$. Two shaded areas under the curve represent the numbers of molecules possessing adequate energy (*RT*) to overcome the activation barriers (E_a). A lower activation energy results in a greater fraction of adequately energized molecules and a faster reaction.

The exponential term also describes the effect of temperature on reaction rate. A higher temperature represents a correspondingly greater fraction of molecules possessing sufficient energy (*RT*) to overcome the activation barrier (E_a), as shown in Figure $10.6.3b$. This yields a greater value for the rate constant and a correspondingly faster reaction rate.

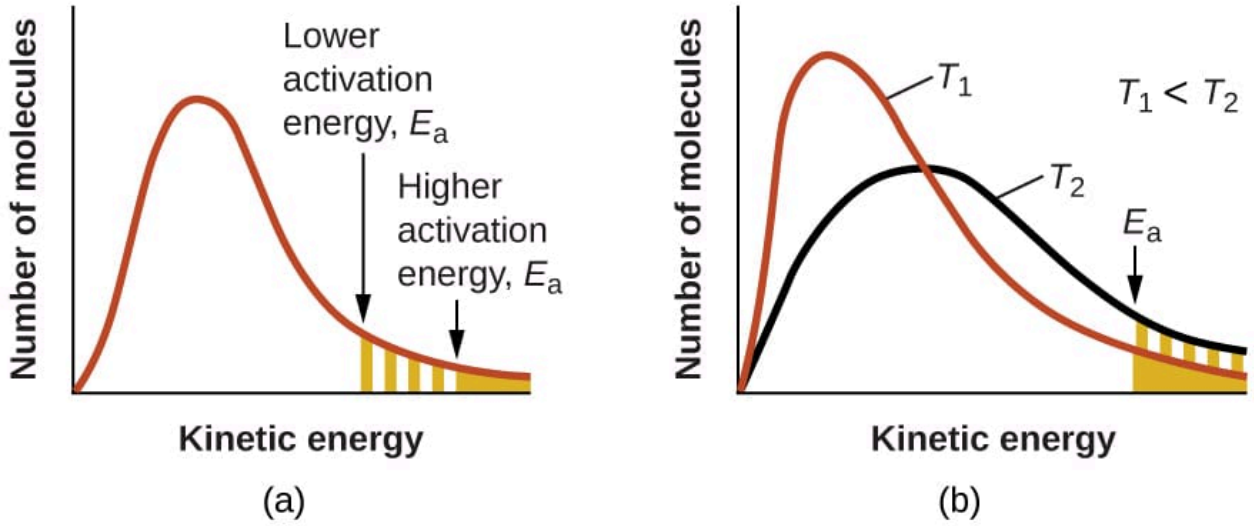


Figure 10.6.3: Molecular energy distributions showing numbers of molecules with energies exceeding (a) two different activation energies at a given temperature, and (b) a given activation energy at two different temperatures.

A convenient approach for determining E_a for a reaction involves the measurement of *k* at two or more different temperatures and using an alternate version of the Arrhenius equation that takes the form of a linear equation

$$\ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$$

$$y = mx + b$$

A plot of $\ln k$ versus $\frac{1}{T}$ is linear with a slope equal to $\frac{-E_a}{R}$ and a y-intercept equal to $\ln A$.

Example 10.6.1: Determination of E_a

The variation of the rate constant with temperature for the decomposition of $\mathrm{HI(g)}$ to $\mathrm{H_2(g)}$ and $\mathrm{I_2(g)}$ is given here. What is the activation energy for the reaction?

$$2\,\mathrm{HI(g)} \longrightarrow \mathrm{H_2(g) + I_2(g)}$$

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

Use the provided data to derive values of $\frac{1}{T}$ and $\ln k$:

$\frac{1}{T}$	$\ln k$
1.80×10^{-3}	−14.860
1.74×10^{-3}	−13.617

$\frac{1}{T}$	$\ln k$
1.55×10^{-3}	−9.362
1.43×10^{-3}	−6.759
1.28×10^{-3}	−3.231

Figure $10.6.4$ is a graph of $\ln k$ versus $\frac{1}{T}$. In practice, the equation of the line (slope and *y*-intercept) that best fits these plotted data points would be derived using a statistical process called regression. This is helpful for most experimental data because a perfect fit of each data point with the line is rarely encountered. For the data here, the fit is nearly perfect and the slope may be estimated using any two of the provided data pairs. Using the first and last data points permits estimation of the slope.

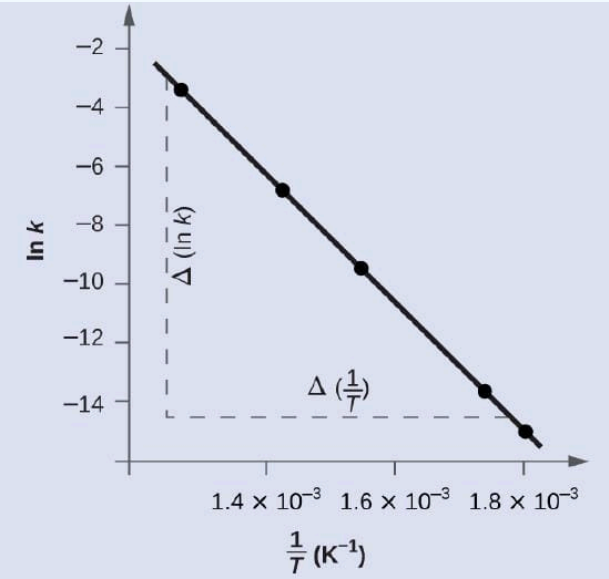


Figure $10.6.4$: This graph shows the linear relationship between $\ln k$ versus $\frac{1}{T}$ for the reaction $2HI \longrightarrow H_2 + I_2$ according to the Arrhenius equation.

$$\begin{aligned}
\text{Slope } &= \frac{\Delta(\ln k)}{\Delta\left(\frac{1}{T}\right)} \\
&= \frac{(-14.860) - (-3.231)}{\left(1.80 \times 10^{-3} K^{-1}\right) - \left(1.28 \times 10^{-3} K^{-1}\right)} \\
&= \frac{-11.629}{0.52 \times 10^{-3} K^{-1}} = -2.2 \times 10^{4} K \\
&= -\frac{E_a}{R} \\
E_a &= -\text{ slope } \times R = -\left(-2.2 \times 10^{4} K \times 8.314 J mol^{-1} K^{-1}\right) \\
&\quad 1.8 \times 10^{5} J mol^{-1} \text{ or } 180 k J mol^{-1}
\end{aligned}$$

Alternative approach: A more expedient approach involves deriving activation energy from measurements of the rate constant at just two temperatures. In this approach, the Arrhenius equation is rearranged to a convenient two-point form:

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Rearranging this equation to isolate activation energy yields:

$$E_a = -R\left(\frac{\ln k_2 - \ln k_1}{\left(\frac{1}{T_2}\right) - \left(\frac{1}{T_1}\right)}\right)$$

Any two data pairs may be substituted into this equation—for example, the first and last entries from the above data table:

$$E_a = -8.314 J mol^{-1} K^{-1}\left(\frac{-3.231 - (-14.860)}{1.28 \times 10^{-3} K^{-1} - 1.80 \times 10^{-3} K^{-1}}\right)$$

and the result is E_a = 1.8 10^5 J mol^{-1} or 180 kJ mol^{-1}

This approach yields the same result as the more rigorous graphical approach used above, as expected. In practice, the graphical approach typically provides more reliable results when working with actual experimental data.

Exercise 10.6.1

The rate constant for the rate of decomposition of $\mathrm{N_2O_5}$ to NO and $\mathrm{O_2}$ in the gas phase is 1.66 L/mol/s at 650 K and 7.39 L/mol/s at 700 K:

$$2\,\mathrm{N_2O_5\,(g)} \longrightarrow 4\,\mathrm{NO\,(g)} + 3\,\mathrm{O_2\,(g)}$$

Assuming the kinetics of this reaction are consistent with the Arrhenius equation, calculate the activation energy for this decomposition.

Answer available at the end of this section.

Answers

Exercise 10.6.1

1.1 10^5 J mol^{-1} or 110 kJ mol^{-1}

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10.7: Reaction Mechanisms

Learning Objectives

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

- 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

Chemical reactions very often occur in a step-wise fashion, involving two or more distinct reactions taking place in sequence. A balanced equation indicates what is reacting and what is produced, but it reveals no details about how the reaction actually takes place. The reaction mechanism (or reaction path) provides details regarding the precise, step-by-step process by which a reaction occurs.

The decomposition of ozone, for example, appears to follow a mechanism with two steps:

$$O_3(g) \longrightarrow O_2(g) + O$$
$$O + O_3(g) \longrightarrow 2O_2(g)$$

Each of the steps in a reaction mechanism is an **elementary reaction**. These elementary reactions occur precisely as represented in the step equations, and they must sum to yield the balanced chemical equation representing the overall reaction:

$$2O_3(g) \longrightarrow 3O_2(g)$$

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 direct collision and reaction of two ozone molecules*. Instead, one O_3 decomposes to yield O_2 and an oxygen atom, and a second O_3 molecule subsequently reacts with the oxygen atom to yield two additional O_2 molecules.

Unlike balanced equations representing an overall reaction, the equations for elementary reactions are explicit representations of the chemical change taking place. The reactant(s) in an elementary reaction's equation undergo only the bond-breaking and/or making events depicted to yield the product(s). For this reason, *the rate law for an elementary reaction may be derived directly from the balanced chemical equation describing the reaction*. This is not the case for typical chemical reactions, for which rate laws may be reliably determined only via experimentation.

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 reaction of a *single* reactant species to produce one or more molecules of product:

$$A \longrightarrow \text{ products}$$

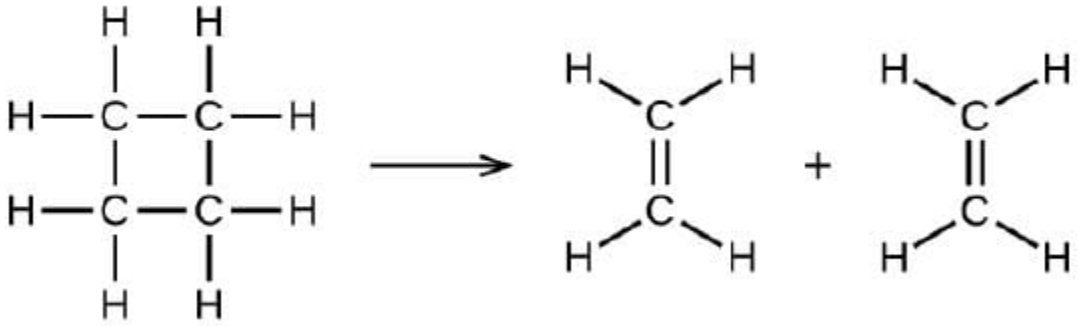
The rate law for a unimolecular reaction is first order:

$$\text{rate } = k[A]$$

A unimolecular reaction may be one of several elementary reactions in a complex mechanism. For example, the reaction:

$$O_3 \longrightarrow O_2 + O$$

illustrates a unimolecular elementary reaction that occurs as one part of a two-step reaction mechanism as described above. However, some unimolecular reactions may be the only step of a single-step reaction mechanism. (In other words, an "overall" reaction may also be an elementary reaction in some cases.) For example, the gas-phase decomposition of cyclobutane, C_4H_8, to ethylene, C_2H_4, is represented by the following chemical equation:



This equation represents the overall reaction observed, and it might also represent a legitimate unimolecular elementary reaction. The rate law predicted from this equation, assuming it is an elementary reaction, turns out to be the same as the rate law derived experimentally for the overall reaction, namely, one showing first-order behavior:

$$\text{rate } = -\frac{\Delta\left[C_4H_8\right]}{\Delta t} = k\left[C_4H_8\right]$$

This agreement between observed and predicted rate laws is interpreted to mean that the proposed unimolecular, single-step process is a reasonable mechanism for the butadiene reaction.

Bimolecular Elementary Reactions

A bimolecular reaction involves two reactant species, for example:

$$A + B \longrightarrow \text{ products}$$

and

$$2A \longrightarrow \text{ products}$$

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* (second-order overall):

$$\text{rate } = k[A][B]$$

For the second type, in which two identical molecules collide and react, the rate law is second order in *A*:

$$\text{rate } = k[A][A] = k[A]^2$$

Some chemical reactions occur by mechanisms that consist of a single bimolecular elementary reaction. One example is the reaction of nitrogen dioxide with carbon monoxide:

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

(see Figure 10.7.1)



Figure 10.7.1: The probable mechanism for the reaction between NO_2 and CO to yield NO and CO_2.

Bimolecular elementary reactions may also be involved as steps in a multistep reaction mechanism. The reaction of atomic oxygen with ozone is the second step of the two-step ozone decomposition mechanism discussed earlier in this section:

$$O(g) + O_3(g) \longrightarrow 2O_2(g)$$

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:

$$2NO + O_2 \longrightarrow 2NO_2$$
$$\text{rate } = k[NO]^2\,[O_2]$$

Likewise, the reaction of nitric oxide with chlorine appears to involve termolecular steps:

$$2NO + Cl_2 \longrightarrow 2NOCl$$
$$\text{rate } = k[NO]^2\,[Cl_2]$$

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 10.7.2.



Figure 10.7.2: 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)

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, the rate law must be determined from experimental data and the reaction mechanism subsequently deduced from the rate law (and sometimes from other data). The reaction of NO_2 and CO provides an illustrative example:

$$NO_2(g) + CO(g) \longrightarrow CO_2(g) + NO(g)$$

For temperatures above 225 °C, the rate law has been found to be:

$$\text{rate } = k\,[NO_2]\,[CO]$$

The reaction is first order with respect to 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 NO_2:

$$\text{rate } = k\,[NO_2]^2$$

This rate law is not consistent with the single-step mechanism, but is consistent with the following two-step mechanism:

$$NO_2(g) + NO_2(g) \longrightarrow NO_3(g) + NO(g)\ \text{(slow)}$$
$$NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)\ \text{(fast)}$$

The rate-determining (slower) 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 a rapidly reversible reaction the rate law for the overall reaction may be more difficult to derive.

As discussed in several chapters of this text, a reversible reaction is at *equilibrium* when the rates of the forward and reverse processes are equal. Consider the reversible elementary reaction in which NO dimerizes to yield an intermediate species N_2O_2.

$$NO + NO \rightleftharpoons N_2O_2$$

When this reaction is at equilibrium:

$$\text{rate}_{\text{ forward}} = \text{rate}_{\text{ reverse}}$$
$$k_1[NO]^2 = k_{-1}\,[N_2O_2]$$

This expression may be rearranged to express the concentration of the intermediate in terms of the reactant NO:

$$\left(\frac{k_1[NO]^2}{k_{-1}}\right) = [N_2O_2]$$

Since intermediate species concentrations are not used in formulating rate laws for overall reactions, this approach is sometimes necessary, as illustrated in the following example exercise.

Example 10.7.1: Deriving a Rate Law from a Reaction Mechanism

The two-step mechanism below has been proposed for a reaction between nitrogen monoxide and molecular chlorine:

$$\text{Step 1:}\quad \mathrm{NO\,(g) + Cl_2\,(g) \rightleftharpoons NOCl_2\,(g)} \qquad \text{(fast)}$$
$$\text{Step 2:}\quad \mathrm{NOCl_2\,(g) + NO\,(g) \rightleftharpoons 2\,NOCl\,(g)} \qquad \text{(slow)}$$

Use this mechanism to derive the equation and predicted rate law for the overall reaction.

Solution

The equation for the overall reaction is obtained by adding the two elementary reactions:

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$$

To derive a rate law from this mechanism, first write rates laws for each of the two steps.

$$\text{rate}_{\ 1} = k_1[NO]\,[Cl_2] \text{ for the forward reaction of step 1}$$
$$\text{rate}_{\ -1} = k_{-1}\,[NOCl_2] \text{ for the reverse reaction of step 1}$$
$$\text{rate}_{\ 2} = k_2\,[NOCl_2]\,[NO] \text{ for step 2}$$

Step 2 is the rate-determining step, and so the rate law for the overall reaction should be the same as for this step. However, the step 2 rate law, as written, contains an intermediate species concentration, [$NOCl_2$]. To remedy this, use the first step's rate laws to derive an expression for the intermediate concentration in terms of the reactant concentrations.

Assuming step 1 is at equilibrium:

$$\text{rate}_{\ 1} = \text{rate}_{\ -1}$$
$$k_1[NO]\,[Cl_2] = k_{-1}\,[NOCl_2]$$
$$[NOCl_2] = \left(\frac{k_1}{k_{-1}}\right)[NO]\,[Cl_2]$$

Substituting this expression into the rate law for step 2 yields:

$$\text{rate}_{\ 2} = \text{rate}_{\ \text{overall}} = \left(\frac{k_2 k_1}{k_{-1}}\right)[NO]^2\,[Cl_2]$$

Exercise 10.7.1

The first step of a proposed multistep mechanism is:

\[\ce{F2(g) <=> 2 F(g) \tag{fast} \]

Derive the equation relating atomic fluorine concentration to molecular fluorine concentration.

Answer available at the end of this section.

Answers

Exercise 10.7.1

$$[\text{F}] = \left(\frac{k_1\,[F_2]}{k_{-1}}\right)^{1/2}$$

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10.8: Catalysis

Learning Objectives

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

- Explain the function of a catalyst in terms of reaction mechanisms and potential energy diagrams
- List examples of catalysis in natural and industrial processes

Catalysts Do Not Affect Equilibrium

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

$$\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \rightleftharpoons 2\mathrm{NH_3}(g)$$

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.

Portrait of a Chemist

Fritz Haber

In the early 20th century, German chemist Fritz Haber (Figure 17.19) developed a practical process for converting diatomic nitrogen, which cannot be used by plants as a nutrient, to ammonia, a form of nitrogen that is easiest for plants to absorb.

$$\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \rightleftharpoons 2\mathrm{NH_3}(g)$$

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).

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. 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. 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.



Figure 17.19 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.

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.

$$\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \rightleftharpoons 2\mathrm{NH_3}(g)$$

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:

$$\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \longrightarrow 2\mathrm{NH_3}(g) \qquad \Delta H = -92.2\,\mathrm{kJ}$$

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 17.20).

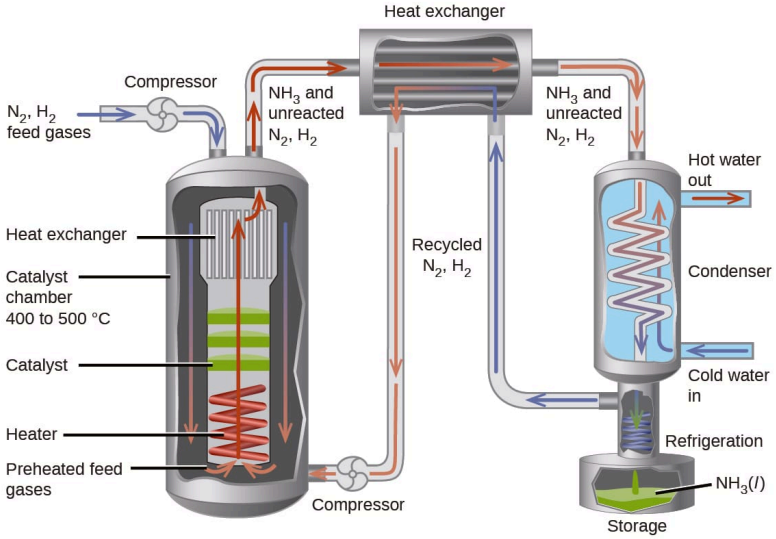


Figure 17.20 Commercial production of ammonia requires heavy equipment to handle the high temperatures and pressures required. This schematic outlines the design of an ammonia plant.

Among the factors affecting chemical reaction rates discussed earlier in this chapter was the presence of a *catalyst*, a substance that can increase the reaction rate without being consumed in the reaction. The concepts introduced in the previous section on reaction mechanisms provide the basis for understanding how catalysts are able to accomplish this very important function.

Figure 17.21 shows reaction diagrams for a chemical process in the absence and presence of a catalyst. Inspection of the diagrams reveals several traits of these reactions. Consistent with the fact that the two diagrams represent the same overall reaction, both curves begin and end at the same energies (in this case, because products are more energetic than reactants, the reaction is endothermic). The reaction mechanisms, however, are clearly different. The uncatalyzed reaction proceeds via a one-step mechanism (one transition state observed), whereas the catalyzed reaction follows a two-step mechanism (two transition states observed) with *a notably lesser activation energy*. This difference illustrates the means by which a catalyst functions to accelerate reactions, namely, by providing an alternative reaction mechanism with a lower activation energy. Although the catalyzed reaction mechanism for a reaction needn't necessarily involve a different number of steps than the uncatalyzed mechanism, it must provide a reaction path whose rate determining step is faster (lower E_a).

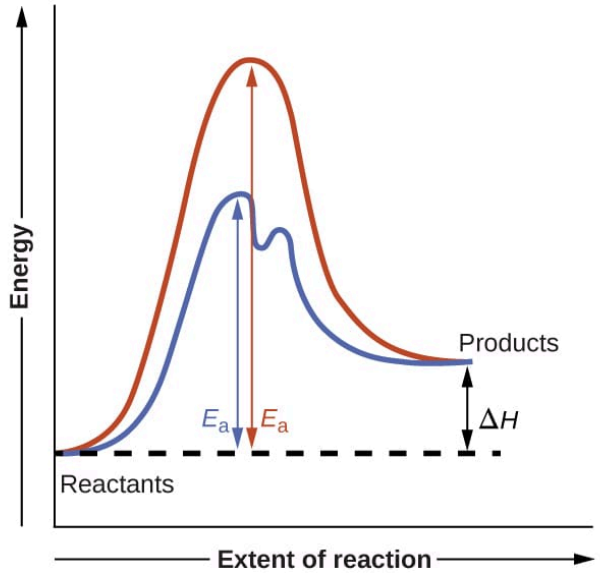
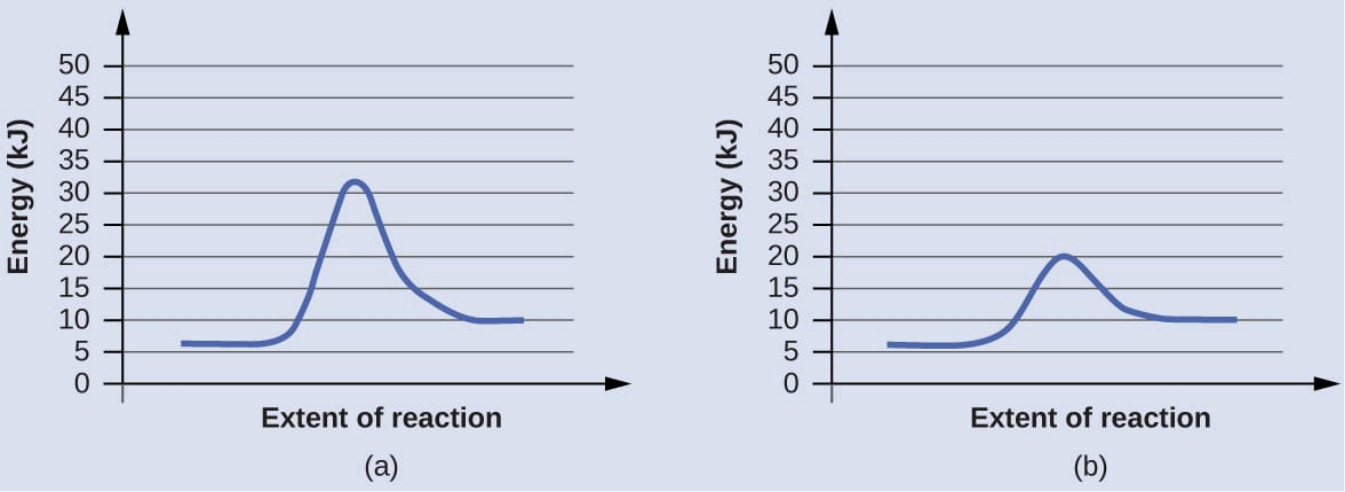


Figure 17.21 Reaction diagrams for an endothermic process in the absence (red curve) and presence (blue curve) of a catalyst. The catalyzed pathway involves a two-step mechanism (note the presence of two transition states) and an intermediate species (represented by the valley between the two transitions states).

Example 17.15

Reaction Diagrams for Catalyzed Reactions

The two reaction diagrams here represent the same reaction: one without a catalyst and one with a catalyst. Estimate the activation energy for each process, and identify which one involves a catalyst.



Solution

Activation energies are calculated by subtracting the reactant energy from the transition state energy.

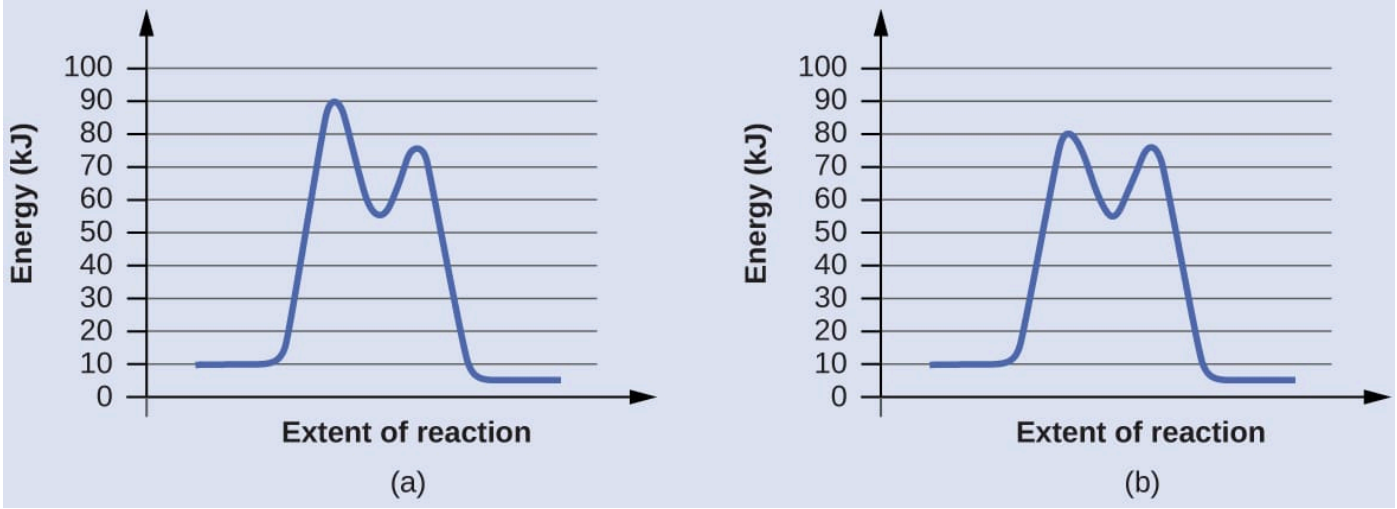
$$\text{diagram (a): } E_a = 32\ \text{kJ} - 6\ \text{kJ} = 26\ \text{kJ}$$

$$\text{diagram (b): } E_a = 20\ \text{kJ} - 6\ \text{kJ} = 14\ \text{kJ}$$

The catalyzed reaction is the one with lesser activation energy, in this case represented by diagram (b).

Check Your Learning

Reaction diagrams for a chemical process with and without a catalyst are shown below. Both reactions involve a two-step mechanism with a rate-determining first step. Compute activation energies for the first step of each mechanism, and identify which corresponds to the catalyzed reaction. How do the second steps of these two mechanisms compare?



Answer:

For the first step, E_a = 80 kJ for (a) and 70 kJ for (b), so diagram (b) depicts the catalyzed reaction. Activation energies for the second steps of both mechanisms are the same, 20 kJ.

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:

$$3O_2(g) \xrightarrow{h\nu} 2O_3(g)$$

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 two-step mechanism:

$$\begin{aligned} O_3 &\longrightarrow O_2 + O \\ O + O_3 &\longrightarrow 2O_2 \end{aligned}$$

A number of substances can catalyze the decomposition of ozone. For example, the nitric oxide -catalyzed decomposition of ozone is believed to occur via the following three-step mechanism:

$$\begin{aligned} NO(g) + O_3(g) &\longrightarrow NO_2(g) + O_2(g) \\ O_3(g) &\longrightarrow O_2(g) + O(g) \\ NO_2(g) + O(g) &\longrightarrow NO(g) + O_2(g) \end{aligned}$$

As required, the overall reaction is the same for both the two-step uncatalyzed mechanism and the three-step NO-catalyzed mechanism:

$$2O_3(g) \longrightarrow 3O_2(g)$$

Notice that NO is a reactant in the first step of the mechanism and a product in the last step. This is another characteristic trait of a catalyst: Though it participates in the chemical reaction, it is not consumed by the reaction.

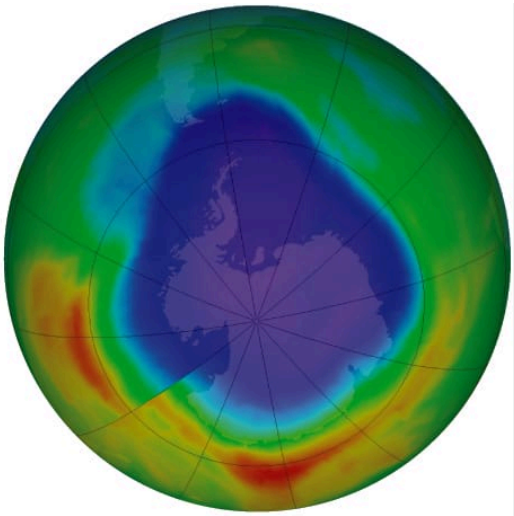
Portrait of a Chemist

Mario J. Molina

The 1995 Nobel Prize in Chemistry was shared by Paul J. Crutzen, Mario J. Molina (Figure 17.22), and F. Sherwood Rowland "for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone."[2] Molina, a Mexican citizen, carried out the majority of his work at the Massachusetts Institute of Technology (MIT).



(a)



(b)

Figure 17.22 (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* 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:

$$\mathrm{CH_3Cl + OH \longrightarrow Cl + \text{other products}}$$

Chlorine radicals break down ozone and are regenerated by the following catalytic cycle:

$$\mathrm{Cl + O_3 \longrightarrow ClO + O_2}$$
$$\mathrm{ClO + O \longrightarrow Cl + O_2}$$
$$\mathrm{\text{overall Reaction: } O_3 + O \longrightarrow 2O_2}$$

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 $ClONO_2$.

Since receiving his portion of the Nobel Prize, Molina has continued his work in atmospheric chemistry at MIT.

How Sciences Interconnect

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 17.23, is the rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells (Figure 17.24).

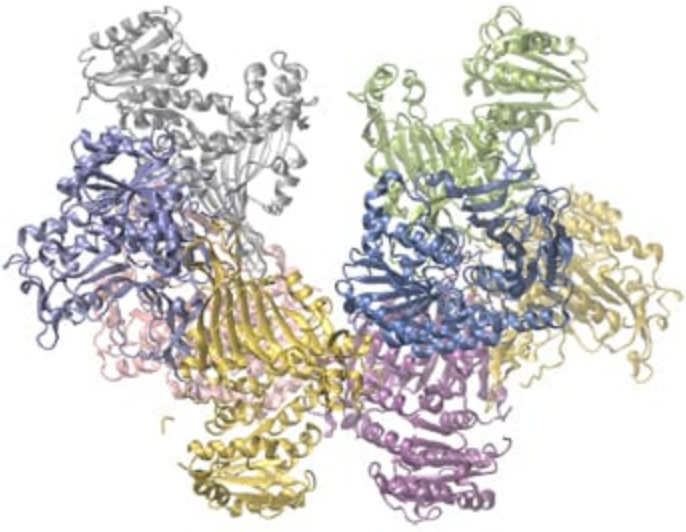


Figure 17.23 Glucose-6-phosphate dehydrogenase is a rate-limiting enzyme for the metabolic pathway that supplies NADPH to cells.

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.

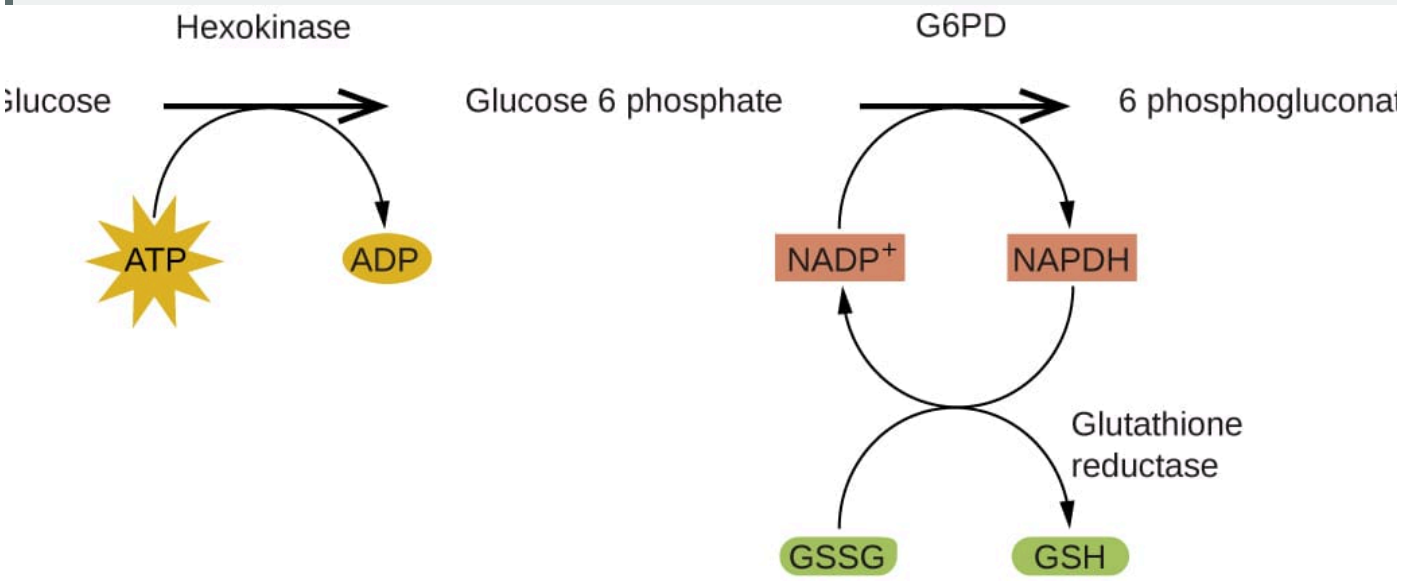


Figure 17.24 In the mechanism for the pentose phosphate pathway, G6PD catalyzes the reaction that regulates NADPH, a co-enzyme that regulates glutathione, an antioxidant that protects red blood cells and other cells from oxidative damage.

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 typically involves the following processes:

1. Adsorption of the reactant(s) onto the surface of the catalyst
2. Activation of the adsorbed reactant(s)

3. Reaction of the adsorbed reactant(s)
4. Desorption of product(s) from the surface of the catalyst

Figure 17.25 illustrates the steps of a mechanism for 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).

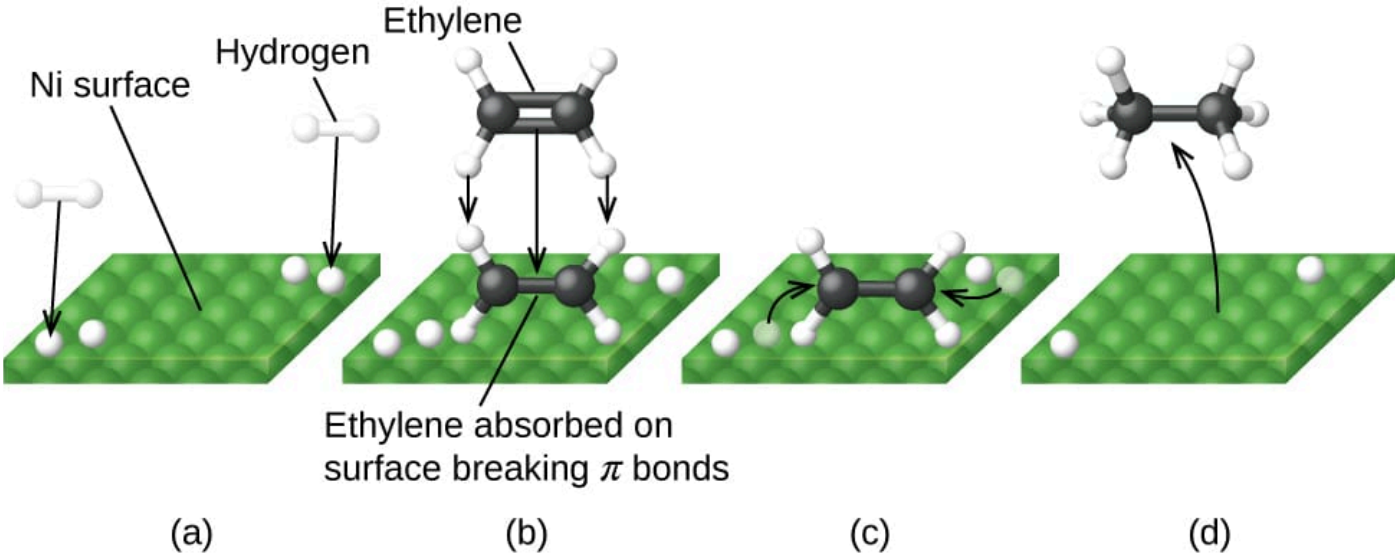


Figure 17.25 Mechanism for the Ni-catalyzed reaction $C_2H_4 + H_2 \longrightarrow C_2H_6$. (a) Hydrogen is adsorbed on the surface, breaking the H–H bonds and forming Ni–H bonds. (b) Ethylene is adsorbed on the surface, breaking the C-C π-bond and forming Ni–C bonds. (c) Atoms diffuse across the surface and form new C–H bonds when they collide. (d) C_2H_6 molecules desorb from the Ni surface.

Many important chemical products are prepared via industrial processes that use heterogeneous catalysts, including ammonia, nitric acid, sulfuric acid, and methanol. Heterogeneous catalysts are also used in the catalytic converters found on most gasoline-powered automobiles (Figure 17.26).

Chemistry in Everyday Life

Automobile Catalytic Converters

Scientists developed catalytic converters to reduce the amount of toxic emissions produced by burning gasoline in internal combustion engines. 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 17.26).

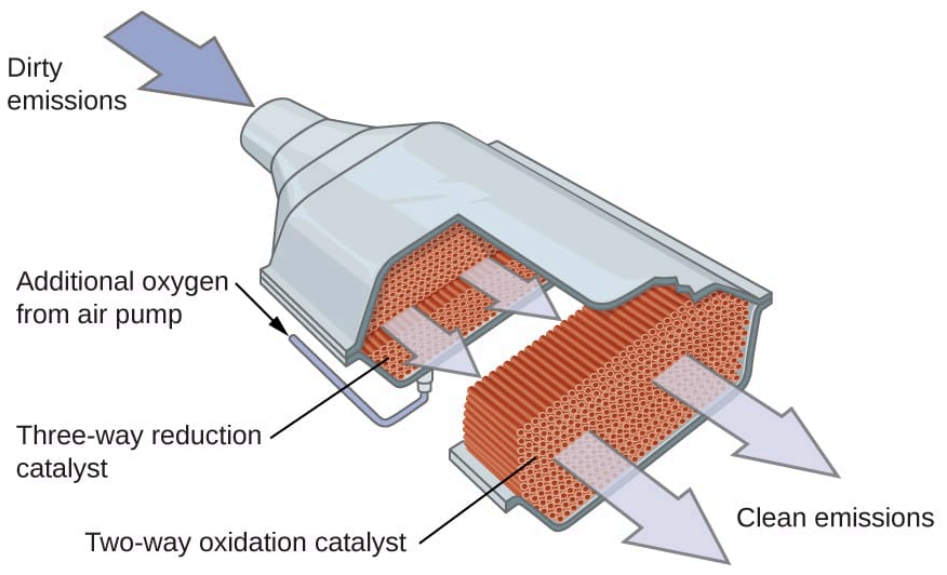


Figure 17.26 A catalytic converter allows for the combustion of all carbon-containing compounds to carbon dioxide, while at the same time reducing the output of nitrogen oxide and other pollutants in emissions from gasoline-burning engines.

Most modern, three-way catalytic converters possess a surface impregnated with a platinum-rhodium catalyst, which catalyzes the conversion of 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:

$$2\mathrm{NO}_2(g) \longrightarrow \mathrm{N}_2(g) + 2\mathrm{O}_2(g)$$
$$2\mathrm{CO}(g) + \mathrm{O}_2(g) \longrightarrow 2\mathrm{CO}_2(g)$$
$$2\mathrm{C}_8\mathrm{H}_{18}(g) + 25\mathrm{O}_2(g) \longrightarrow 16\mathrm{CO}_2(g) + 18\mathrm{H}_2\mathrm{O}(g)$$

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.

Link to Learning

The University of California at Davis' "ChemWiki" provides a thorough explanation of how catalytic converters work.

How Sciences Interconnect

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 17.3.

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

Class	Function
isomerases	isomerization
ligases	bond formation with ATP hydrolysis

Table 17.3

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 17.27).

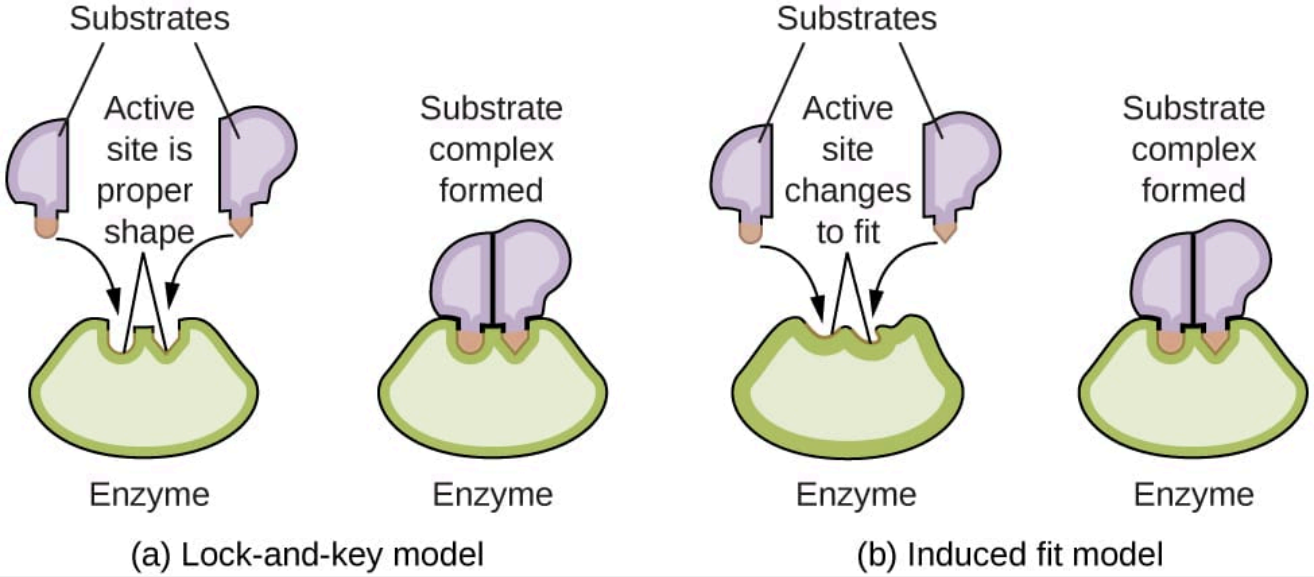


Figure 17.27 (a) According to the lock-and-key model, the shape of an enzyme's active site is a perfect fit for the substrate. (b) According to the induced fit model, the active site is somewhat flexible, and can change shape in order to bond with the substrate.

Link to Learning

The Royal Society of Chemistry provides an excellent introduction to enzymes for students and teachers.

The connection between the rate of a reaction and its equilibrium constant is one we can easily determine with just a bit of algebraic substitution. For a reaction where substance A forms B (and the reverse)

$$A \rightleftharpoons B$$

The rate of the forward reaction is

$$\text{Rate}\,(f) = k\,(f)\,[A]$$

And the rate of the reverse reaction is

$$\text{Rate}\,(r) = k\,(r)\,[B]$$

Once equilibrium is established, the rates of the forward and reverse reactions are equal:

$$\text{Rate}\,(f) = \text{Rate}\,(r) = k\,(f)\,[A] = k\,(r)\,[B]$$

Rearranging a bit, we get

$$\text{Rate}_f = \text{Rate}_r \text{ so } k\,(f)\,[A] = k\,(r)\,[B]$$

Also recall that the equilibrium constant is simply the ratio of product to reactant concentration at equilibrium:

$$\frac{k\,(f)}{k\,(r)} = \frac{[B]}{[A]}$$

$$K = \frac{[B]}{[A]}$$

So the equilibrium constant turns out to be the ratio of the forward to the reverse rate constants. This relationship also helps cement our understanding of the nature of a catalyst. That is, a catalyst does not change the fundamental equilibrium (or the underlying thermodynamics) of a reaction. Rather, what it does is alter the rate constant for the reaction – that is, both rate constants, forward and reverse, equally. In doing so, catalysts usually speed up the rate at which reactions attain equilibrium (though they can be used to slow down the rate of reaction as well!).

Footnotes

- 1Herrlich, 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.
- 2"The Nobel Prize in Chemistry 1995," Nobel Prize.org, accessed February 18, 2015, http://www.nobelprize.org/nobel_priz...aureates/1995/.

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10.9: Key Terms

Example and Directions

Words (or words that have the same definition)	The definition is case sensitive	(Optional) Image to display with the definition [Not displayed in Glossary, only in pop-up on pages]	(Optional) Caption for Image	(Optional) External or Internal Link	(Optional) Source for Definition
(Eg. "Genetic, Hereditary, DNA ...")	(Eg. "Relating to genes or heredity")		The infamous double helix	https://bio.libretexts.org/	CC-BY-SA; Delmar Larsen

Glossary Entries

Word(s)	Definition	Image	Caption	Link	Source
activated complex	(also, transition state) unstable combination of reactant species formed during a chemical reaction				
activation energy (E_a)	minimum energy necessary in order for a reaction to take place				
Arrhenius equation	mathematical relationship between a reaction's rate constant, activation energy, and temperature				
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				
bimolecular reaction	elementary reaction involving two reactant species				
catalyst	substance that increases the rate of a reaction without itself being consumed by the reaction				
collision theory	model that emphasizes the energy and orientation of molecular collisions to explain and predict reaction kinetics				
elementary reaction	reaction that takes place in a single step, precisely as depicted in its chemical equation				
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				
half-life of a reaction ($t_{1/2}$)	time required for half of a given amount of reactant to be consumed				
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				
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				
integrated rate law	equation that relates the concentration of a reactant to elapsed time of reaction				

Word(s)	Definition	Image	Caption	Link	Source
intermediate	species produced in one step of a reaction mechanism and consumed in a subsequent step				
method of initial rates	common experimental approach to determining rate laws that involves measuring reaction rates at varying initial reactant concentrations				
molecularity	number of reactant species involved in an elementary reaction				
overall reaction order	sum of the reaction orders for each substance represented in the rate law				
rate constant (k)	proportionality constant in a rate law				
rate expression	mathematical representation defining reaction rate as change in amount, concentration, or pressure of reactant or product species per unit time				
rate law	(also, rate equation) (also, differential rate laws) 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				
rate-determining step	(also, rate-limiting step) slowest elementary reaction in a reaction mechanism; determines the rate of the overall reaction				
reaction diagram	used in chemical kinetics to illustrate various properties of a reaction				
reaction mechanism	stepwise sequence of elementary reactions by which a chemical change takes place				
reaction order	value of an exponent in a rate law (for example, zero order for 0, first order for 1, second order for 2, and so on)				
termolecular reaction	elementary reaction involving three reactant species				
unimolecular reaction	elementary reaction involving a single reactant species				

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10.10: Key Equations

relative reaction rates for $a\ \mathrm{A} \longrightarrow b\ \mathrm{B} = -\frac{1}{a}\frac{\Delta[\ \mathrm{A}]}{\Delta t} = \frac{1}{b}\frac{\Delta[\ \mathrm{B}]}{\Delta t}$

integrated rate law for zero-order reactions: $[A]_t = -kt + [A]_0$,

half-life for a zero-order reaction $t_{1/2} = \frac{[A]_0}{2k}$

integrated rate law for first-order reactions: $\ln [A]_t = -kt + \ln [A]_0$,

half-life for a first-order reaction $t_{1/2} = \frac{0.693}{k}$

integrated rate law for second-order reactions: $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$,

half-life for a second-order reaction $t_{1/2} = \frac{1}{[A]_0 k}$

$k = Ae^{-E_a/RT}$

$\ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$

$\ln \frac{k_1}{k_0} = \frac{E_a}{R}\left(\frac{1}{T_0} - \frac{1}{T_1}\right)$

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10.11: 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.

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 with a lower activation energy.

Rate laws (*differential rate laws*) provide a mathematical description of how changes in the concentration 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 concentration 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.

Integrated rate laws are mathematically derived from differential rate laws, and they describe the time dependence of reactant and product concentrations.

The half-life of a reaction is the time required to decrease the amount of a given reactant by one-half. A reaction's half-life varies with rate constant and, for some reaction orders, reactant concentration. 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.

Chemical reactions typically 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, activation energy, temperature, and dependence on collision orientation.

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 molecularity of an elementary reaction is the number of reactant species involved, typically one (unimolecular), two (bimolecular), or, less commonly, three (termolecular). The overall rate of a reaction is determined by the rate of the slowest in its mechanism, 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.

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).

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10.12: Exercises

1.

What is the difference between average rate, initial rate, and instantaneous rate?

2.

Ozone decomposes to oxygen according to the equation $2O_3(g) \longrightarrow 3O_2(g)$. Write the equation that relates the rate expressions for this reaction in terms of the disappearance of O_3 and the formation of oxygen.

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 $Cl_2(g) + 3F_2(g) \longrightarrow 2ClF_3(g)$. 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.

4.

A study of the rate of dimerization of C_4H_6 gave the data shown in the table:
$2C_4H_6 \longrightarrow C_8H_{12}$

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).

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	0.775	0.625	0.465	0.360	0.285	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.

6.

Consider the following reaction in aqueous solution:
$5\mathrm{Br}^-(aq) + \mathrm{BrO_3}^-(aq) + 6\mathrm{H}^+(aq) \longrightarrow 3\mathrm{Br_2}(aq) + 3\mathrm{H_2O}(l)$

If the rate of disappearance of $Br^-(aq)$ at a particular moment during the reaction is 3.5×10^{-4} mol L^{-1} s^{-1}, what is the rate of appearance of $Br_2(aq)$ at that moment?

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.

8.

Explain why an egg cooks more slowly in boiling water in Denver than in New York City. (Hint: Consider the effect of temperature on reaction rate and the effect of pressure on boiling point.)

9.

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.

10.

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?

11.

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.

12.

How do the rate of a reaction and its rate constant differ?

13.

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?

14.

Tripling the concentration of a reactant increases the rate of a reaction nine-fold. 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-fold. What is the order of the reaction with respect to that reactant?

15.

How will the rate of reaction change for the process: $\mathrm{CO}(g) + \mathrm{NO_2}(g) \longrightarrow \mathrm{CO_2}(g) + \mathrm{NO}(g)$ 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*.

16.

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*.

17.

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*?

18.

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*?

19.

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):
$^{14}_{6}\mathrm{C} \longrightarrow {}^{14}_{7}\mathrm{N} + \mathrm{e}^{-}$
$\text{rate} = k\left[^{14}_{6}\mathrm{C}\right]$

What is the instantaneous rate of production of N atoms in a sample with a carbon-14 content of 6.5 × 10^{-9} *M*?

20.

The decomposition of acetaldehyde is a second order reaction with a rate constant of 4.71 × 10^{-8} L mol^{-1} s^{-1}. What is the instantaneous rate of decomposition of acetaldehyde in a solution with a concentration of 5.55 × 10^{-4} *M*?

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^{-1} h^{-1})	2.0 × 10^{-2}	2.0 × 10^{-2}	2.0 × 10^{-2}

Determine the rate law, the rate constant, and the overall order for this reaction.

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^{-1} h^{-1})	1.5 × 10^{-6}	1.5 × 10^{-6}	1.5 × 10^{-6}

Determine the rate law, the rate constant, and the overall order for this reaction.

23.

Nitrosyl chloride, NOCl, decomposes to NO and Cl_2.
$2\mathrm{NOCl}(g) \longrightarrow 2\mathrm{NO}(g) + \mathrm{Cl}_2(g)$

Determine the rate law, 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^{-1} h^{-1})	8.0 × 10^{-10}	3.2 × 10^{-9}	7.2 × 10^{-9}

24.

From the following data, determine the rate law, 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^{-1} h^{-1})	3.80 × 10^{-7}	1.52 × 10^{-6}	3.42 × 10^{-6}

25.

Nitrogen monoxide reacts with chlorine according to the equation:
$2\text{NO}(g) + \text{Cl}_2(g) \longrightarrow 2\text{NOCl}(g)$

The following initial rates of reaction have been observed for certain reactant concentrations:

[NO] (mol/L)	[Cl_2] (mol/L)	Rate (mol L^{-1} h^{-1})
0.50	0.50	1.14
1.00	0.50	4.56
1.00	1.00	9.12

What is the rate law 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?

26.

Hydrogen reacts with nitrogen monoxide to form dinitrogen monoxide (laughing gas) according to the equation: $\text{H}_2(g) + 2\text{NO}(g) \longrightarrow \text{N}_2\text{O}(g) + \text{H}_2\text{O}(g)$

Determine the rate law, 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^{-1} s^{-1})	2.835×10^{-3}	1.134×10^{-2}	2.268×10^{-2}

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^{-1} s^{-1})	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 law?

(b) What is the rate constant?

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^{-1} s^{-1})	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 law?

(b) What is the rate constant?

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}.

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

What is the rate of the reaction when $[N_2O_5]$ = 0.40 *M*?

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) $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$

(b) $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

(c) $3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$

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^{-1}.

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^{-1} s^{-1})	3.05×10^{-4}	6.20×10^{-4}	1.83×10^{-4}

Determine the rate law and the rate constant for this reaction.

32.

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.

33.

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
$[SO_2Cl_2]$ (*M*)	0.100	0.0896	0.0802	0.0719
Time (s)	2.50×10^4	3.00×10^4	4.00×10^4	
$[SO_2Cl_2]$ (*M*)	0.0577	0.0517	0.0415	

34.

Pure ozone decomposes slowly to oxygen, $2O_3(g) \longrightarrow 3O_2(g)$. 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	1.00×10^4
$[O_3]$ (*M*)	1.00×10^{-5}	4.98×10^{-6}	2.07×10^{-6}	1.66×10^{-6}
Time (h)	1.23×10^4	1.43×10^4	1.70×10^4	
$[O_3]$ (*M*)	1.39×10^{-6}	1.22×10^{-6}	1.05×10^{-6}	

35.

From the given data, use a graphical method to determine the order and rate constant of the following reaction:
$2X \longrightarrow Y + Z$

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

36.

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}.

37.

What is the half-life for the first-order decay of carbon-14? $\left({}^{14}_{6}\mathrm{C} \longrightarrow {}^{14}_{7}\mathrm{N} + \mathrm{e}^-\right)$ The rate constant for the decay is 1.21×10^{-4} year^{-1}.

38.

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^{-1} s^{-1}.

39.

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^{-1} h^{-1}.

40.

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^{-1} s^{-1}. If the initial concentration is 0.500 mol/L, what is the value of $t_{1/2}$?

41.

The half-life of a reaction of compound *A* to give compounds *D* and *E* is 8.50 min when the initial concentration of *A* is 0.150 M. How long will it take for the concentration to drop to 0.0300 M if the reaction is (a) first order with respect to *A* or (b) second

order with respect to *A*?

42.

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 law 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.

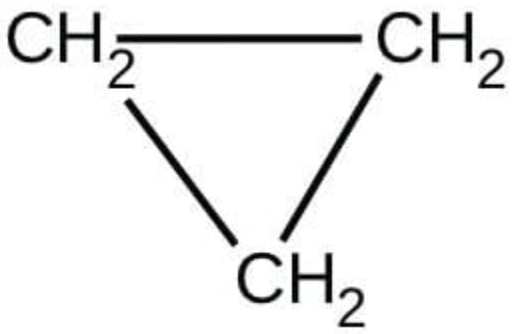
[Penicillin] (*M*)	Rate (mol L^{-1} min^{-1})
2.0×10^{-6}	1.0×10^{-10}
3.0×10^{-6}	1.5×10^{-10}
4.0×10^{-6}	2.0×10^{-10}

43.

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)?

44.

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 5.95×10^{-4} s^{-1}. What is the half-life of this reaction? What fraction of the cyclopropane remains after 0.75 h at 499 °C?

45.

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 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 take for 99.99% of the ^{18}F to decay?

46.

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?

47.

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.

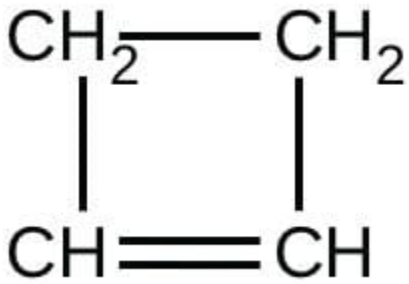
48.

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

49.

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.

50.

Chemical reactions occur when reactants collide. What are two factors that may prevent a collision from producing a chemical reaction?

51.

When every collision between reactants leads to a reaction, what determines the rate at which the reaction occurs?

52.

What is the activation energy of a reaction, and how is this energy related to the activated complex of the reaction?

53.

Account for the relationship between the rate of a reaction and its activation energy.

54.

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.

55.

How does an increase in temperature affect rate of reaction? Explain this effect in terms of the collision theory of the reaction rate.

56.

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?

57.

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? (Hint: Assume the rate doubles for each 10 °C rise in temperature.)

58.

The rate constant at 325 °C for the decomposition reaction $\mathrm{C_4H_8 \longrightarrow 2C_2H_4}$ 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.

59.

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^{-1} s^{-1} at 703 K and 4.95 L mol^{-1} s^{-1} at 865 K. Determine the activation energy for this decomposition.

60.

An elevated level of the enzyme alkaline phosphatase (ALP) in human 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?

61.

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

62.

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* (L mol^{-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?

63.

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})
293	0.054
298	0.100

64.

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 law 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

$\times 10^{-7}$ *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)?

65.

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?

66.

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?

67.

Why are elementary reactions involving three or more reactants very uncommon?

68.

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?

69.

Define these terms:

(a) unimolecular reaction

(b) bimolecular reaction

(c) elementary reaction

(d) overall reaction

70.

What is the rate law for the elementary termolecular reaction $A + 2B \longrightarrow \text{products}$? For $3A \longrightarrow \text{products}$?

71.

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) $\mathrm{Cl_2 + CO \longrightarrow Cl_2CO}$

$\text{rate} = k[\mathrm{Cl_2}]^{3/2}\,[\mathrm{CO}]$

(b) $PCl_3 + Cl_2 \longrightarrow PCl_5$
$\text{rate} = k\,[PCl_3]\,[Cl_2]$

(c) $2NO + H_2 \longrightarrow N_2 + H_2O_2$
$\text{rate} = k\,[NO]\,[H_2]$

(d) $2NO + O_2 \longrightarrow 2NO_2$
$\text{rate} = k[NO]^2\,[O_2]$

(e) $NO + O_3 \longrightarrow NO_2 + O_2$
$\text{rate} = k\,[NO]\,[O_3]$

72.

Write the rate law for each of the following elementary reactions:

(a) $O_3 \xrightarrow{\text{sunlight}} O_2 + O$

(b) $O_3 + Cl \longrightarrow O_2 + ClO$

(c) $ClO + O \longrightarrow Cl + O_2$

(d) $O_3 + NO \longrightarrow NO_2 + O_2$

(e) $NO_2 + O \longrightarrow NO + O_2$

73.

Nitrogen monoxide, NO, reacts with hydrogen, H_2, according to the following equation:
$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$

What would the rate law be if the mechanism for this reaction were:
$2NO + H_2 \longrightarrow N_2 + H_2O_2\ (\text{slow})$
$H_2O_2 + H_2 \longrightarrow 2H_2O\ (\text{fast})$

74.

Experiments were conducted to study the rate of the reaction represented by this equation.[3]
$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$

Initial concentrations and rates of reaction are given here.

Experiment	Initial Concentration [NO] (mol L^{-1})	Initial Concentration, [H_2] (mol L^{-1} min^{-1})	Initial Rate of Formation of N_2 (mol L^{-1} min^{-1})
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.

75.

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:
$\mathrm{Cl_2}(g) \rightleftharpoons 2\mathrm{Cl}(g)$ (fast, k_1 represents the forward rate constant, k_{-1} the reverse rate constant)
$\mathrm{CO}(g) + \mathrm{Cl}(g) \longrightarrow \mathrm{COCl}(g)$ (slow, k_2 the rate constant)
$\mathrm{COCl}(g) + \mathrm{Cl}(g) \longrightarrow \mathrm{COCl_2}(g)$ (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.

76.

Account for the increase in reaction rate brought about by a catalyst.

77.

Compare the functions of homogeneous and heterogeneous catalysts.

78.

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:

$\mathrm{O_3} \xrightarrow{\text{sunlight}} \mathrm{O_2} + \mathrm{O}$
$\mathrm{O_3} + \mathrm{Cl} \longrightarrow \mathrm{O_2} + \mathrm{ClO}$
$\mathrm{ClO} + \mathrm{O} \longrightarrow \mathrm{Cl} + \mathrm{O_2}$

(a) Explain why chlorine atoms are catalysts in the gas-phase transformation:
$2\mathrm{O_3} \longrightarrow 3\mathrm{O_2}$

(b) Nitric oxide is also involved in the decomposition of ozone by the mechanism:

$$O_3 \xrightarrow{\text{sunlight}} O_2 + O$$
$$O_3 + NO \longrightarrow NO_2 + O_2$$
$$NO_2 + O \longrightarrow NO + O_2$$

Is NO a catalyst for the decomposition? Explain your answer.

79.

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: $H_2O(g) + C(s) \rightleftharpoons H_2(g) + CO(g)$. 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. What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more catalyst is added?

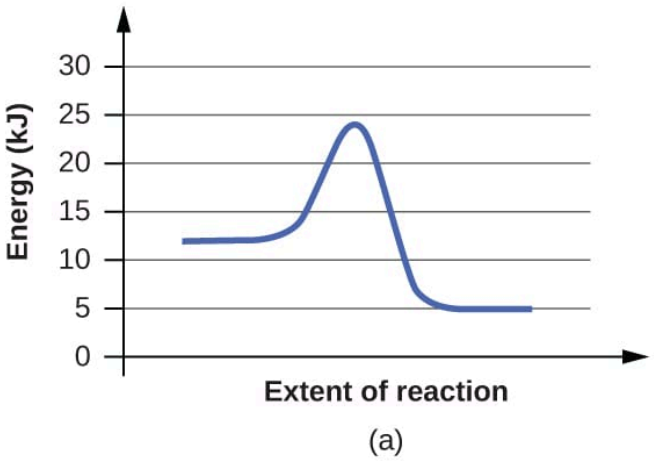
80.

Nitrogen and oxygen react at high temperatures. What will happen to the concentrations of N_2, O_2, and NO at equilibrium if a catalyst is added?

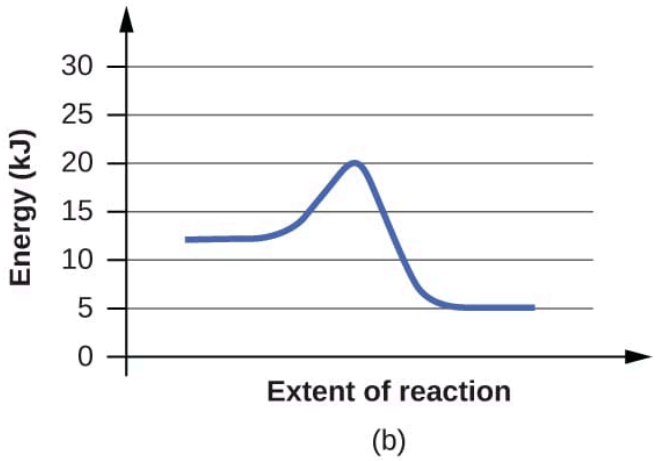
81.

For each of the following pairs of reaction diagrams, identify which of the pair is catalyzed:

(a)

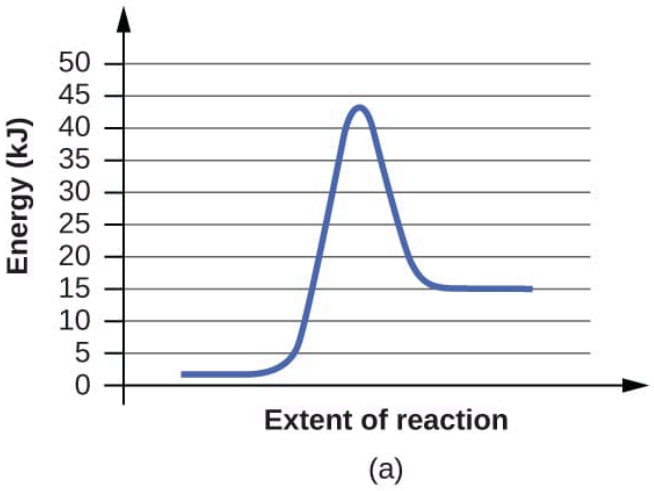


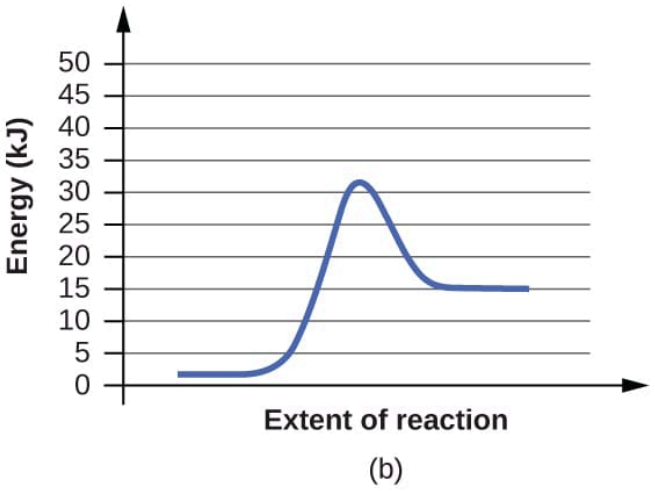
(a)



(b)

(b)

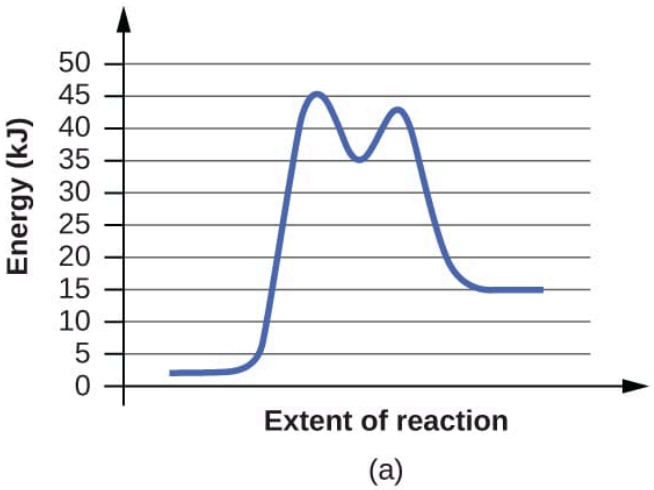


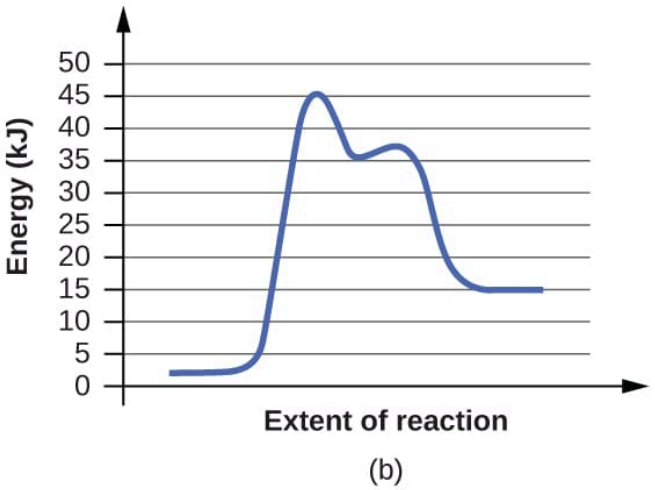


82.

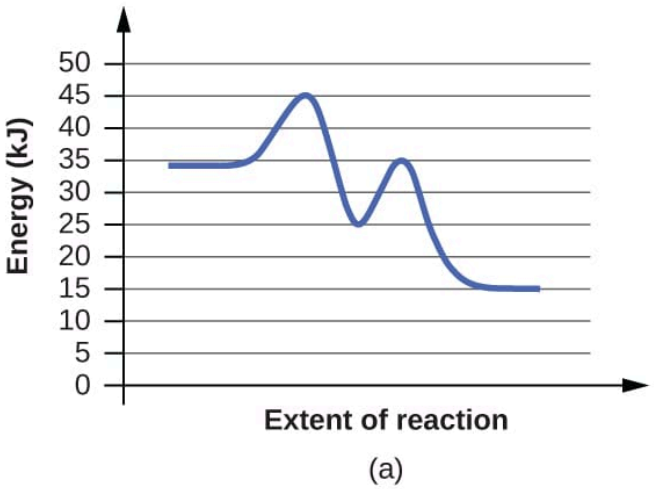
For each of the following pairs of reaction diagrams, identify which of the pairs is catalyzed:

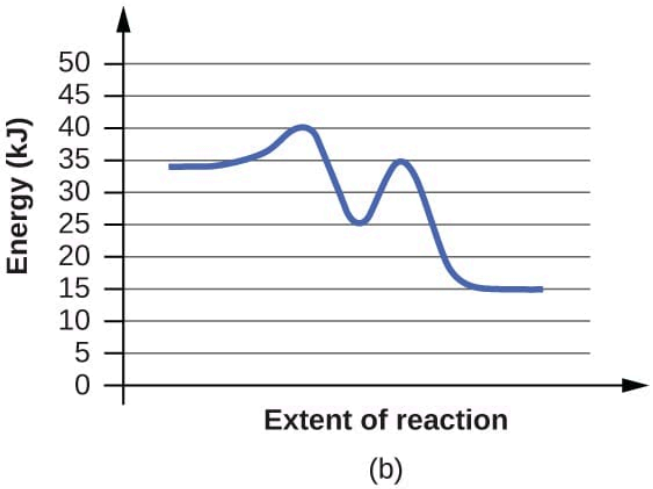
(a)





(b)

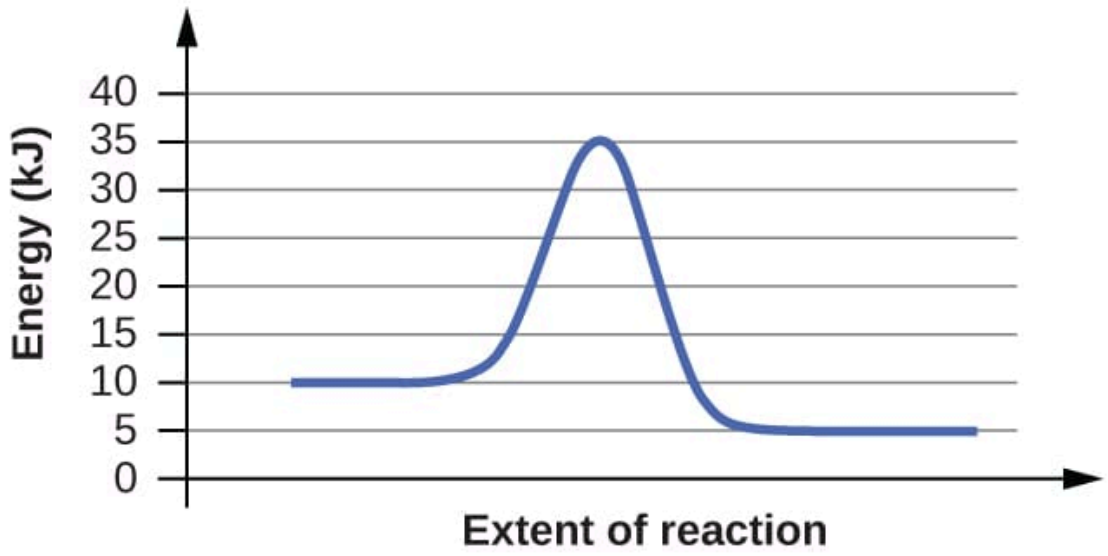




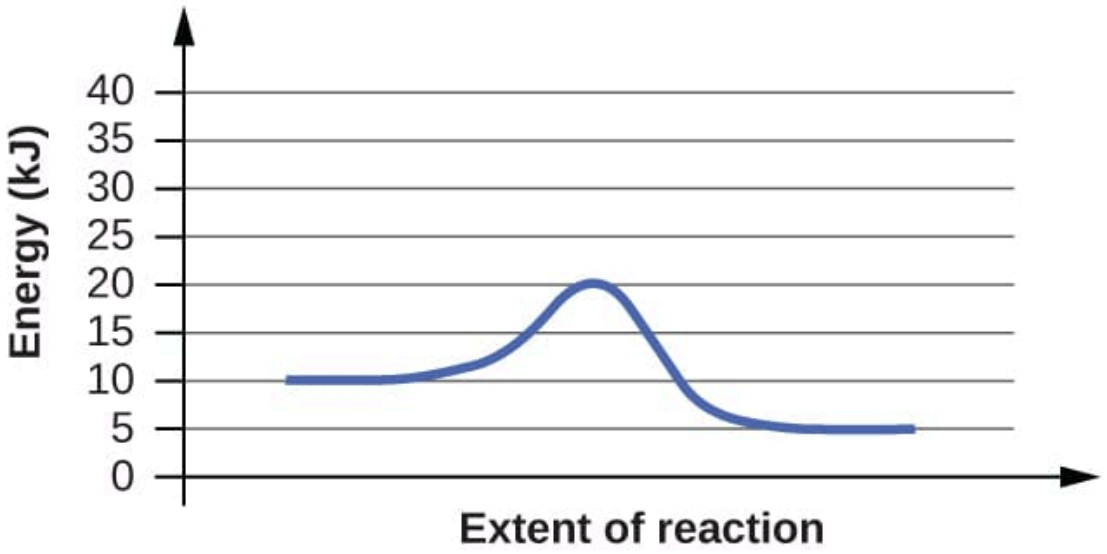
83.

For each of the following reaction diagrams, estimate the activation energy (E_a) of the reaction:

(a)



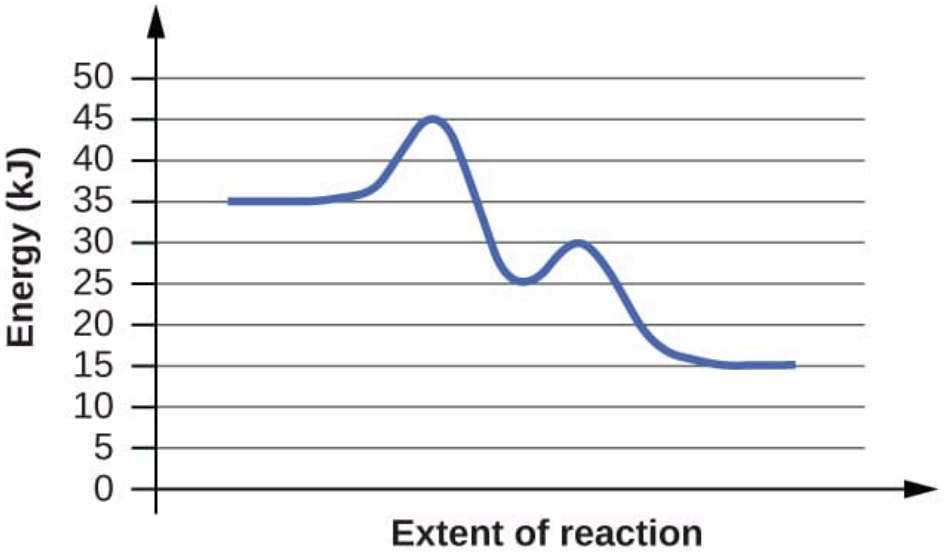
(b)



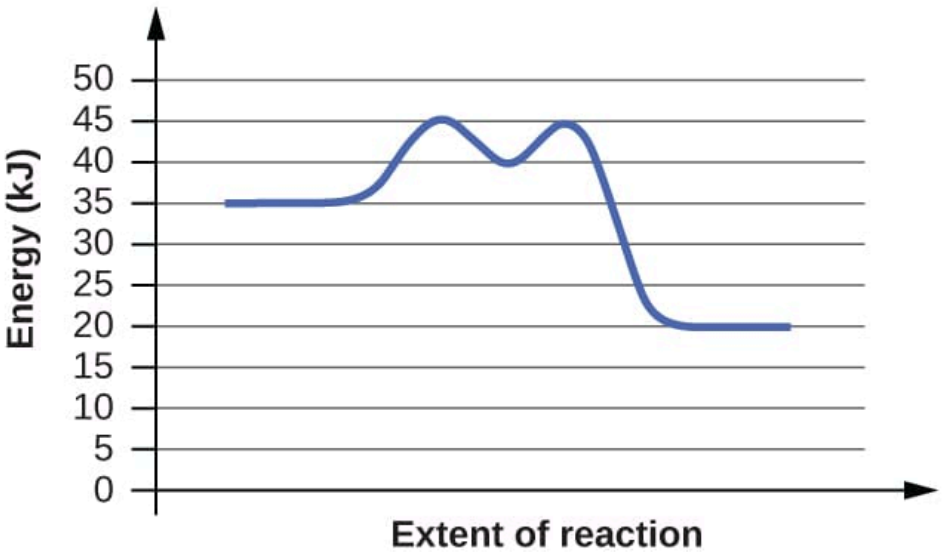
84.

For each of the following reaction diagrams, estimate the activation energy (E_a) of the reaction:

(a)



(b)



85.

Assuming the diagrams in Exercise 17.83 represent different mechanisms for the same reaction, which of the reactions has the faster rate?

86.

Consider the similarities and differences in the two reaction diagrams shown in Exercise 17.84. Do these diagrams represent two different overall reactions, or do they represent the same overall reaction taking place by two different mechanisms? Explain your answer.

Footnotes

- 3This question is taken from the Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

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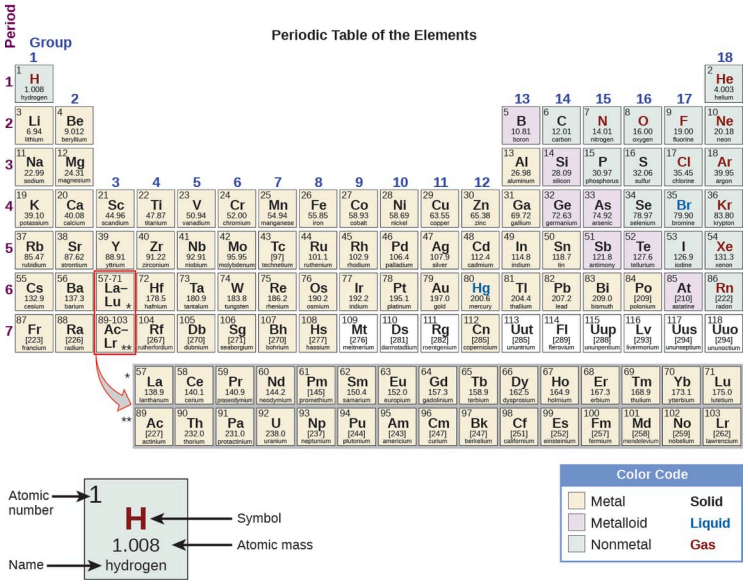
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11.1: The Periodic Table



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11.2: Essential Mathematics

Exponential Arithmetic

Exponential notation is used to express very large and very small numbers as a product of two numbers. The first number of the product, the *digit term*, is usually a number not less than 1 and not greater than 10. The second number of the product, the *exponential term*, is written as 10 with an exponent. Some examples of exponential notation are:

$$1000 = 1 \times 10^3 \tag{11.2.1}$$
$$100 = 1 \times 10^2 \tag{11.2.2}$$
$$10 = 1 \times 10^1 \tag{11.2.3}$$
$$1 = 1 \times 10^0 \tag{11.2.4}$$
$$0.1 = 1 \times 10^{-1} \tag{11.2.5}$$
$$0.001 = 1 \times 10^{-3} \tag{11.2.6}$$
$$2386 = 2.386 \times 1000 = 2.386 \times 10^3 \tag{11.2.7}$$
$$0.123 = 1.23 \times 0.1 = 1.23 \times 10^{-1} \tag{11.2.8}$$

The power (exponent) of 10 is equal to the number of places the decimal is shifted to give the digit number. The exponential method is particularly useful notation for every large and very small numbers. For example, 1,230,000,000 = 1.23×10^9, and $0.000000000036 \times 10^{-10}$.

Addition of Exponentials

Convert all numbers to the same power of 10, add the digit terms of the numbers, and if appropriate, convert the digit term back to a number between 1 and 10 by adjusting the exponential term.

Adding Exponentials Add 5.00×10^{-5} and 3.00×10^{-3}.

Solution

$$3.00 \times 10^{-3} = 300 \times 10^{-5} \tag{11.2.9}$$
$$(5.00 \times 10^{-5}) + (300 \times 10^{-5}) = 305 \times 10^{-5} = 3.05 \times 10^{-3} \tag{11.2.10}$$

Subtraction of Exponentials

Convert all numbers to the same power of 10, take the difference of the digit terms, and if appropriate, convert the digit term back to a number between 1 and 10 by adjusting the exponential term.

Subtracting Exponentials Subtract 4.0×10^{-7} from 5.0×10^{-6}.

Solution

$$4.0 \times 10^{-7} = 0.40 \times 10^{-6} \tag{11.2.11}$$
$$(5.0 \times 10^{-6}) - (0.40 \times 10^{-6}) = 4.6 \times 10^{-6}$$

Multiplication of Exponentials

Multiply the digit terms in the usual way and add the exponents of the exponential terms.

Multiplying Exponentials Multiply 4.2×10^{-8} by 2.0×10^{3}.

Solution

$$(4.2 \times 10^{-8}) \times (2.0 \times 10^{3}) = (4.2 \times 2.0) \times 10^{(-8)+(+3)} = 8.4 \times 10^{-5} \tag{11.2.12}$$

Division of Exponentials

Divide the digit term of the numerator by the digit term of the denominator and subtract the exponents of the exponential terms.

Dividing Exponentials Divide 3.6×10^{5} by 6.0×10^{-4}.

Solution

$$\frac{3.6 \times 10^{-5}}{6.0 \times 10^{-4}} = \left(\frac{3.6}{6.0}\right) \times 10^{(-5)-(-4)} = 0.60 \times 10^{-1} = 6.0 \times 10^{-2} \tag{11.2.13}$$

Squaring of Exponentials

Square the digit term in the usual way and multiply the exponent of the exponential term by 2.

Squaring Exponentials Square the number 4.0×10^{-6}.

Solution

$$(4.0 \times 10^{-6})^{2} = 4 \times 4 \times 10^{2\times(-6)} = 16 \times 10^{-12} = 1.6 \times 10^{-11} \tag{11.2.14}$$

Cubing of Exponentials

Cube the digit term in the usual way and multiply the exponent of the exponential term by 3.

Cubing Exponentials Cube the number 2×10^{4}.

Solution

$$(2 \times 10^{4})^{3} = 2 \times 2 \times 2 \times 10^{3\times4} = 8 \times 10^{12} \tag{11.2.15}$$

Taking Square Roots of Exponentials

If necessary, decrease or increase the exponential term so that the power of 10 is evenly divisible by 2. Extract the square root of the digit term and divide the exponential term by 2.

Finding the Square Root of Exponentials Find the square root of 1.6×10^{-7}.

Solution

$$1.6 \times 10^{-7} = 16 \times 10^{-8} \tag{11.2.16}$$

$$\sqrt{16 \times 10^{-8}} = \sqrt{16} \times \sqrt{10^{-8}} = \sqrt{16} \times 10^{-\frac{8}{2}} = 4.0 \times 10^{-4} \tag{11.2.17}$$

Significant Figures

A beekeeper reports that he has 525,341 bees. The last three figures of the number are obviously inaccurate, for during the time the keeper was counting the bees, some of them died and others hatched; this makes it quite difficult to determine the exact

number of bees. It would have been more accurate if the beekeeper had reported the number 525,000. In other words, the last three figures are not significant, except to set the position of the decimal point. Their exact values have no meaning useful in this situation. In reporting any information as numbers, use only as many significant figures as the accuracy of the measurement warrants.

The importance of significant figures lies in their application to fundamental computation. In addition and subtraction, the sum or difference should contain as many digits to the right of the decimal as that in the least certain of the numbers used in the computation (indicated by underscoring in the following example).

Addition and Subtraction with Significant Figures Add 4.383 g and 0.0023 g.

Solution

$$4.38\underline{3}\ \text{g} \tag{11.2.18}$$
$$\underline{0.002\underline{3}\ \text{g}} \tag{11.2.19}$$
$$4.38\underline{5}\ \text{g} \tag{11.2.20}$$

In multiplication and division, the product or quotient should contain no more digits than that in the factor containing the least number of significant figures.

Multiplication and Division with Significant Figures Multiply 0.6238 by 6.6.

Solution

$$0.623\underline{8} \times 6.\underline{6} = 4.\underline{1} \tag{11.2.21}$$

When rounding numbers, increase the retained digit by 1 if it is followed by a number larger than 5 (“round up”). Do not change the retained digit if the digits that follow are less than 5 (“round down”). If the retained digit is followed by 5, round up if the retained digit is odd, or round down if it is even (after rounding, the retained digit will thus always be even).

The Use of Logarithms and Exponential Numbers

The common logarithm of a number (log) is the power to which 10 must be raised to equal that number. For example, the common logarithm of 100 is 2, because 10 must be raised to the second power to equal 100. Additional examples follow.

Logarithms and Exponential Numbers

Number	Number Expressed Exponentially	Common Logarithm
1000	10^3	3
10	10^1	1
1	10^0	0
0.1	10^{-1}	–1
0.001	10^{-3}	–3

What is the common logarithm of 60? Because 60 lies between 10 and 100, which have logarithms of 1 and 2, respectively, the logarithm of 60 is 1.7782; that is,

$$60 = 10^{1.7782} \tag{11.2.22}$$

The common logarithm of a number less than 1 has a negative value. The logarithm of 0.03918 is –1.4069, or

$$0.03918 = 10^{-1.4069} = \frac{1}{10^{1.4069}} \tag{11.2.23}$$

To obtain the common logarithm of a number, use the *log* button on your calculator. To calculate a number from its logarithm, take the inverse log of the logarithm, or calculate 10^x (where x is the logarithm of the number).

The natural logarithm of a number (ln) is the power to which e must be raised to equal the number; e is the constant 2.7182818. For example, the natural logarithm of 10 is 2.303; that is,

$$10 = e^{2.303} = 2.7182818^{2.303} \tag{11.2.24}$$

To obtain the natural logarithm of a number, use the *ln* button on your calculator. To calculate a number from its natural logarithm, enter the natural logarithm and take the inverse ln of the natural logarithm, or calculate e^x (where x is the natural logarithm of the number).

Logarithms are exponents; thus, operations involving logarithms follow the same rules as operations involving exponents.

1. The logarithm of a product of two numbers is the sum of the logarithms of the two numbers.
$$\log xy = \log x + \log y, \text{ and } \ln xy = \ln x + \ln y \tag{11.2.25}$$
2. The logarithm of the number resulting from the division of two numbers is the difference between the logarithms of the two numbers.
$$\log \frac{x}{y} = \log x - \log y, \text{ and } \ln \frac{x}{y} = \ln x - \ln y \tag{11.2.26}$$
3. The logarithm of a number raised to an exponent is the product of the exponent and the logarithm of the number.
$$\log x^n = n \log x \text{ and } \ln x^n = n \ln x \tag{11.2.27}$$

The Solution of Quadratic Equations

Mathematical functions of this form are known as second-order polynomials or, more commonly, quadratic functions.

$$ax^2 + bx + c = 0 \tag{11.2.28}$$

The solution or roots for any quadratic equation can be calculated using the following formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \tag{11.2.29}$$

Solving Quadratic Equations Solve the quadratic equation $3x^2 + 13x - 10 = 0$.

Solution Substituting the values $a = 3$, $b = 13$, $c = -10$ in the formula, we obtain

$$x = \frac{-13 \pm \sqrt{(13)^2 - 4 \times 3 \times (-10)}}{2 \times 3} \tag{11.2.30}$$

$$x = \frac{-13 \pm \sqrt{169 + 120}}{6} = \frac{-13 \pm \sqrt{289}}{6} = \frac{-13 \pm 17}{6} \tag{11.2.31}$$

The two roots are therefore

$$x = \frac{-13 + 17}{6} = \frac{2}{3} \text{ and } x = \frac{-13 - 17}{6} = -5 \tag{11.2.32}$$

Quadratic equations constructed on physical data always have real roots, and of these real roots, often only those having positive values are of any significance.

Two-Dimensional (*x*-*y*) Graphing

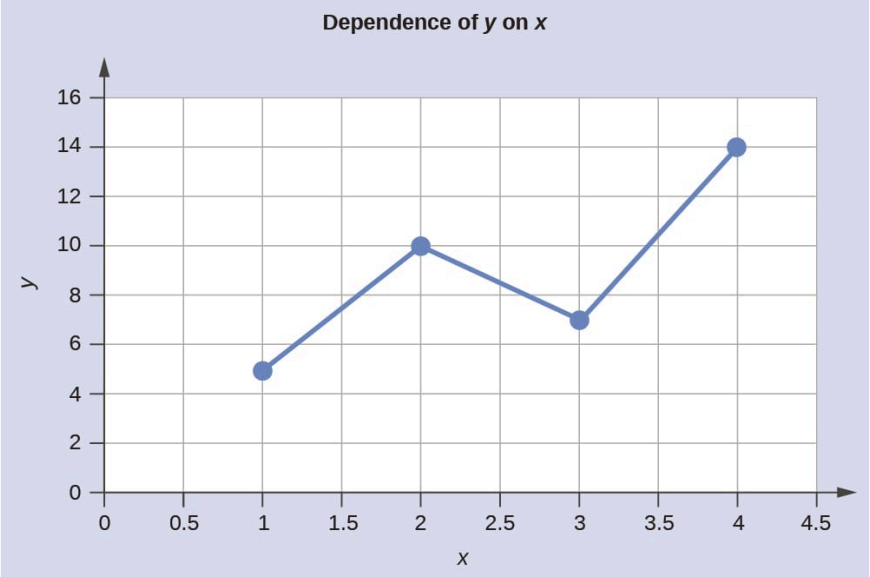
The relationship between any two properties of a system can be represented graphically by a two-dimensional data plot. Such a graph has two axes: a horizontal one corresponding to the independent variable, or the variable whose value is being controlled (x), and a vertical axis corresponding to the dependent variable, or the variable whose value is being observed or measured (y).

When the value of y is changing as a function of x (that is, different values of x correspond to different values of y), a graph of this change can be plotted or sketched. The graph can be produced by using specific values for (x,y) data pairs.

Graphing the Dependence of y on x

x	y
1	5
2	10
3	7
4	14

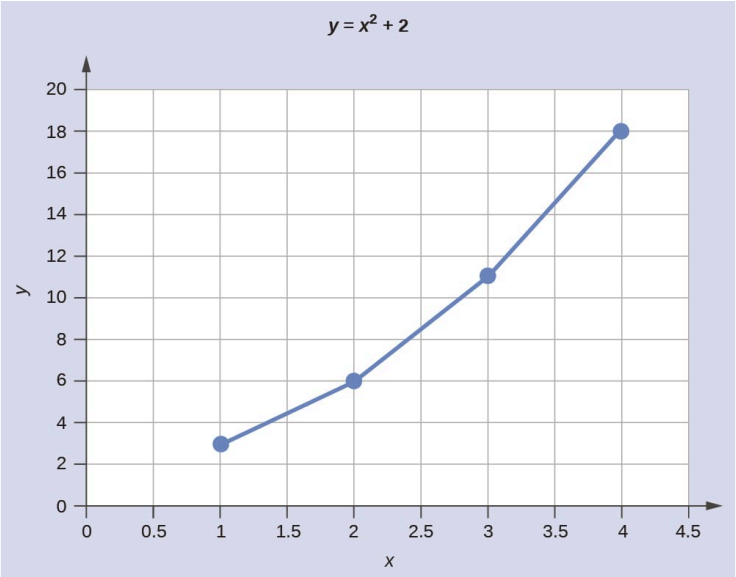
This table contains the following points: (1,5), (2,10), (3,7), and (4,14). Each of these points can be plotted on a graph and connected to produce a graphical representation of the dependence of y on x.



If the function that describes the dependence of y on x is known, it may be used to compute x,y data pairs that may subsequently be plotted.

Plotting Data Pairs If we know that $y = x^2 + 2$, we can produce a table of a few (x,y) values and then plot the line based on the data shown here.

x	$y = x^2 + 2$
1	3
2	6
3	11
4	18



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11.3: Units and Conversion Factors

Units of Length			
meter (m)	= 39.37 inches (in.) = 1.094 yards (yd)	angstrom (Å)	= 10^{-8} cm (exact, definition) = 10^{-10} m (exact, definition)
centimeter (cm)	= 0.01 m (exact, definition)	yard (yd)	= 0.9144 m
millimeter (mm)	= 0.001 m (exact, definition)	inch (in.)	= 2.54 cm (exact, definition)
kilometer (km)	= 1000 m (exact, definition)	mile (US)	= 1.60934 km

Units of Volume			
liter (L)	= 0.001 m^3 (exact, definition) = 1000 cm^3 (exact, definition) = 1.057 (US) quarts	liquid quart (US)	= 32 (US) liquid ounces (exact, definition) = 0.25 (US) gallon (exact, definition) = 0.9463 L
milliliter (mL)	= 0.001 L (exact, definition) = 1 cm^3 (exact, definition)	dry quart	= 1.1012 L
microliter (µL)	= 10^{-6} L (exact, definition) = 10^{-3} cm^3 (exact, definition)	cubic foot (US)	= 28.316 L

Units of Mass			
gram (g)	= 0.001 kg (exact, definition)	ounce (oz) (avoirdupois)	= 28.35 g
milligram (mg)	= 0.001 g (exact, definition)	pound (lb) (avoirdupois)	= 0.4535924 kg
kilogram (kg)	= 1000 g (exact, definition) = 2.205 lb	ton (short)	=2000 lb (exact, definition) = 907.185 kg
ton (metric)	=1000 kg (exact, definition) = 2204.62 lb	ton (long)	= 2240 lb (exact, definition) = 1.016 metric ton

Units of Energy	
4.184 joule (J)	= 1 thermochemical calorie (cal)
1 thermochemical calorie (cal)	= 4.184 × 10^7 erg
erg	= 10^{-7} J (exact, definition)
electron-volt (eV)	= 1.60218 × 10^{-19} J = 23.061 kcal mol^{-1}
liter·atmosphere	= 24.217 cal = 101.325 J (exact, definition)
nutritional calorie (Cal)	= 1000 cal (exact, definition) = 4184 J
British thermal unit (BTU)	= 1054.804 J[1]

Units of Pressure	
torr	= 1 mm Hg (exact, definition)
pascal (Pa)	= N m^{-2} (exact, definition) = kg m^{-1} s^{-2} (exact, definition)
atmosphere (atm)	= 760 mm Hg (exact, definition) = 760 torr (exact, definition) = 101,325 N m^{-2} (exact, definition) = 101,325 Pa (exact, definition)

Units of Pressure	
bar	= 10^5 Pa (exact, definition) = 10^5 kg m^{-1} s^{-2} (exact, definition)

Footnotes

1. 1 BTU is the amount of energy needed to heat one pound of water by one degree Fahrenheit. Therefore, the exact relationship of BTU to joules and other energy units depends on the temperature at which BTU is measured. 59 °F (15 °C) is the most widely used reference temperature for BTU definition in the United States. At this temperature, the conversion factor is the one provided in this table.

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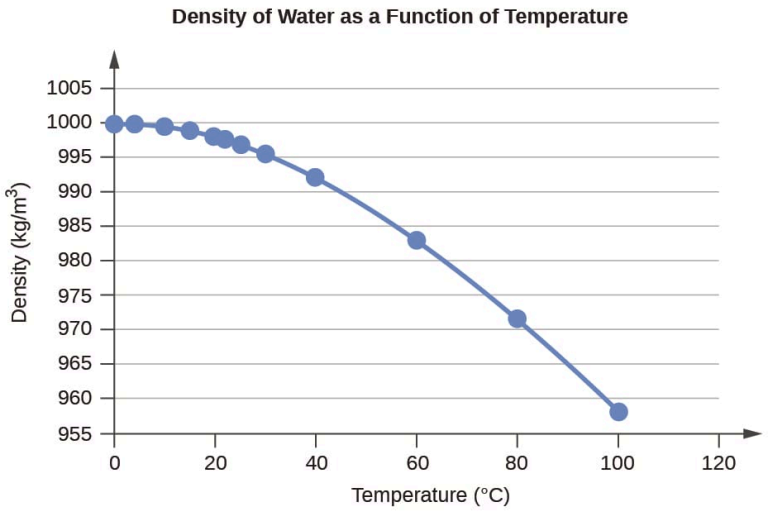
11.4: Fundamental Physical Constants

Fundamental Physical Constants	
Name and Symbol	**Value**
atomic mass unit (amu)	$1.6605402 \times 10^{-27}$ kg
Avogadro's number	6.0221367×10^{23} mol^{-1}
Boltzmann's constant (k)	1.380658×10^{-23} J K^{-1}
charge-to-mass ratio for electron (e/m_e)	$1.75881962 \times 10^{11}$ C kg^{-1}
electron charge (e)	$1.60217733 \times 10^{-19}$ C
electron rest mass (m_e)	$9.1093897 \times 10^{-31}$ kg
Faraday's constant (F)	9.6485309×10^{4} C mol^{-1}
gas constant (R)	8.205784×10^{-2} L atm mol^{-1} K^{-1} = 8.314510 J mol^{-1} K^{-1}
molar volume of an ideal gas, 1 atm, 0 °C	22.41409 L mol^{-1}
molar volume of an ideal gas, 1 bar, 0 °C	22.71108 L mol^{-1}
neutron rest mass (m_n)	$1.6749274 \times 10^{-27}$ kg
Planck's constant (h)	$6.6260755 \times 10^{-34}$ J s
proton rest mass (m_p)	$1.6726231 \times 10^{-27}$ kg
Rydberg constant (R)	$1.0973731534 \times 10^{7}$ m^{-1} = $2.1798736 \times 10^{-18}$ J
speed of light (in vacuum) (c)	2.99792458×10^{8} m s^{-1}

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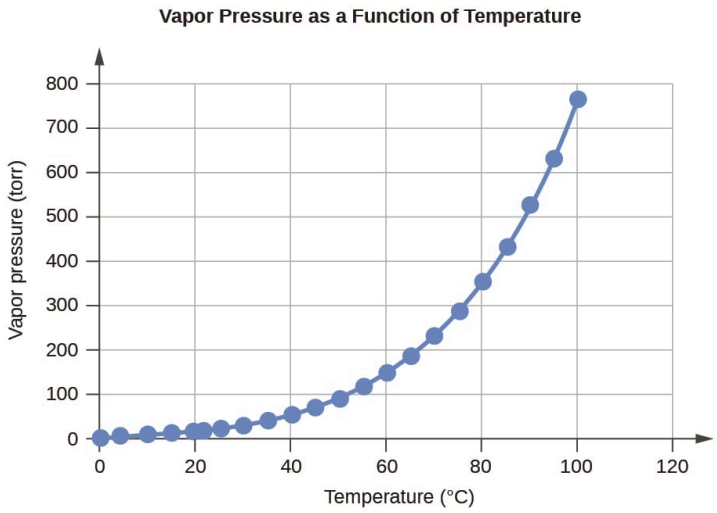
11.5: Water Properties

Water Density (kg/m^3) at Different Temperatures (°C)	
Temperature[1]	Density
0	999.8395
4	999.9720 (density maximum)
10	999.7026
15	999.1026
20	998.2071
22	997.7735
25	997.0479
30	995.6502
40	992.2
60	983.2
80	971.8
100	958.4



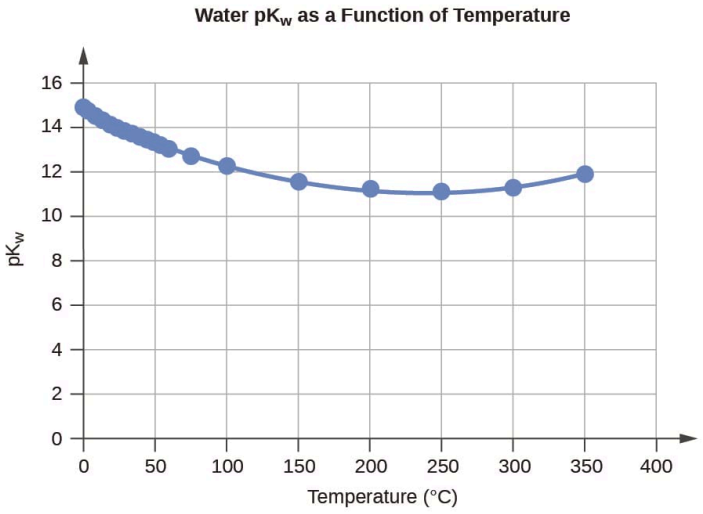
Water Vapor Pressure at Different Temperatures (°C)		
Temperature	Vapor Pressure (torr)	Vapor Pressure (Pa)
0	4.6	613.2812
4	6.1	813.2642
10	9.2	1226.562
15	12.8	1706.522
20	17.5	2333.135

Water Vapor Pressure at Different Temperatures (°C)		
Temperature	**Vapor Pressure (torr)**	**Vapor Pressure (Pa)**
22	19.8	2639.776
25	23.8	3173.064
30	31.8	4239.64
35	42.2	5626.188
40	55.3	7372.707
45	71.9	9585.852
50	92.5	12332.29
55	118.0	15732
60	149.4	19918.31
65	187.5	24997.88
70	233.7	31157.35
75	289.1	38543.39
80	355.1	47342.64
85	433.6	57808.42
90	525.8	70100.71
95	633.9	84512.82
100	760.0	101324.7



Water K_w and pK_w at Different Temperatures (°C)		
Temperature	**K_w 10^{-14}**	**pK_w**
0	0.112	14.95
5	0.182	14.74
10	0.288	14.54

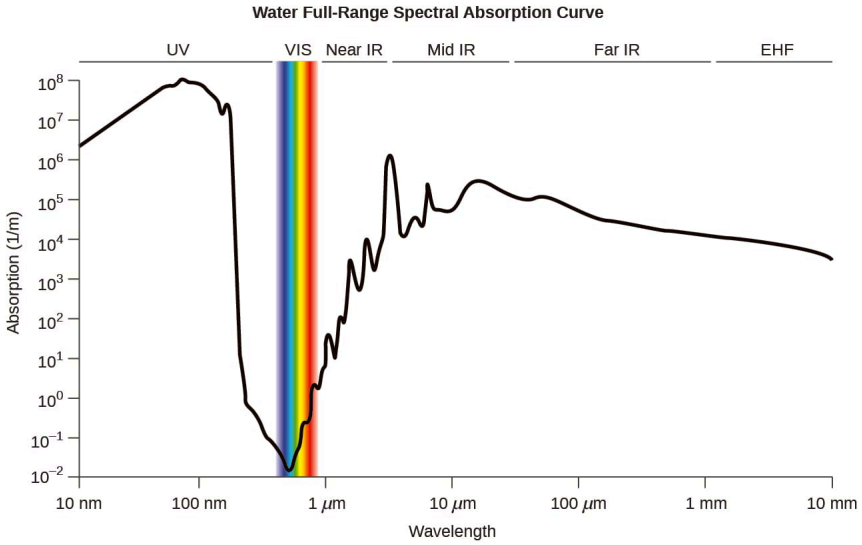
Water K_w and pK_w at Different Temperatures (°C)		
Temperature	K_w 10^{-14}	pK_w[2]
15	0.465	14.33
20	0.671	14.17
25	0.991	14.00
30	1.432	13.84
35	2.042	13.69
40	2.851	13.55
45	3.917	13.41
50	5.297	13.28
55	7.080	13.15
60	9.311	13.03
75	19.95	12.70
100	56.23	12.25



Specific Heat Capacity for Water
$C°(H_2O(l)) = 4184\ J{\cdot}K^{-1}{\cdot}kg^{-1} = 4.184\ J{\cdot}g^{-1}{\cdot}°C^{-1}$
$C°(H_2O(s)) = 1864\ J{\cdot}K^{-1}{\cdot}kg^{-1}$
$C°(H_2O(g)) = 2093\ J{\cdot}K^{-1}{\cdot}kg^{-1}$

Standard Water Melting and Boiling Temperatures and Enthalpies of the Transitions		
	Temperature (K)	ΔH (kJ/mol)
melting	273.15	6.008
boiling	373.15	40.656 (44.016 at 298 K)

Water Cryoscopic (Freezing Point Depression) and Ebullioscopic (Boiling Point Elevation) Constants
K_f = 1.86°C·kg·mol^{-1} (cryoscopic constant)
K_b = 0.51°C·kg·mol^{-1} (ebullioscopic constant)



Water full-range spectral absorption curve. This curve shows the full-range spectral absorption for water. The *y*-axis signifies the absorption in 1/cm. If we divide 1 by this value, we will obtain the length of the path (in cm) after which the intensity of a light beam passing through water decays by a factor of the base of the natural logarithm e (e = 2.718281828).

Footnotes

1. 1 Data for t < 0 °C are for supercooled water
2. 2 $pK_w = -\log_{10}(K_w)$

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11.6: Composition of Commercial Acids and Bases

Composition of Commercial Acids and Bases			
Acid or Base[1]	Density (g/mL)[2]	Percentage by Mass	Molarity
acetic acid, glacial	1.05	99.5%	17.4
aqueous ammonia[3]	0.90	28%	14.8
hydrochloric acid	1.18	36%	11.6
nitric acid	1.42	71%	16.0
perchloric acid	1.67	70%	11.65
phosphoric acid	1.70	85%	14.7
sodium hydroxide	1.53	50%	19.1
sulfuric acid	1.84	96%	18.0

Footnotes

1. 1 Acids and bases are commercially available as aqueous solutions. This table lists properties (densities and concentrations) of common acid and base solutions. Nominal values are provided in cases where the manufacturer cites a range of concentrations and densities.
2. 2 This column contains specific gravity data. In the case of this table, specific gravity is the ratio of density of a substance to the density of pure water at the same conditions. Specific gravity is often cited on commercial labels.
3. 3 This solution is sometimes called “ammonium hydroxide,” although this term is not chemically accurate.

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11.7: Standard Thermodynamic Properties for Selected Substances

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° **(kJ mol⁻)**	ΔG_f° **(kJ mol^{-1})**	S_{298}° **(J K^{-1} mol^{-1})**
aluminum			
Al(s)	0	0	28.3
Al(*g*)	324.4	285.7	164.54
Al_2O_3(s)	−1676	−1582	50.92
AlF_3(s)	−1510.4	−1425	66.5
$AlCl_3$(s)	−704.2	−628.8	110.67
$AlCl_3 \cdot 6H_2O$(s)	−2691.57	−2269.40	376.56
Al_2S_3(s)	−724.0	−492.4	116.9
$Al_2(SO_4)_3$(s)	−3445.06	−3506.61	239.32
antimony			
Sb(s)	0	0	45.69
Sb(*g*)	262.34	222.17	180.16
Sb_4O_6(s)	−1440.55	−1268.17	220.92
$SbCl_3$(*g*)	−313.8	−301.2	337.80
$SbCl_5$(*g*)	−394.34	−334.29	401.94
Sb_2S_3(s)	−174.89	−173.64	182.00
$SbCl_3$(s)	−382.17	−323.72	184.10
SbOCl(s)	−374.0	—	—
arsenic			
As(s)	0	0	35.1
As(*g*)	302.5	261.0	174.21
As_4(*g*)	143.9	92.4	314
As_4O_6(s)	−1313.94	−1152.52	214.22
As_2O_5(s)	−924.87	−782.41	105.44
$AsCl_3$(*g*)	−261.50	−248.95	327.06
As_2S_3(s)	−169.03	−168.62	163.59
AsH_3(*g*)	66.44	68.93	222.78
H_3AsO_4(s)	−906.3	—	—
barium			
Ba(s)	0	0	62.5

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
Ba(g)	180	146	170.24
BaO(s)	−548.0	−520.3	72.1
$BaCl_2$(s)	−855.0	−806.7	123.7
$BaSO_4$(s)	−1473.2	−1362.3	132.2
beryllium			
Be(s)	0	0	9.50
Be(g)	324.3	286.6	136.27
BeO(s)	−609.4	−580.1	13.8
bismuth			
Bi(s)	0	0	56.74
Bi(g)	207.1	168.2	187.00
Bi_2O_3(s)	−573.88	−493.7	151.5
$BiCl_3$(s)	−379.07	−315.06	176.98
Bi_2S_3(s)	−143.1	−140.6	200.4
boron			
B(s)	0	0	5.86
B(g)	565.0	521.0	153.4
B_2O_3(s)	−1273.5	−1194.3	53.97
B_2H_6(g)	36.4	87.6	232.1
H_3BO_3(s)	−1094.33	−968.92	88.83
BF_3(g)	−1136.0	−1119.4	254.4
BCl_3(g)	−403.8	−388.7	290.1
$B_3N_3H_6$(l)	−540.99	−392.79	199.58
HBO_2(s)	−794.25	−723.41	37.66
bromine			
Br_2(l)	0	0	152.23
Br_2(g)	30.91	3.142	245.5
Br(g)	111.88	82.429	175.0
BrF_3(g)	−255.60	−229.45	292.42
HBr(g)	−36.3	−53.43	198.7
cadmium			
Cd(s)	0	0	51.76
Cd(g)	112.01	77.41	167.75
CdO(s)	−258.2	−228.4	54.8
$CdCl_2$(s)	−391.5	−343.9	115.3

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° **(kJ mol⁻)**	ΔG_f° **(kJ mol^{-1})**	S_{298}° **(J K^{-1} mol^{-1})**
$CdSO_4(s)$	−933.3	−822.7	123.0
$CdS(s)$	−161.9	−156.5	64.9
calcium			
$Ca(s)$	0	0	41.6
$Ca(g)$	178.2	144.3	154.88
$CaO(s)$	−634.9	−603.3	38.1
$Ca(OH)_2(s)$	−985.2	−897.5	83.4
$CaSO_4(s)$	−1434.5	−1322.0	106.5
$CaSO_4{\cdot}2H_2O(s)$	−2022.63	−1797.45	194.14
$CaCO_3(s)$ (calcite)	−1220.0	−1081.4	110.0
$CaSO_3{\cdot}H_2O(s)$	−1752.68	−1555.19	184.10
carbon			
$C(s)$ (graphite)	0	0	5.740
$C(s)$ (diamond)	1.89	2.90	2.38
$C(g)$	716.681	671.2	158.1
$CO(g)$	−110.52	−137.15	197.7
$CO_2(g)$	−393.51	−394.36	213.8
$CH_4(g)$	−74.6	−50.5	186.3
$CH_3OH(l)$	−239.2	−166.6	126.8
$CH_3OH(g)$	−201.0	−162.3	239.9
$CCl_4(l)$	−128.2	−62.5	214.4
$CCl_4(g)$	−95.7	−58.2	309.7
$CHCl_3(l)$	−134.1	−73.7	201.7
$CHCl_3(g)$	−103.14	−70.34	295.71
$CS_2(l)$	89.70	65.27	151.34
$CS_2(g)$	116.9	66.8	238.0
$C_2H_2(g)$	227.4	209.2	200.9
$C_2H_4(g)$	52.4	68.4	219.3
$C_2H_6(g)$	−84.0	−32.0	229.2
$CH_3CO_2H(l)$	−484.3	−389.9	159.8
$CH_3CO_2H(g)$	−434.84	−376.69	282.50
$C_2H_5OH(l)$	−277.6	−174.8	160.7
$C_2H_5OH(g)$	−234.8	−167.9	281.6
$C_3H_8(g)$	−103.8	−23.4	270.3

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° **(kJ mol⁻)**	ΔG_f° **(kJ mol^{-1})**	S_{298}° **(J K^{-1} mol^{-1})**
$C_6H_6(g)$	82.927	129.66	269.2
$C_6H_6(l)$	49.1	124.50	173.4
$CH_2Cl_2(l)$	−124.2	−63.2	177.8
$CH_2Cl_2(g)$	−95.4	−65.90	270.2
$CH_3Cl(g)$	−81.9	−60.2	234.6
$C_2H_5Cl(l)$	−136.52	−59.31	190.79
$C_2H_5Cl(g)$	−112.17	−60.39	276.00
$C_2N_2(g)$	308.98	297.36	241.90
$HCN(l)$	108.9	125.0	112.8
$HCN(g)$	135.5	124.7	201.8
chlorine			
$Cl_2(g)$	0	0	223.1
$Cl(g)$	121.3	105.70	165.2
$ClF(g)$	−54.48	−55.94	217.78
$ClF_3(g)$	−158.99	−118.83	281.50
$Cl_2O(g)$	80.3	97.9	266.2
$Cl_2O_7(l)$	238.1	—	—
$Cl_2O_7(g)$	272.0	—	—
$HCl(g)$	−92.307	−95.299	186.9
$HClO_4(l)$	−40.58	—	—
chromium			
Cr(s)	0	0	23.77
$Cr(g)$	396.6	351.8	174.50
$Cr_2O_3(s)$	−1139.7	−1058.1	81.2
$CrO_3(s)$	−589.5	—	—
$(NH_4)_2Cr_2O_7(s)$	−1806.7	—	—
cobalt			
Co(s)	0	0	30.0
CoO(s)	−237.9	−214.2	52.97
$Co_3O_4(s)$	−910.02	−794.98	114.22
$Co(NO_3)_2(s)$	−420.5	—	—
copper			
Cu(s)	0	0	33.15
$Cu(g)$	338.32	298.58	166.38
CuO(s)	−157.3	−129.7	42.63

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° **(kJ mol⁻)**	ΔG_f° **(kJ mol^{-1})**	S_{298}° **(J K^{-1} mol^{-1})**
$Cu_2O(s)$	−168.6	−146.0	93.14
CuS(s)	−53.1	−53.6	66.5
$Cu_2S(s)$	−79.5	−86.2	120.9
$CuSO_4(s)$	−771.36	−662.2	109.2
$Cu(NO_3)_2(s)$	−302.9	—	—
fluorine			
$F_2(g)$	0	0	202.8
F(*g*)	79.4	62.3	158.8
$F_2O(g)$	24.7	41.9	247.43
HF(*g*)	−273.3	−275.4	173.8
hydrogen			
$H_2(g)$	0	0	130.7
H(*g*)	217.97	203.26	114.7
$H_2O(l)$	−285.83	−237.1	70.0
$H_2O(g)$	−241.82	−228.59	188.8
$H_2O_2(l)$	−187.78	−120.35	109.6
$H_2O_2(g)$	−136.3	−105.6	232.7
HF(*g*)	−273.3	−275.4	173.8
HCl(*g*)	−92.307	−95.299	186.9
HBr(*g*)	−36.3	−53.43	198.7
HI(*g*)	26.48	1.70	206.59
$H_2S(g)$	−20.6	−33.4	205.8
$H_2Se(g)$	29.7	15.9	219.0
iodine			
$I_2(s)$	0	0	116.14
$I_2(g)$	62.438	19.3	260.7
I(*g*)	106.84	70.2	180.8
IF(*g*)	95.65	−118.49	236.06
ICl(*g*)	17.78	−5.44	247.44
IBr(*g*)	40.84	3.72	258.66
$IF_7(g)$	−943.91	−818.39	346.44
HI(*g*)	26.48	1.70	206.59
iron			
Fe(s)	0	0	27.3
Fe(*g*)	416.3	370.7	180.5

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° **(kJ mol⁻)**	ΔG_f° **(kJ mol^{-1})**	S_{298}° **(J K^{-1} mol^{-1})**
$Fe_2O_3(s)$	−824.2	−742.2	87.40
$Fe_3O_4(s)$	−1118.4	−1015.4	146.4
$Fe(CO)_5(l)$	−774.04	−705.42	338.07
$Fe(CO)_5(g)$	−733.87	−697.26	445.18
$FeCl_2(s)$	−341.79	−302.30	117.95
$FeCl_3(s)$	−399.49	−334.00	142.3
FeO(s)	−272.0	−255.2	60.75
$Fe(OH)_2(s)$	−569.0	−486.5	88.
$Fe(OH)_3(s)$	−823.0	−696.5	106.7
FeS(s)	−100.0	−100.4	60.29
$Fe_3C(s)$	25.10	20.08	104.60
lead			
Pb(s)	0	0	64.81
Pb(g)	195.2	162.	175.4
PbO(s) (yellow)	−217.32	−187.89	68.70
PbO(s) (red)	−218.99	−188.93	66.5
$Pb(OH)_2(s)$	−515.9	—	—
PbS(s)	−100.4	−98.7	91.2
$Pb(NO_3)_2(s)$	−451.9	—	—
$PbO_2(s)$	−277.4	−217.3	68.6
$PbCl_2(s)$	−359.4	−314.1	136.0
lithium			
Li(s)	0	0	29.1
Li(g)	159.3	126.6	138.8
LiH(s)	−90.5	−68.3	20.0
Li(OH)(s)	−487.5	−441.5	42.8
LiF(s)	−616.0	−587.5	35.7
$Li_2CO_3(s)$	−1216.04	−1132.19	90.17
manganese			
Mn(s)	0	0	32.0
Mn(g)	280.7	238.5	173.7
MnO(s)	−385.2	−362.9	59.71
$MnO_2(s)$	−520.03	−465.1	53.05
$Mn_2O_3(s)$	−958.97	−881.15	110.46
$Mn_3O_4(s)$	−1378.83	−1283.23	155.64

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° (kJ mol^{-})	ΔG_f° (kJ mol^{-1})	S_{298}° (J K^{-1} mol^{-1})
mercury			
Hg(*l*)	0	0	75.9
Hg(*g*)	61.4	31.8	175.0
HgO(s) (red)	−90.83	−58.5	70.29
HgO(s) (yellow)	−90.46	−58.43	71.13
$HgCl_2$(s)	−224.3	−178.6	146.0
Hg_2Cl_2(s)	−265.4	−210.7	191.6
HgS(s) (red)	−58.16	−50.6	82.4
HgS(s) (black)	−53.56	−47.70	88.28
$HgSO_4$(s)	−707.51	−594.13	0.00
nitrogen			
N_2(*g*)	0	0	191.6
N(*g*)	472.704	455.5	153.3
NO(*g*)	90.25	87.6	210.8
NO_2(*g*)	33.2	51.30	240.1
N_2O(*g*)	81.6	103.7	220.0
N_2O_3(*g*)	83.72	139.41	312.17
N_2O_4(*g*)	11.1	99.8	304.4
N_2O_5(*g*)	11.3	115.1	355.7
NH_3(*g*)	−45.9	−16.5	192.8
N_2H_4(*l*)	50.63	149.43	121.21
N_2H_4(*g*)	95.4	159.4	238.5
NH_4NO_3(s)	−365.56	−183.87	151.08
NH_4Cl(s)	−314.43	−202.87	94.6
NH_4Br(s)	−270.8	−175.2	113.0
NH_4I(s)	−201.4	−112.5	117.0
NH_4NO_2(s)	−256.5	—	—
HNO_3(*l*)	−174.1	−80.7	155.6
HNO_3(*g*)	−133.9	−73.5	266.9
oxygen			
O_2(*g*)	0	0	205.2
O(*g*)	249.17	231.7	161.1
O_3(*g*)	142.7	163.2	238.9
phosphorus			
P_4(s)	0	0	164.4

Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° **(kJ mol⁻)**	ΔG_f° **(kJ mol^{-1})**	S_{298}° **(J K^{-1} mol^{-1})**
$P_4(g)$	58.91	24.4	280.0
$P(g)$	314.64	278.25	163.19
$PH_3(g)$	5.4	13.5	210.2
$PCl_3(g)$	−287.0	−267.8	311.78
$PCl_5(g)$	−374.9	−305.0	364.4
$P_4O_6(s)$	−1640.1	—	—
$P_4O_{10}(s)$	−2984.0	−2697.0	228.86
$HPO_3(s)$	−948.5	—	—
$H_3PO_2(s)$	−604.6	—	—
$H_3PO_3(s)$	−964.4	—	—
$H_3PO_4(s)$	−1279.0	−1119.1	110.50
$H_3PO_4(l)$	−1266.9	−1124.3	110.5
$H_4P_2O_7(s)$	−2241.0	—	—
$POCl_3(l)$	−597.1	−520.8	222.5
$POCl_3(g)$	−558.5	−512.9	325.5
potassium			
K(s)	0	0	64.7
K(*g*)	89.0	60.5	160.3
KF(s)	−576.27	−537.75	66.57
KCl(s)	−436.5	−408.5	82.6
silicon			
Si(s)	0	0	18.8
Si(*g*)	450.0	405.5	168.0
$SiO_2(s)$	−910.7	−856.3	41.5
$SiH_4(g)$	34.3	56.9	204.6
$H_2SiO_3(s)$	−1188.67	−1092.44	133.89
$H_4SiO_4(s)$	−1481.14	−1333.02	192.46
$SiF_4(g)$	−1615.0	−1572.8	282.8
$SiCl_4(l)$	−687.0	−619.8	239.7
$SiCl_4(g)$	−662.75	−622.58	330.62
SiC(s, *beta cubic*)	−73.22	−70.71	16.61
SiC(s, *alpha hexagonal*)	−71.55	−69.04	16.48
silver			
Ag(s)	0	0	42.55
Ag(*g*)	284.9	246.0	172.89

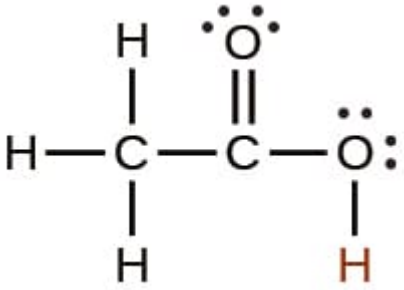
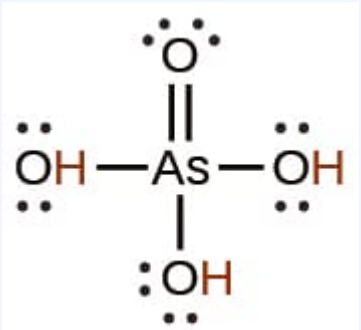
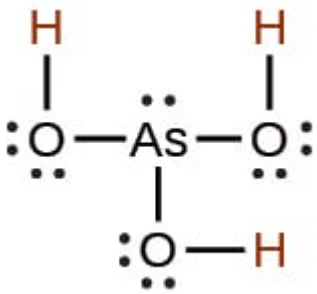
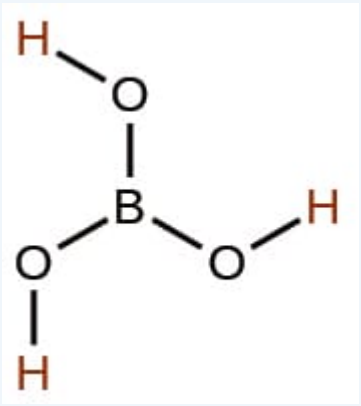
Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° **(kJ mol⁻)**	ΔG_f° **(kJ mol^{-1})**	S_{298}° **(J K^{-1} mol^{-1})**
$Ag_2O(s)$	−31.05	−11.20	121.3
AgCl(s)	−127.0	−109.8	96.3
$Ag_2S(s)$	−32.6	−40.7	144.0
sodium			
Na(s)	0	0	51.3
Na(*g*)	107.5	77.0	153.7
$Na_2O(s)$	−414.2	−375.5	75.1
NaCl(s)	−411.2	−384.1	72.1
sulfur			
$S_8(s)$ (rhombic)	0	0	256.8
S(*g*)	278.81	238.25	167.82
$SO_2(g)$	−296.83	−300.1	248.2
$SO_3(g)$	−395.72	−371.06	256.76
$H_2S(g)$	−20.6	−33.4	205.8
$H_2SO_4(l)$	−813.989	690.00	156.90
$H_2S_2O_7(s)$	−1273.6	—	—
$SF_4(g)$	−728.43	−684.84	291.12
$SF_6(g)$	−1220.5	−1116.5	291.5
$SCl_2(l)$	−50	—	—
$SCl_2(g)$	−19.7	—	—
$S_2Cl_2(l)$	−59.4	—	—
$S_2Cl_2(g)$	−19.50	−29.25	319.45
$SOCl_2(g)$	−212.55	−198.32	309.66
$SOCl_2(l)$	−245.6	—	—
$SO_2Cl_2(l)$	−394.1	—	—
SO_2Cl_2(g)	−354.80	−310.45	311.83
tin			
Sn(s)	0	0	51.2
Sn(*g*)	301.2	266.2	168.5
SnO(s)	−285.8	−256.9	56.5
$SnO_2(s)$	−577.6	−515.8	49.0
$SnCl_4(l)$	−511.3	−440.1	258.6
$SnCl_4(g)$	−471.5	−432.2	365.8
titanium			
Ti(s)	0	0	30.7

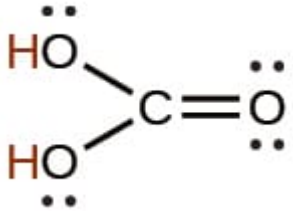
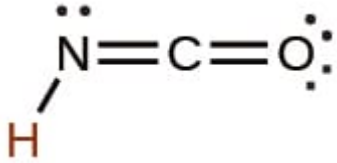
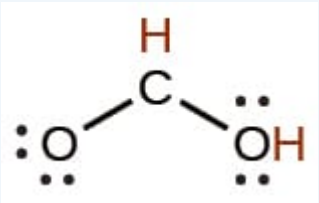
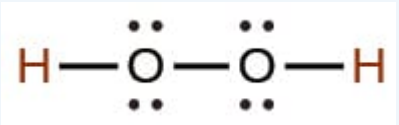
Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° **(kJ mol⁻)**	ΔG_f° **(kJ mol^{-1})**	S_{298}° **(J K^{-1} mol^{-1})**
Ti(*g*)	473.0	428.4	180.3
TiO_2(s)	−944.0	−888.8	50.6
$TiCl_4$(*l*)	−804.2	−737.2	252.4
$TiCl_4$(*g*)	−763.2	−726.3	353.2
tungsten			
W(s)	0	0	32.6
W(*g*)	849.4	807.1	174.0
WO_3(s)	−842.9	−764.0	75.9
zinc			
Zn(s)	0	0	41.6
Zn(*g*)	130.73	95.14	160.98
ZnO(s)	−350.5	−320.5	43.7
$ZnCl_2$(s)	−415.1	−369.43	111.5
ZnS(s)	−206.0	−201.3	57.7
$ZnSO_4$(s)	−982.8	−871.5	110.5
$ZnCO_3$(s)	−812.78	−731.57	82.42
complexes			
$[Co(NH_3)_4(NO_2)_2]NO_3$, *cis*	−898.7	—	—
$[Co(NH_3)_4(NO_2)_2]NO_3$, *trans*	−896.2	—	—
$NH_4[Co(NH_3)_2(NO_2)_4]$	−837.6	—	—
$[Co(NH_3)_6][Co(NH_3)_2(NO_2)_4]_3$	−2733.0	—	—
$[Co(NH_3)_4Cl_2]Cl$, *cis*	−874.9	—	—
$[Co(NH_3)_4Cl_2]Cl$, *trans*	−877.4	—	—
$[Co(en)_2(NO_2)_2]NO_3$, *cis*	−689.5	—	—
$[Co(en)_2Cl_2]Cl$, *cis*	−681.2	—	—
$[Co(en)_2Cl_2]Cl$, *trans*	−677.4	—	—
$[Co(en)_3](ClO_4)_3$	−762.7	—	—
$[Co(en)_3]Br_2$	−595.8	—	—
$[Co(en)_3]I_2$	−475.3	—	—
$[Co(en)_3]I_3$	−519.2	—	—
$[Co(NH_3)_6](ClO_4)_3$	−1034.7	−221.1	615
$[Co(NH_3)_5NO_2](NO_3)_2$	−1088.7	−412.9	331
$[Co(NH_3)_6](NO_3)_3$	−1282.0	−524.5	448
$[Co(NH_3)_5Cl]Cl_2$	−1017.1	−582.5	366.1

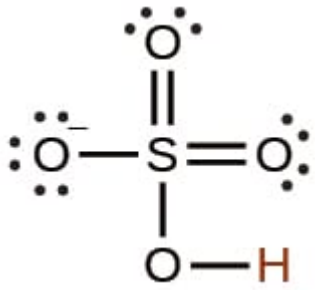
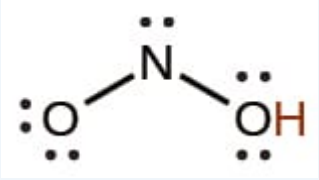
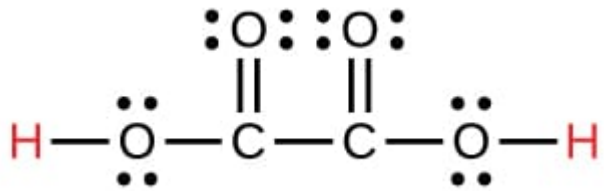
Standard Thermodynamic Properties for Selected Substances			
Substance	ΔH_f° **(kJ mol⁻)**	ΔG_f° **(kJ mol^{-1})**	S_{298}° **(J K^{-1} mol^{-1})**
$[Pt(NH_3)_4]Cl_2$	–725.5	—	—
$[Ni(NH_3)_6]Cl_2$	–994.1	—	—
$[Ni(NH_3)_6]Br_2$	–923.8	—	—
$[Ni(NH_3)_6]I_2$	–808.3	—	—

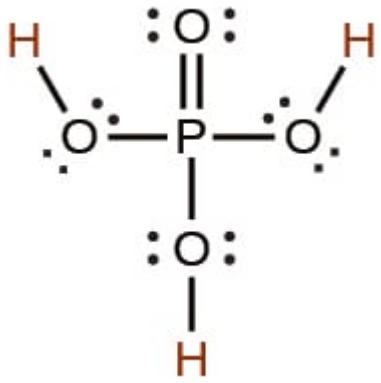
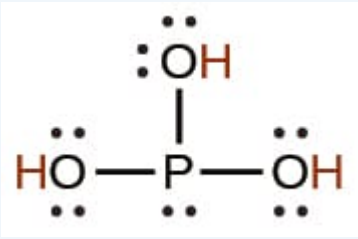
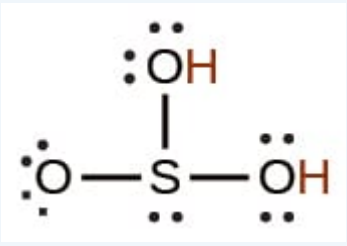
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11.8: Ionization Constants of Weak Acids

Ionization Constants of Weak Acids			
Acid	**Formula**	**K_a at 25 °C**	**Lewis Structure**
acetic	$CH_3CO_2\mathbf{H}$	1.8×10^{-5}	
arsenic	$\mathbf{H_3}AsO_4$	5.5×10^{-3}	
	$H_2AsO_4^-$	1.7×10^{-7}	
	$HAsO_4^{2-}$	5.1×10^{-12}	
arsenous	$\mathbf{H_3}AsO_3$	5.1×10^{-10}	
boric	$\mathbf{H_3}BO_3$	5.4×10^{-10}	

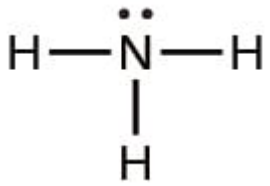
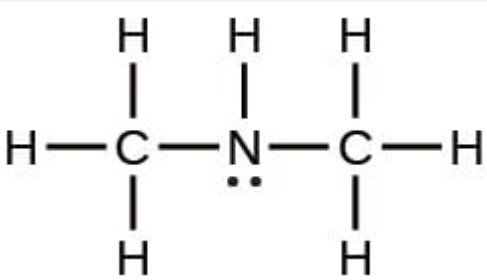
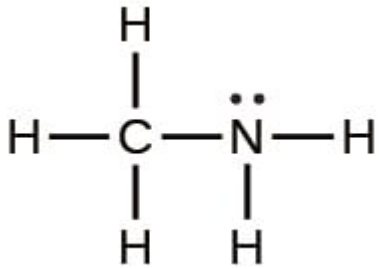
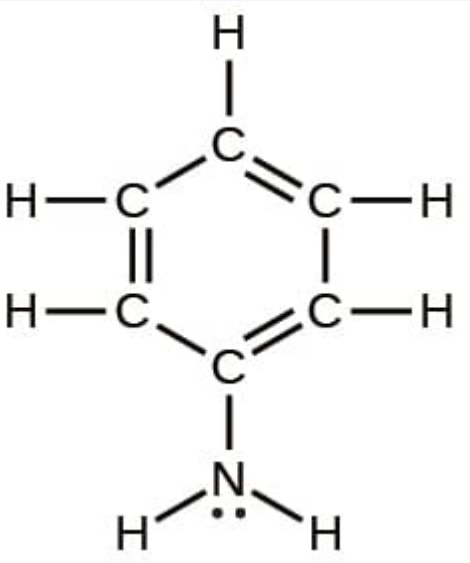
Ionization Constants of Weak Acids			
Acid	**Formula**	K_a at 25 °C	**Lewis Structure**
carbonic	$\mathbf{H_2}CO_3$	4.3×10^{-7}	
	HCO_3^-	5.6×10^{-11}	
cyanic	**H**CNO	2×10^{-4}	
formic	$HCO_2\mathbf{H}$	1.8×10^{-4}	
hydrazoic	$\mathbf{H}N_3$	2.5×10^{-5}	
hydrocyanic	**H**CN	4.9×10^{-10}	
hydrofluoric	**H**F	3.5×10^{-4}	
hydrogen peroxide	$\mathbf{H_2}O_2$	2.4×10^{-12}	
hydrogen selenide	$\mathbf{H_2}Se$	1.29×10^{-4}	
	$\mathbf{H}Se^-$	1×10^{-12}	

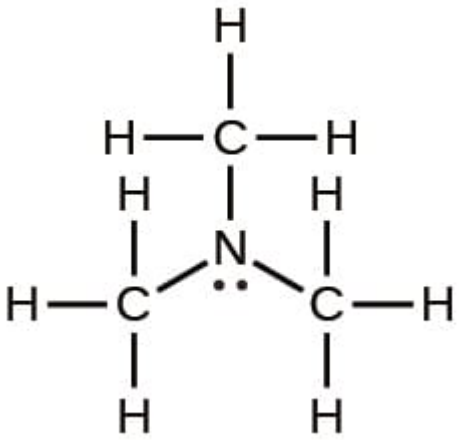
Ionization Constants of Weak Acids			
Acid	**Formula**	**K_a at 25 °C**	**Lewis Structure**
hydrogen sulfate ion	HSO_4^-	1.2×10^{-2}	
hydrogen sulfide	$\mathbf{H_2}S$	8.9×10^{-8}	
	$\mathbf{H}S^-$	1.0×10^{-19}	
hydrogen telluride	$\mathbf{H_2}Te$	2.3×10^{-3}	
	$\mathbf{H}Te^-$	1.6×10^{-11}	
hypobromous	$\mathbf{H}BrO$	2.8×10^{-9}	
hypochlorous	$\mathbf{H}ClO$	2.9×10^{-8}	
nitrous	$\mathbf{H}NO_2$	4.6×10^{-4}	
oxalic	$\mathbf{H_2}C_2O_4$	6.0×10^{-2}	
	$HC_2O_4^-$	6.1×10^{-5}	

Ionization Constants of Weak Acids			
Acid	**Formula**	K_a at 25 °C	**Lewis Structure**
phosphoric	$\mathbf{H_3PO_4}$	7.5×10^{-3}	
	$H_2PO_4^-$	6.2×10^{-8}	
	HPO_4^{2-}	4.2×10^{-13}	
phosphorous	$\mathbf{H_3PO_3}$	5×10^{-2}	
	$H_2PO_3^-$	2.0×10^{-7}	
sulfurous	$\mathbf{H_2SO_3}$	1.6×10^{-2}	
	HSO_3^-	6.4×10^{-8}	

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11.9: Ionization Constants of Weak Bases

Ionization Constants of Weak Bases		
Base	**Lewis Structure**	**K_b at 25 °C**
ammonia		1.8×10^{-5}
dimethylamine		5.9×10^{-4}
methylamine		4.4×10^{-4}
phenylamine (aniline)		4.3×10^{-10}

Ionization Constants of Weak Bases		
Base	**Lewis Structure**	**K_b at 25 °C**
trimethylamine		6.3×10^{-5}

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11.10: Solubility Products

Solubility Products	
Substance	**K_{sp} at 25 °C**
aluminum	
$Al(OH)_3$	2×10^{-32}
barium	
$BaCO_3$	1.6×10^{-9}
$BaC_2O_4 \cdot 2H_2O$	1.1×10^{-7}
$BaSO_4$	2.3×10^{-8}
$BaCrO_4$	8.5×10^{-11}
BaF_2	2.4×10^{-5}
$Ba(OH)_2 \cdot 8H_2O$	5.0×10^{-3}
$Ba_3(PO_4)_2$	6×10^{-39}
$Ba_3(AsO_4)_2$	1.1×10^{-13}
bismuth	
BiO(OH)	4×10^{-10}
BiOCl	1.8×10^{-31}
Bi_2S_3	1×10^{-97}
cadmium	
$Cd(OH)_2$	5.9×10^{-15}
CdS	1.0×10^{-28}
$CdCO_3$	5.2×10^{-12}
calcium	
$Ca(OH)_2$	1.3×10^{-6}
$CaCO_3$	8.7×10^{-9}
$CaSO4 \cdot 2H_2O$	6.1×10^{-5}
$CaC_2O_4 \cdot H_2O$	1.96×10^{-8}
$Ca_3(PO_4)_2$	1.3×10^{-32}
$CaHPO_4$	7×10^{-7}
CaF_2	4.0×10^{-11}
chromium	
$Cr(OH)_3$	6.7×10^{-31}

Solubility Products	
Substance	**K_{sp} at 25 °C**
cobalt	
$Co(OH)_2$	2.5×10^{-16}
$CoS(\alpha)$	5×10^{-22}
$CoS(\beta)$	3×10^{-26}
$CoCO_3$	1.4×10^{-13}
$Co(OH)_3$	2.5×10^{-43}
copper	
CuCl	1.2×10^{-6}
CuBr	6.27×10^{-9}
CuI	1.27×10^{-12}
CuSCN	1.6×10^{-11}
Cu_2S	2.5×10^{-48}
$Cu(OH)_2$	2.2×10^{-20}
CuS	8.5×10^{-45}
$CuCO_3$	2.5×10^{-10}
iron	
$Fe(OH)_2$	1.8×10^{-15}
$FeCO_3$	2.1×10^{-11}
FeS	3.7×10^{-19}
$Fe(OH)_3$	4×10^{-38}
lead	
$Pb(OH)_2$	1.2×10^{-15}
PbF_2	4×10^{-8}
$PbCl_2$	1.6×10^{-5}
$PbBr_2$	4.6×10^{-6}
PbI_2	1.4×10^{-8}
$PbCO_3$	1.5×10^{-15}
PbS	7×10^{-29}
$PbCrO_4$	2×10^{-16}
$PbSO_4$	1.3×10^{-8}
$Pb_3(PO_4)_2$	1×10^{-54}

Solubility Products	
Substance	**K_{sp} at 25 °C**
magnesium	
$Mg(OH)_2$	8.9×10^{-12}
$MgCO_3 \cdot 3H_2O$	*ca* 1×10^{-5}
$MgNH_4PO_4$	3×10^{-13}
MgF_2	6.4×10^{-9}
MgC_2O_4	7×10^{-7}
manganese	
$Mn(OH)_2$	2×10^{-13}
$MnCO_3$	8.8×10^{-11}
MnS	2.3×10^{-13}
mercury	
$Hg_2O \cdot H_2O$	3.6×10^{-26}
Hg_2Cl_2	1.1×10^{-18}
Hg_2Br_2	1.3×10^{-22}
Hg_2I_2	4.5×10^{-29}
Hg_2CO_3	9×10^{-15}
Hg_2SO_4	7.4×10^{-7}
Hg_2S	1.0×10^{-47}
Hg_2CrO_4	2×10^{-9}
HgS	1.6×10^{-54}
nickel	
$Ni(OH)_2$	1.6×10^{-16}
$NiCO_3$	1.4×10^{-7}
NiS(α)	4×10^{-20}
NiS(β)	1.3×10^{-25}
potassium	
$KClO_4$	1.05×10^{-2}
K_2PtCl_6	7.48×10^{-6}
$KHC_4H_4O_6$	3×10^{-4}
silver	
$\frac{1}{2}Ag_2O(Ag^+ + OH^-)$	2×10^{-8}
AgCl	1.6×10^{-10}

Solubility Products	
Substance	**K_{sp} at 25 °C**
$AgBr$	5.0×10^{-13}
AgI	1.5×10^{-16}
$AgCN$	1.2×10^{-16}
$AgSCN$	1.0×10^{-12}
Ag_2S	1.6×10^{-49}
Ag_2CO_3	8.1×10^{-12}
Ag_2CrO_4	9.0×10^{-12}
$Ag_4Fe(CN)_6$	1.55×10^{-41}
Ag_2SO_4	1.2×10^{-5}
Ag_3PO_4	1.8×10^{-18}
strontium	
$Sr(OH)_2 \cdot 8H_2O$	3.2×10^{-4}
$SrCO_3$	7×10^{-10}
$SrCrO_4$	3.6×10^{-5}
$SrSO_4$	3.2×10^{-7}
$SrC_2O_4 \cdot H_2O$	4×10^{-7}
thallium	
$TlCl$	1.7×10^{-4}
$TlSCN$	1.6×10^{-4}
Tl_2S	6×10^{-22}
$Tl(OH)_3$	6.3×10^{-46}
tin	
$Sn(OH)_2$	3×10^{-27}
SnS	1×10^{-26}
$Sn(OH)_4$	1.0×10^{-57}
zinc	
$ZnCO_3$	2×10^{-10}

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11.11: Formation Constants for Complex Ions

Formation Constants for Complex Ions	
Equilibrium	K_f
$Al^{3+} + 6\,F^- \rightleftharpoons [AlF_6]^{3-}$	7×10^{19}
$Cd^{2+} + 4\,NH_3 \rightleftharpoons [Cd(NH_3)_4]^{2+}$	1.3×10^{7}
$Cd^{2+} + 4\,CN^- \rightleftharpoons [Cd(CN)_4]^{2-}$	3×10^{18}
$Co^{2+} + 6\,NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+}$	1.3×10^{5}
$Co^{3+} + 6\,NH_3 \rightleftharpoons [Co(NH_3)_6]^{3+}$	2.3×10^{33}
$Cu^{+} + 2\,CN \rightleftharpoons [Cu(CN)_2]^-$	1.0×10^{16}
$Cu^{2+} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	1.7×10^{13}
$Fe^{2+} + 6\,CN^- \rightleftharpoons [Fe(CN)_6]^{4-}$	1.5×10^{35}
$Fe^{3+} + 6\,CN^- \rightleftharpoons [Fe(CN)_6]^{3-}$	2×10^{43}
$Fe^{3+} + 6\,SCN^- \rightleftharpoons [Fe(SCN)_6]^{3-}$	3.2×10^{3}
$Hg^{2+} + 4\,Cl^- \rightleftharpoons [HgCl_4]^{2-}$	1.1×10^{16}
$Ni^{2+} + 6\,NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}$	2.0×10^{8}
$Ag^{+} + 2\,Cl^- \rightleftharpoons [AgCl_2]^-$	1.8×10^{5}
$Ag^{+} + 2\,CN^- \rightleftharpoons [Ag(CN)_2]^-$	1×10^{21}
$Ag^{+} + 2\,NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$	1.7×10^{7}
$Zn^{2+} + 4\,CN^- \rightleftharpoons [Zn(CN)_4]^{2-}$	2.1×10^{19}
$Zn^{2+} + 4\,OH^- \rightleftharpoons [Zn(OH)_4]^{2-}$	2×10^{15}
$Fe^{3+} + SCN^- \rightleftharpoons [Fe(SCN)]^{2+}$	8.9×10^{2}
$Ag^{+} + 4\,SCN^- \rightleftharpoons [Ag(SCN)_4]^{3-}$	1.2×10^{10}
$Pb^{2+} + 4\,I^- \rightleftharpoons [PbI_4]^{2-}$	3.0×10^{4}
$Pt^{2+} + 4\,Cl^- \rightleftharpoons [PtCl_4]^{2-}$	1×10^{16}
$Cu^{2+} + 4\,CN \rightleftharpoons [Cu(CN)_4]^{2-}$	1.0×10^{25}
$Co^{2+} + 4\,SCN^- \rightleftharpoons [Co(SCN)_4]^{2-}$	1×10^{3}

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11.12: Standard Electrode (Half-Cell) Potentials

Standard Electrode (Half-Cell) Potentials	
Half-Reaction	***E*° (V)**
$Ag^+ + e^- \longrightarrow Ag$	+0.7996
$AgCl + e^- \longrightarrow Ag + Cl^-$	+0.22233
$[Ag(CN)_2]^- + e^- \longrightarrow Ag + 2\,CN^-$	−0.31
$Ag_2CrO_4 + 2\,e^- \longrightarrow 2\,Ag + {CrO_4}^{2-}$	+0.45
$[Ag(NH_3)_2]^+ + e^- \longrightarrow Ag + 2\,NH_3$	+0.373
$[Ag(S_2O_3)_2]^{3+} + e^- \longrightarrow Ag + 2\,{S_2O_3}^{2-}$	+0.017
$[AlF_6]^{3-} + 3\,e^- \longrightarrow Al + 6\,F^-$	−2.07
$Al^{3+} + 3\,e^- \longrightarrow Al$	−1.662
$Am^{3+} + 3\,e^- \longrightarrow Am$	−2.048
$Au^{3+} + 3\,e^- \longrightarrow Au$	+1.498
$Au^+ + e^- \longrightarrow Au$	+1.692
$Ba^{2+} + 2\,e^- \longrightarrow Ba$	−2.912
$Be^{2+} + 2\,e^- \longrightarrow Be$	−1.847
$Br_2(aq) + 2\,e^- \longrightarrow 2\,Br^-$	+1.0873
$Ca^{2+} + 2\,e^- \longrightarrow Ca$	−2.868
$Ce^3 + 3\,e^- \longrightarrow Ce$	−2.483
$Ce^{4+} + e^- \longrightarrow Ce^{3+}$	+1.61
$Cd^{2+} + 2\,e^- \longrightarrow Cd$	−0.4030
$[Cd(CN)_4]^{2-} + 2\,e^- \longrightarrow Cd + 4\,CN^-$	−1.09
$[Cd(NH_3)_4]^{2+} + 2\,e^- \longrightarrow Cd + 4\,NH_3$	−0.61
$CdS + 2\,e^- \longrightarrow Cd + S^{2-}$	−1.17
$Cl_2 + 2\,e^- \longrightarrow 2\,Cl^-$	+1.35827
$ClO_4^- + H_2O + 2\,e^- \longrightarrow ClO_3^- + 2\,OH^-$	+0.36
$ClO_3^- + H_2O + 2\,e^- \longrightarrow ClO_2^- + 2\,OH^-$	+0.33
$ClO_2^- + H_2O + 2\,e^- \longrightarrow ClO^- + 2\,OH^-$	+0.66
$ClO^- + H_2O + 2\,e^- \longrightarrow Cl^- + 2\,OH^-$	+0.89
$ClO_4^- + 2\,H_3O^+ + 2\,e^- \longrightarrow ClO_3^- + 3\,H_2O$	+1.189
$ClO_3^- + 3\,H_3O^+ + 2\,e^- \longrightarrow HClO_2 + 4\,H_2O$	+1.21
$HClO + H_3O^+ + 2\,e^- \longrightarrow Cl^- + 2\,H_2O$	+1.482
$HClO + H_3O^+ + e^- \longrightarrow \frac{1}{2}Cl_2 + 2\,H_2O$	+1.611
$HClO_2 + 2\,H_3O^+ + 2\,e^- \longrightarrow HClO + 3\,H_2O$	+1.628
$Co^{3+} + e^- \longrightarrow Co^{2+}\ \ (2\,mol\,//\,H_2SO_4)$	+1.83

Standard Electrode (Half-Cell) Potentials	
Half-Reaction	***E*° (V)**
$Co^{2+} + 2\,e^- \longrightarrow Co$	−0.28
$[Co(NH_3)_6]^{3+} + e^- \xrightarrow{Co(NH_3)_6} {}^{2+}$	+0.1
$Co(OH)_3 + e^- \longrightarrow Co(OH)_2 + OH^-$	+0.17
$Cr^3 + 3\,e^- \longrightarrow Cr$	−0.744
$Cr^{3+} + e^- \longrightarrow Cr^{2+}$	−0.407
$Cr^{2+} + 2\,e^- \longrightarrow Cr$	−0.913
$[Cu(CN)_2]^- + e^- \longrightarrow Cu + 2\,CN^-$	−0.43
$CrO_4{}^{2-} + 4\,H_2O + 3\,e^- \longrightarrow Cr(OH)_3 + 5\,OH^-$	−0.13
$Cr_2O_7{}^{2-} + 14\,H_3O^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 21\,H_2O$	+1.232
$[Cr(OH)_4]^- + 3\,e^- \longrightarrow Cr + 4\,OH^-$	−1.2
$Cr(OH)_3 + 3\,e^- \longrightarrow Cr + 3\,OH^-$	−1.48
$Cu^{2+} + e^- \longrightarrow Cu^+$	+0.153
$Cu^{2+} + 2\,e^- \longrightarrow Cu$	+0.34
$Cu^+ + e^- \longrightarrow Cu$	+0.521
$F_2 + 2\,e^- \longrightarrow 2\,F^-$	+2.866
$Fe^{2+} + 2\,e^- \longrightarrow Fe$	−0.447
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+0.771
$[Fe(CN)_6]^{3-} + e^- \xrightarrow{Fe(CN)_6} {}^{4-}$	+0.36
$Fe(OH)_2 + 2\,e^- \longrightarrow Fe + 2\,OH^-$	−0.88
$FeS + 2\,e^- \longrightarrow Fe + S^{2-}$	−1.01
$Ga^{3+} + 3\,e^- \longrightarrow Ga$	−0.549
$Gd^{3+} + 3\,e^- \longrightarrow Gd$	−2.279
$\frac{1}{2}H_2 + e^- \longrightarrow H^-$	−2.23
$2\,H_2O + 2\,e^- \longrightarrow H_2 + 2\,OH^-$	−0.8277
$H_2O_2 + 2\,H_3O^+ + 2\,e^- \longrightarrow 4\,H_2O$	+1.776
$2\,H_3O^+ + 2\,e^- \longrightarrow H_2 + 2\,H_2O$	0.00
$HO_2{}^- + H_2O + 2\,e^- \longrightarrow 3\,OH^-$	+0.878
$Hf^{4+} + 4\,e^- \longrightarrow Hf$	−1.55
$Hg^{2+} + 2\,e^- \longrightarrow Hg$	+0.851
$2\,Hg^{2+} + 2\,e^- \longrightarrow Hg_2{}^{2+}$	+0.92
$Hg_2{}^{2+} + 2\,e^- \longrightarrow 2\,Hg$	+0.7973
$[HgBr_4]^{2-} + 2\,e^- \longrightarrow Hg + 4\,Br^-$	+0.21
$Hg_2Cl_2 + 2\,e^- \longrightarrow 2\,Hg + 2\,Cl^-$	+0.26808
$[Hg(CN)_4]^{2-} + 2\,e^- \longrightarrow Hg + 4\,CN^-$	−0.37
$[HgI_4]^{2-} + 2\,e^- \longrightarrow Hg + 4\,I^-$	−0.04

Standard Electrode (Half-Cell) Potentials	
Half-Reaction	***E*° (V)**
$HgS + 2\,e^- \longrightarrow Hg + S^{2-}$	−0.70
$I_2 + 2\,e^- \longrightarrow 2\,I^-$	+0.5355
$In^{3+} + 3\,e^- \longrightarrow In$	−0.3382
$K^+ + e^- \longrightarrow K$	−2.931
$La^{3+} + 3\,e^- \longrightarrow La$	−2.52
$Li^+ + e^- \longrightarrow Li$	−3.04
$Lu^{3+} + 3\,e^- \longrightarrow Lu$	−2.28
$Mg^{2+} + 2\,e^- \longrightarrow Mg$	−2.372
$Mn^{2+} + 2\,e^- \longrightarrow Mn$	−1.185
$MnO_2 + 2\,H_2O + 2\,e^- \longrightarrow Mn(OH)_2 + 2\,OH^-$	−0.05
$MnO_4^- + 2\,H_2O + 3\,e^- \longrightarrow MnO_2 + 4\,OH^-$	+0.558
$MnO_2 + 4\,H^+ + 2\,e^- \longrightarrow Mn^{2+} + 2\,H_2O$	+1.23
$MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O$	+1.507
$Na^+ + e^- \longrightarrow Na$	−2.71
$Nd^{3+} + 3\,e^- \longrightarrow Nd$	−2.323
$Ni^{2+} + 2\,e^- \longrightarrow Ni$	−0.257
$[Ni(NH_3)_6]^{2+} + 2\,e^- \longrightarrow Ni + 6\,NH_3$	−0.49
$NiO_2 + 4\,H^+ + 2\,e^- \longrightarrow Ni^{2+} + 2\,H_2O$	+1.593
$NiO_2 + 2\,H_2O + 2\,e^- \longrightarrow Ni(OH)_2 + 2\,OH^-$	+0.49
$NiS + 2\,e^- \longrightarrow Ni + S^{2-}$	+0.76
$NO_3^- + 4\,H^+ + 3\,e^- \longrightarrow NO + 2\,H_2O$	+0.957
$NO_3^- + 3\,H^+ + 2\,e^- \longrightarrow HNO_2 + H_2O$	+0.92
$NO_3^- + H_2O + 2\,e^- \longrightarrow NO_2^- + 2\,OH^-$	+0.10
$Np^{3+} + 3\,e^- \longrightarrow Np$	−1.856
$O_2 + 2\,H_2O + 4\,e^- \longrightarrow 4\,OH^-$	+0.401
$O_2 + 2\,H^+ + 2\,e^- \longrightarrow H_2O_2$	+0.695
$O_2 + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O$	+1.229
$Pb^{2+} + 2\,e^- \longrightarrow Pb$	−0.1262
$PbO_2 + SO_4^{2-} + 4\,H^+ + 2\,e^- \longrightarrow PbSO_4 + 2\,H_2O$	+1.69
$PbS + 2\,e^- \longrightarrow Pb + S^{2-}$	−0.95
$PbSO_4 + 2\,e^- \longrightarrow Pb + SO_4^{2-}$	−0.3505
$Pd^{2+} + 2\,e^- \longrightarrow Pd$	+0.987
$[PdCl_4]^{2-} + 2\,e^- \longrightarrow Pd + 4\,Cl^-$	+0.591
$Pt^{2+} + 2\,e^- \longrightarrow Pt$	+1.20
$[PtBr_4]^{2-} + 2\,e^- \longrightarrow Pt + 4\,Br^-$	+0.58
$[PtCl_4]^{2-} + 2\,e^- \longrightarrow Pt + 4\,Cl^-$	+0.755

Standard Electrode (Half-Cell) Potentials	
Half-Reaction	***E*° (V)**
$[PtCl_6]^{2-} + 2\,e^- \xrightarrow{PtCl_4} {}^{2-} + 2\,Cl^-$	+0.68
$Pu^3 + 3\,e^- \longrightarrow Pu$	−2.03
$Ra^{2+} + 2\,e^- \longrightarrow Ra$	−2.92
$Rb^+ + e^- \longrightarrow Rb$	−2.98
$[RhCl_6]^{3-} + 3\,e^- \longrightarrow Rh + 6\,Cl^-$	+0.44
$S + 2\,e^- \longrightarrow S^{2-}$	−0.47627
$S + 2\,H^+ + 2\,e^- \longrightarrow H_2S$	+0.142
$Sc^{3+} + 3\,e^- \longrightarrow Sc$	−2.09
$Se + 2\,H^+ + 2\,e^- \longrightarrow H_2Se$	−0.399
$[SiF_6]^{2-} + 4\,e^- \longrightarrow Si + 6\,F^-$	−1.2
$SiO_3{}^{2-} + 3\,H_2O + 4\,e^- \longrightarrow Si + 6\,OH^-$	−1.697
$SiO_2 + 4\,H^+ + 4\,e^- \longrightarrow Si + 2\,H_2O$	−0.86
$Sm^{3+} + 3\,e^- \longrightarrow Sm$	−2.304
$Sn^{4+} + 2\,e^- \longrightarrow Sn^{2+}$	+0.151
$Sn^{2+} + 2\,e^- \longrightarrow Sn$	−0.1375
$[SnF_6]^{2-} + 4\,e^- \longrightarrow Sn + 6\,F^-$	−0.25
$SnS + 2\,e^- \longrightarrow Sn + S^{2-}$	−0.94
$Sr^{2+} + 2\,e^- \longrightarrow Sr$	−2.89
$TeO_2 + 4\,H^+ + 4\,e^- \longrightarrow Te + 2\,H_2O$	+0.593
$Th^{4+} + 4\,e^- \longrightarrow Th$	−1.90
$Ti^{2+} + 2\,e^- \longrightarrow Ti$	−1.630
$U^{3+} + 3\,e^- \longrightarrow U$	−1.79
$V^{2+} + 2\,e^- \longrightarrow V$	−1.19
$Y^{3+} + 3\,e^- \longrightarrow Y$	−2.37
$Zn^{2+} + 2\,e^- \longrightarrow Zn$	−0.7618
$[Zn(CN)_4]^{2-} + 2\,e^- \longrightarrow Zn + 4\,CN^-$	−1.26
$[Zn(NH_3)_4]^{2+} + 2\,e^- \longrightarrow Zn + 4\,NH_3$	−1.04
$Zn(OH)_2 + 2\,e^- \longrightarrow Zn + 2\,OH^-$	−1.245
$[Zn(OH)_4]^2 + 2\,e^- \longrightarrow Zn + 4\,OH^-$	−1.199
$ZnS + 2\,e^- \longrightarrow Zn + S^{2-}$	−1.40
$Zr^4 + 4\,e^- \longrightarrow Zr$	−1.539

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11.13: Half-Lives for Several Radioactive Isotopes

Isotope	Half-Life[1]	Type of Emission[2]	Isotope	Half-Life[3]	Type of Emission[4]
$^{14}_{6}C$	5730 y	(β^-)	$^{210}_{83}Bi$	5.01 d	(β^-)
$^{13}_{7}N$	9.97 m	(β^+)	$^{212}_{83}Bi$	60.55 m	$(\alpha\ or\ beta^-)$
$^{15}_{9}F$	$4.1 \times 10^{-22} s$	(p)	$^{210}_{84}Po$	138.4 d	(α)
$^{24}_{11}Na$	15.00 h	(β^-)	$^{212}_{84}Po$	$3 \times 10^{-7} s$	(α)
$^{32}_{15}P$	14.29 d	(β^-)	$^{216}_{84}Po$	0.15 s	(α)
$^{40}_{19}K$	$1.27 \times 10^{9} y$	$(\beta\ or\ E.C.)$	$^{218}_{84}Po$	3.05 m	(α)
$^{49}_{26}Fe$	0.08 s	(β^+)	$^{215}_{85}At$	$1.0 \times 10^{-4} s$	(α)
$^{60}_{26}Fe$	$2.6 \times 10^{6} y$	(β^-)	$^{218}_{85}At$	1.6 s	(α)
$^{60}_{27}Co$	5.27 y	(β^-)	$^{220}_{86}Rn$	55.6 s	(α)
$^{87}_{37}Rb$	$4.7 \times 10^{10} y$	(β^-)	$^{222}_{86}Rn$	3.82 d	(α)
$^{90}_{38}Sr$	29 y	(β^-)	$^{224}_{88}Ra$	3.66 d	(α)
$^{115}_{49}In$	$5.1 \times 10^{15} y$	(β^-)	$^{226}_{88}Ra$	1600 y	(α)
$^{131}_{53}I$	8.040 d	(β^-)	$^{228}_{88}Ra$	5.75 y	(β^-)
$^{142}_{58}Ce$	$5 \times 10^{15} y$	(α)	$^{228}_{89}Ac$	6.13 h	(β^-)
$^{208}_{81}Tl$	3.07 m	(β^-)	$^{228}_{90}Th$	$1.913y$	(α)
$^{210}_{82}Pb$	22.3 y	(β^-)	$^{232}_{90}Th$	$1.4 \times 10^{10} y$	(α)
$^{212}_{82}Pb$	10.6 h	(β^-)	$^{233}_{90}Th$	22 m	(β^-)
$^{214}_{82}Pb$	26.8 m	(β^-)	$^{234}_{90}Th$	24.10 d	(β^-)
$^{206}_{83}Bi$	6.243 d	$(E.C.)$	$^{233}_{91}Pa$	$27d$	(β^-)
$^{233}_{92}U$	$1.59 \times 10^{5} y$	(α)	$^{242}_{96}Cm$	162.8 d	(α)
$^{234}_{92}U$	$2.45 \times 10^{5} y$	(α)	$^{243}_{97}Bk$	4.5 h	$(\alpha\ or\ E.C.)$
$^{235}_{92}U$	$7.03 \times 10^{8} y$	(α)	$^{253}_{99}Es$	20.47 d	(α)
$^{238}_{92}U$	$4.47 \times 10^{9} y$	(α)	$^{254}_{100}Fm$	$3.24h$	$(\alpha\ or\ S.F.)$
$^{239}_{92}U$	23.54 m	(β^-)	$^{255}_{100}Fm$	20.1 h	(α)
$^{239}_{93}Np$	2.3 d	(β^-)	$^{256}_{101}Md$	76 m	$(\alpha\ or\ E.C.)$
$^{239}_{94}Pu$	$2.407 \times 10^{4} y$	(α)	$^{254}_{102}No$	55 s	(α)
$^{239}_{94}Pu$	$6.54 \times 10^{3} y$	(α)	$^{257}_{103}Lr$	0.65 s	(α)
$^{241}_{94}Pu$	14.4 y	$(\alpha\ or\ beta^-)$	$^{260}_{105}Ha$	1.5 s	$(\alpha\ or\ S.F.)$
$^{241}_{95}Am$	432.2 y	(α)	$^{263}_{106}Sg$	0.8 s	$(\alpha\ or\ S.F.)$

Footnotes

1. y = years, d = days, h = hours, m = minutes, s = seconds
2. *E.C.* = electron capture, *S.F.* = Spontaneous fission

3. y = years, d = days, h = hours, m = minutes, s = seconds
4. *E.C.* = electron capture, *S.F.* = Spontaneous fission

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11.14: ANSWER KEY

11.14.1: Chapter 1 - Atoms, Molecules and Ions

11.14.2: Chapter 2 - Electronic Structure and Periodic Properties

11.14.3: Chapter 3 - Chemical Bonding and Molecular Geometry

11.14.4: Chapter 4 - Advanced Theories of Bonding

11.14.5: Chapter 5 - Thermochemistry

11.14.6: Chapter 6 - Thermodynamics

11.14.7: Chapter 7 - Fundamental Equilibrium Concepts

11.14.8: Chapter 8 - Acid-Base Equilibria

11.14.9: Chapter 9 - Electrochemistry

11.14.10: Chapter 10 - Kinetics

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11.14.1: Chapter 1 - Atoms, Molecules and Ions

1.

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.

3.

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.

5.

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.

7.

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.

9.

(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).

11.

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

13.

(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.

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

17.

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

19.

(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

21.

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.

23.

79.90 amu

25.

Turkey source: 20.3% (of 10.0129 amu isotope); US source: 19.1% (of 10.0129 amu isotope)

27.

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.

29.

(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

31.

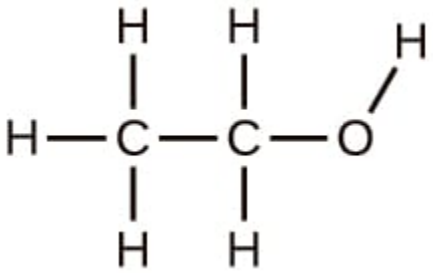
(a) $C_4H_5N_2O$; (b) $C_{12}H_{22}O_{11}$; (c) HO; (d) CH_2O; (e) $C_3H_4O_3$

33.

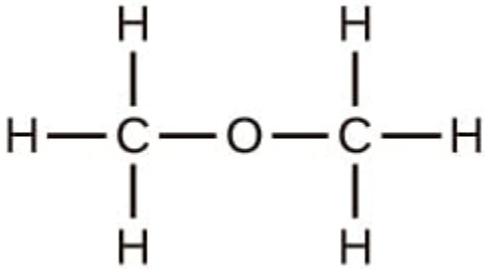
(a) CH_2O; (b) C_2H_4O

35.

(a) ethanol



(b) methoxymethane, more commonly known as dimethyl ether



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

37.

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.

39.

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.

41.

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.

43.

(a) 256.48 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}

45.

(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}

47.

(a) 0.819 g;
(b) 307 g;
(c) 0.23 g;
(d) 1.235×10^{6} g (1235 kg);
(e) 765 g

49.

(a) 99.41 g;
(b) 2.27 g;
(c) 3.5 g;
(d) 222 kg;
(e) 160.1 g

51.

(a) 9.60 g; (b) 19.2 g; (c) 28.8 g

53.

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

55.

$AlPO_4$: 1.000 mol or 26.98 g Al
Al_2Cl_6: 1.994 mol or 53.74 g Al
Al_2S_3: 3.00 mol or 80.94 g Al
The Al_2S_3 sample thus contains the greatest mass of Al.

57.

3.113×10^{25} C atoms

59.

0.865 servings, or about 1 serving.

61.

20.0 g H_2O represents the least number of molecules since it has the least number of moles.

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11.14.2: Chapter 2 - Electronic Structure and Periodic Properties

1.

The spectrum consists of colored lines, at least one of which (probably the brightest) is red.

3.

3.15 m

5.

3.233×10^{-19} J; 2.018 eV

7.

$\nu = 4.568 \times 10^{14}$ s^{-1}; λ = 656.3 nm; Energy $mol^{-1} = 1.823 \times 10^{5}$ J mol^{-1}; red

9.

(a) $\lambda = 8.69 \times 10^{-7}$ m; $E = 2.29 \times 10^{-19}$ J; (b) $\lambda = 4.59 \times 10^{-7}$ m; $E = 4.33 \times 10^{-19}$ J; The color of (a) is red; (b) is blue.

11.

$E = 9.502 \times 10^{-15}$ J; $\nu = 1.434 \times 10^{19}$ s^{-1}

13.

Red: 660 nm; 4.54×10^{14} Hz; 3.01×10^{-19} J. Green: 520 nm; 5.77×10^{14} Hz; 3.82×10^{-19} J. Blue: 440 nm; 6.81×10^{14} Hz; 4.51×10^{-19} J. Somewhat different numbers are also possible.

15.

5.49×10^{14} s^{-1}; no

17.

Quantized energy means that the electrons can possess only certain discrete energy values; values between those quantized values are not permitted.

19.

$2.856\,\mathrm{eV}$

21.

-8.716×10^{-18} J

23.

-3.405×10^{-20} J

25.

33.9 Å

27.

1.471×10^{-17} J

29.

Both involve a relatively heavy nucleus with electrons moving around it, although strictly speaking, the Bohr model works only for one-electron atoms or ions. According to classical mechanics, the Rutherford model predicts a miniature “solar system” with electrons moving about the nucleus in circular or elliptical orbits that are confined to planes. If the requirements of classical electromagnetic theory that electrons in such orbits would emit electromagnetic radiation are ignored, such atoms would be stable, having constant energy and angular momentum, but would not emit any visible light (contrary to observation). If classical electromagnetic theory is applied, then the Rutherford atom would emit electromagnetic radiation of continually increasing frequency (contrary to the observed discrete spectra), thereby losing energy until the atom collapsed in an absurdly short time (contrary to the observed long-term stability of atoms). The Bohr model retains the classical mechanics view of circular orbits confined to planes having constant energy and angular momentum, but restricts these to quantized values dependent on a single quantum number, *n*. The orbiting electron in Bohr’s model is assumed not to emit any electromagnetic radiation while moving about the nucleus in its stationary orbits, but the atom can emit or absorb electromagnetic radiation when the electron changes from one orbit to another. Because of the quantized orbits, such “quantum jumps” will produce discrete spectra, in agreement with observations.

31.

Both models have a central positively charged nucleus with electrons moving about the nucleus in accordance with the Coulomb electrostatic potential. The Bohr model *assumes* that the electrons move in circular orbits that have quantized energies, angular momentum, and radii that are specified by a single quantum number, $n = 1, 2, 3, \ldots$, but this quantization is an ad hoc assumption made by Bohr to incorporate quantization into an essentially classical mechanics description of the atom. Bohr also assumed that electrons orbiting the nucleus normally do not emit or absorb electromagnetic radiation, but do so when the electron switches to a different orbit. In the quantum mechanical model, the electrons do not move in precise orbits (such orbits violate the Heisenberg uncertainty principle) and, instead, a probabilistic interpretation of the electron’s position at any given instant is used, with a mathematical function ψ called a wavefunction that can be used to determine the electron’s spatial probability distribution. These wavefunctions, or orbitals, are three-dimensional stationary waves that can be specified by three quantum numbers that arise naturally from their underlying mathematics (no ad hoc assumptions required): the principal quantum number, *n* (the same one used by Bohr), which specifies shells such that orbitals having the same *n* all have the same energy and approximately the same spatial extent; the angular momentum quantum number *l*, which is a measure of the orbital’s angular momentum and corresponds to the orbitals’ general shapes, as well as specifying subshells such that orbitals having the same *l* (and *n*) all have the same energy; and the orientation quantum number *m*, which is a measure of the *z* component of the angular momentum and corresponds to the orientations of the orbitals. The Bohr model gives the same expression for the energy as the quantum mechanical expression and, hence, both properly account for hydrogen’s discrete spectrum (an example of getting the right answers for the wrong reasons, something that many chemistry students can sympathize with), but gives the wrong expression for the angular momentum (Bohr orbits necessarily all have non-zero angular momentum, but some quantum orbitals [*s* orbitals] can have zero angular momentum).

33.

n determines the general range for the value of energy and the probable distances that the electron can be from the nucleus. *l* determines the shape of the orbital. m_l determines the orientation of the orbitals of the same *l* value with respect to one another. m_s determines the spin of an electron.

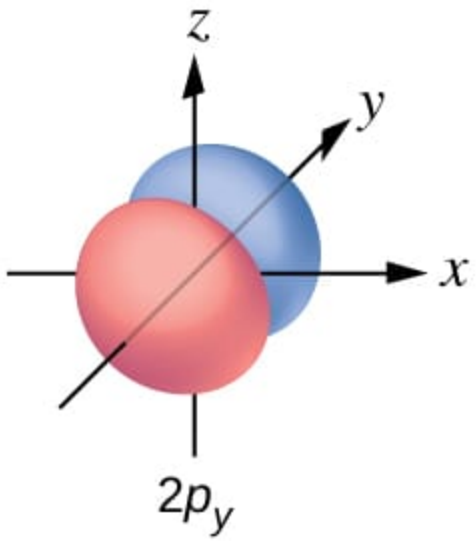
35.

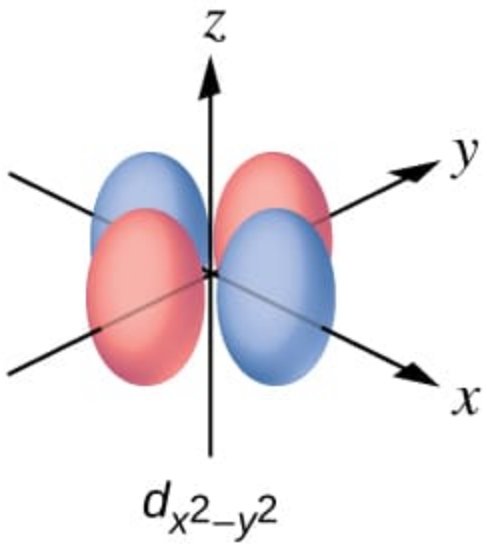
(a) 2*p*; (b) 4*d*; (c) 6*s*

37.

(a) 3*d;* (b) 1s*;* (c) 4*f*

39.





41.

(a) x. 2, y. 2, z. 2; (b) x. 1, y. 3, z. 0; (c) x. 4 0 0 $\frac{1}{2}$, y. 2 1 0 $\frac{1}{2}$, z. 3 2 0 $\frac{1}{2}$; (d) x. 1, y. 2, z. 3; (e) x. $l = 0$, $m_l = 0$, y. $l = 1$, $m_l = -1$, 0, or +1, z. $l = 2$, $m_l = -2, -1, 0, +1, +2$

43.

12

45.

n	l	m_l	s
4	0	0	$+\frac{1}{2}$
4	0	0	$-\frac{1}{2}$
4	1	−1	$+\frac{1}{2}$
4	1	0	$+\frac{1}{2}$
4	1	+1	$+\frac{1}{2}$
4	1	−1	$-\frac{1}{2}$

47.

For example, Na^+: $1s^2 2s^2 2p^6$; Ca^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6$; Sn^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2$; F^-: $1s^2 2s^2 2p^6$; O^{2-}: $1s^2 2s^2 2p^6$; Cl^-: $1s^2 2s^2 2p^6 3s^2 3p^6$.

49.

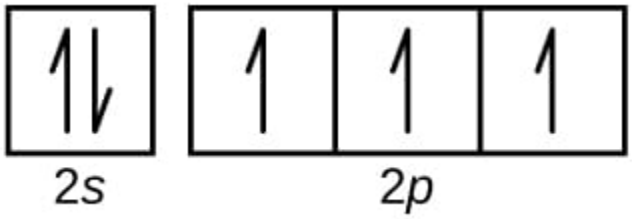
(a) $1s^2 2s^2 2p^3$; (b) $1s^2 2s^2 2p^6 3s^2 3p^2$; (c) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$; (d) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^4$; (e) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^9$

51.

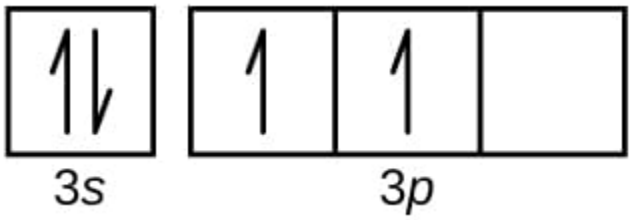
The charge on the ion.

53.

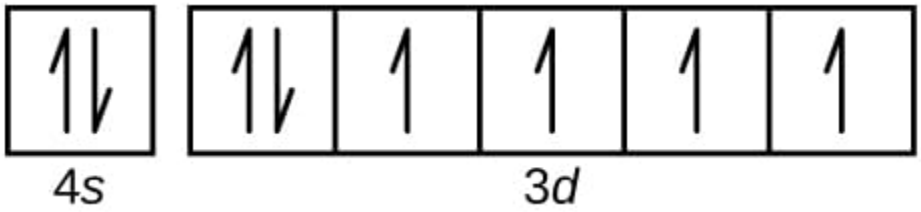
(a)



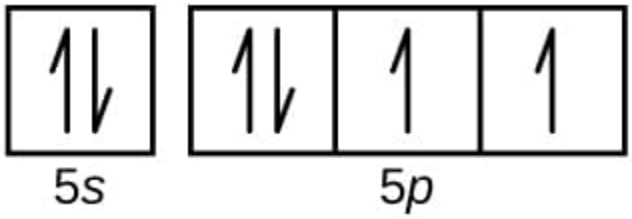
(b)



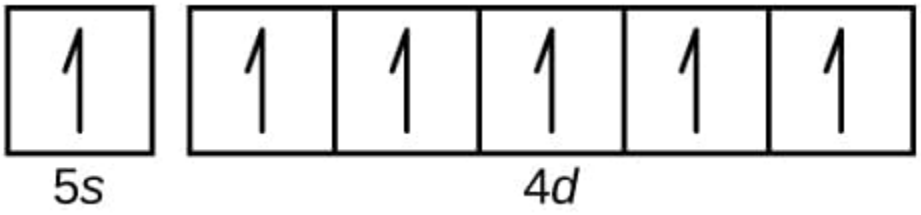
(c)



(d)



(e)



55.

Zr

57.

Rb^{+}, Se^{2-}

59.

Although both (b) and (c) are correct, (e) encompasses both and is the best answer.

61.

K

63.

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

65.

Co has 27 protons, 27 electrons, and 33 neutrons: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$. I has 53 protons, 53 electrons, and 78 neutrons: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^5$.

67.

Cl

69.

O

71.

Rb < Li < N < F

73.

15 (5A)

75.

Mg < Ca < Rb < Cs

77.

$Si^{4+} < Al^{3+} < Ca^{2+} < K^{+}$

79.

Se, As^{-}

81.

$Mg^{2+} < K^{+} < Br^{-} < As^{3-}$

83.

O, IE_1

85.

Ra

87.

(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

89.

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

91.

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

93.

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

95.

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

97.

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

99.

(a) CaS; (b) $(NH_4)_2SO_4$; (c) $AlBr_3$; (d) Na_2HPO_4; (e) $Mg_3\ (PO_4)_2$

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11.14.3: Chapter 3 - Chemical Bonding and Molecular Geometry

1.

The protons in the nucleus do not change during normal chemical reactions. Only the outer electrons move. Positive charges form when electrons are lost.

3.

P, I, Cl, and O would form anions because they are nonmetals. Mg, In, Cs, Pb, and Co would form cations because they are metals.

5.

(a) P^{3-}; (b) Mg^{2+}; (c) Al^{3+}; (d) O^{2-}; (e) Cl^{-}; (f) Cs^{+}

7.

(a) $[Ar]4s^2 3d^{10} 4p^6$; (b) $[Kr]4d^{10} 5s^2 5p^6$ (c) $1s^2$ (d) $[Kr]4d^{10}$; (e) $[He]2s^2 2p^6$; (f) $[Ar]3d^{10}$; (g) $1s^2$ (h) $[He]2s^2 2p^6$ (i) $[Kr]4d^{10} 5s^2$ (j) $[Ar]3d^7$ (k) $[Ar]3d^6$, (l) $[Ar]3d^{10} 4s^2$

9.

(a) $1s^2 2s^2 2p^6 3s^2 3p^1$; Al^{3+}: $1s^2 2s^2 2p^6$; (b) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$; $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$; (c) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$; Sr^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$; (d) $1s^2 2s^1$; Li^{+}: $1s^2$; (e) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$; $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$; (f) $1s^2 2s^2 2p^6 3s^2 3p^4$; $1s^2 2s^2 2p^6 3s^2 3p^6$

11.

NaCl consists of discrete ions arranged in a crystal lattice, not covalently bonded molecules.

13.

ionic: (b), (d), (e), (g), and (i); covalent: (a), (c), (f), (h), (j), and (k)

15.

(a) Cl; (b) O; (c) O; (d) S; (e) N; (f) P; (g) N

17.

(a) H, C, N, O, F; (b) H, I, Br, Cl, F; (c) H, P, S, O, F; (d) Na, Al, H, P, O; (e) Ba, H, As, N, O

19.

N, O, F, and Cl

21.

(a) HF; (b) CO; (c) OH; (d) PCl; (e) NH; (f) PO; (g) CN

23.

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

25.

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

27.

(a) ClO_2; (b) N_2O_4; (c) K_3P; (d) Ag_2S; (e) $AlF_3 \cdot 3H_2O$; (f) SiO_2

29.

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

31.

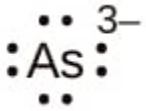
(a) K_3PO_4; (b) $CuSO_4$; (c) $CaCl_2$; (d) TiO_2; (e) NH_4NO_3; (f) $NaHSO_4$

33.

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

34.

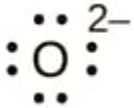
(a) eight electrons:



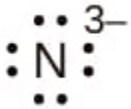
(b) eight electrons:



(c) no electrons Be^{2+}
(d) eight electrons:



(e) no electrons Ga^{3+}
(f) no electrons Li^{+}
(g) eight electrons:



36.

(a)



(b)



(c)



(d)



(e)



(f)

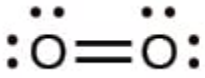


38.



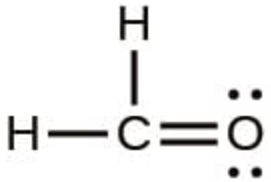
40.

(a)

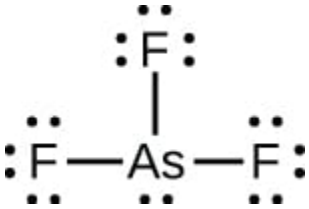


In this case, the Lewis structure is inadequate to depict the fact that experimental studies have shown two unpaired electrons in each oxygen molecule.

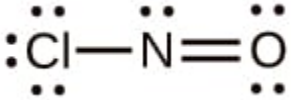
(b)



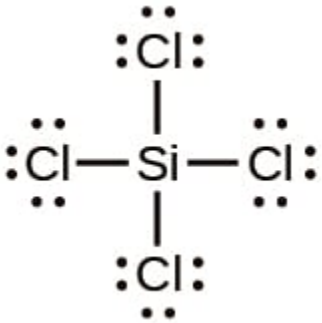
(c)



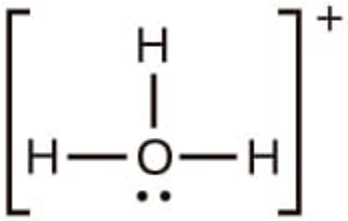
(d)



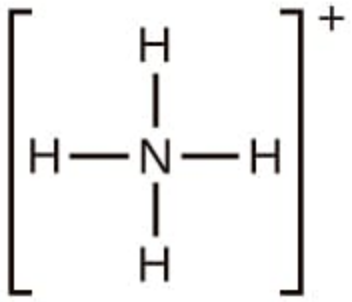
(e)



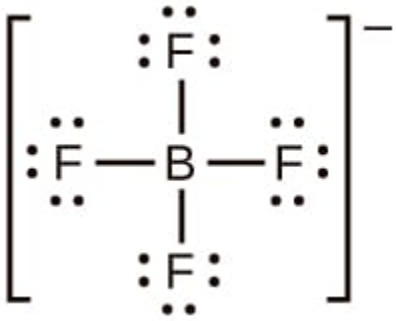
(f)



(g)



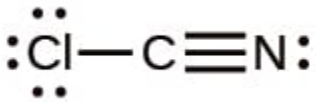
(h)



(i)



(j)

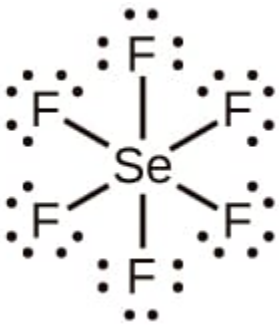


(k)

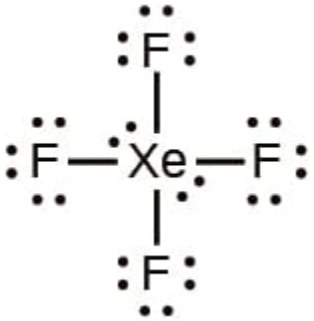


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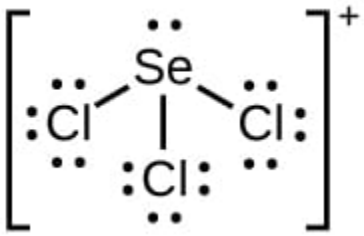
(a) SeF_6:



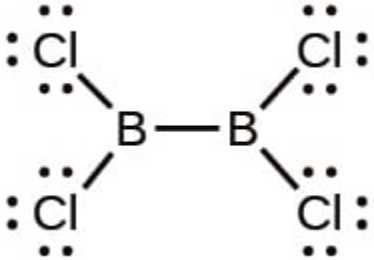
(b) XeF_4:



(c) $SeCl_3^+$:



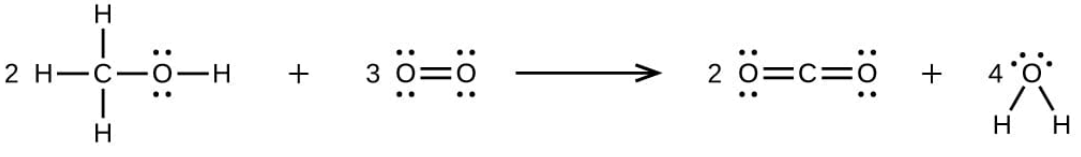
(d) Cl_2BBCl_2:

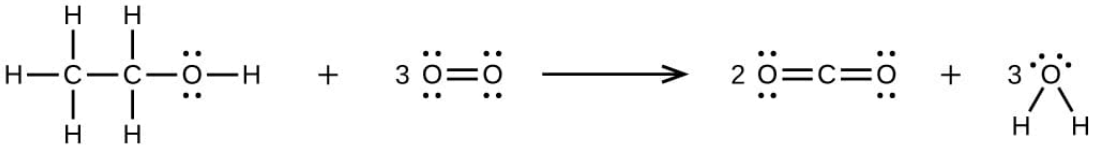


44.

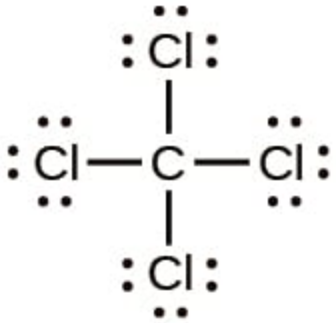
Two valence electrons per Pb atom are transferred to Cl atoms; the resulting Pb^{2+} ion has a $6s^2$ valence shell configuration. Two of the valence electrons in the HCl molecule are shared, and the other six are located on the Cl atom as lone pairs of electrons.

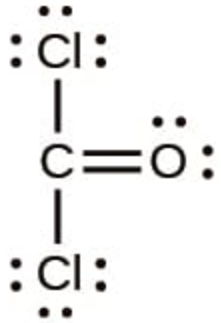
46.





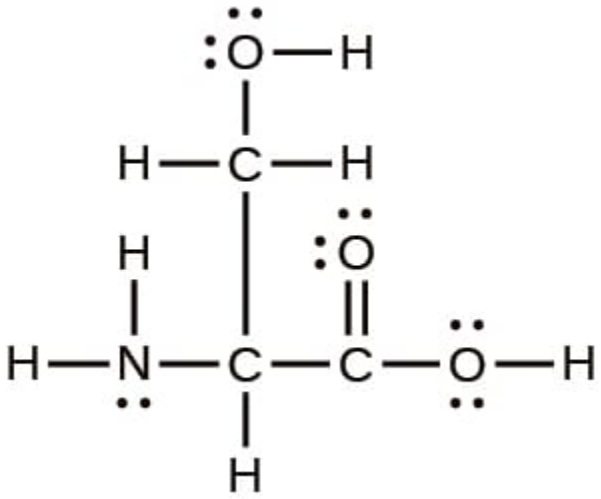
48.



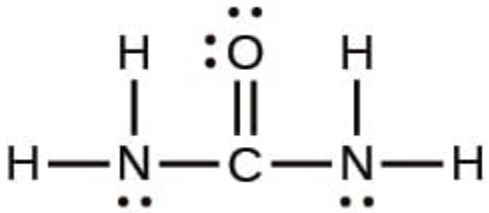


50.

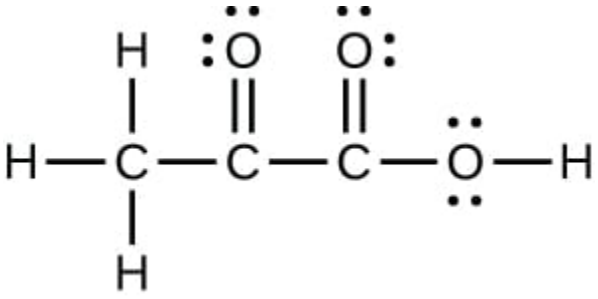
(a)



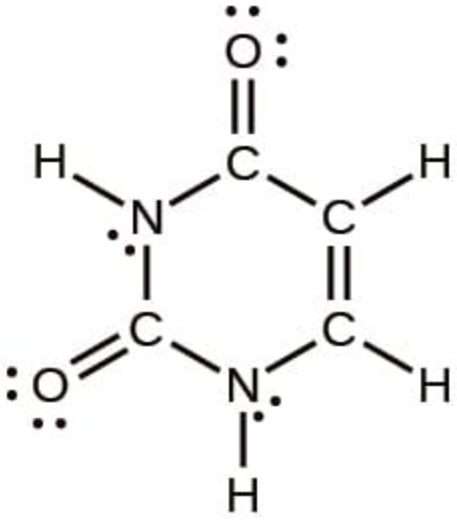
(b)



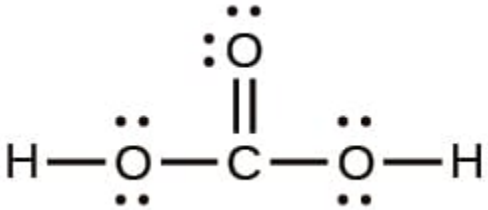
(c)



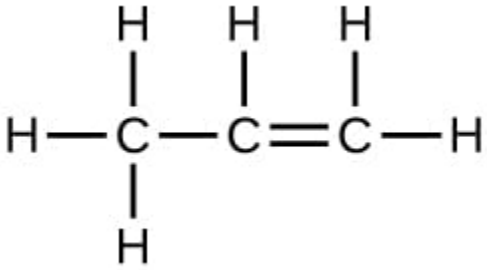
(d)



(e)



52.



54.

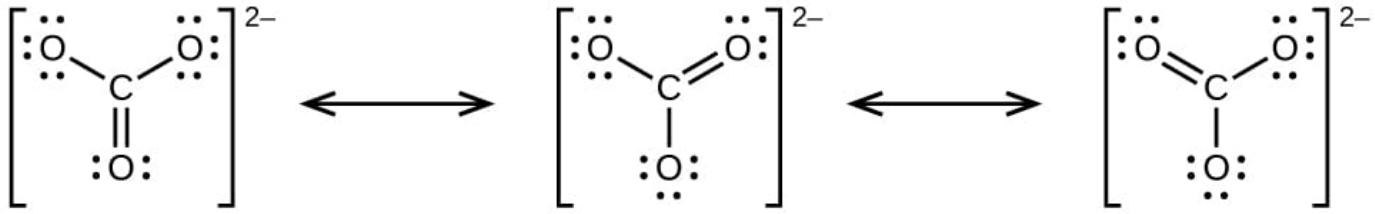
Each bond includes a sharing of electrons between atoms. Two electrons are shared in a single bond; four electrons are shared in a double bond; and six electrons are shared in a triple bond.

56.

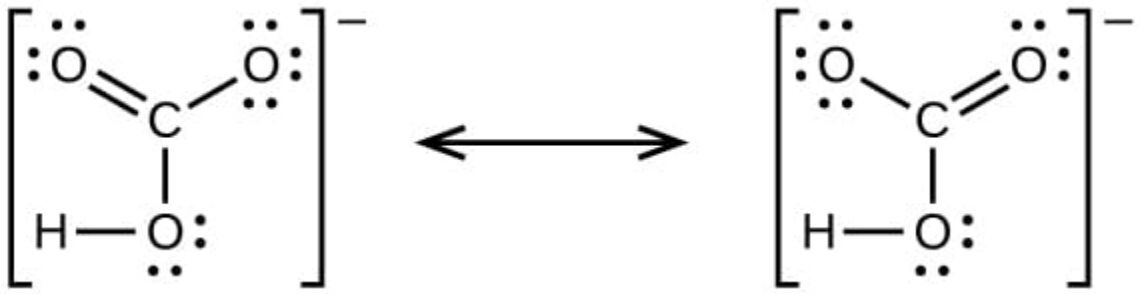
(a)



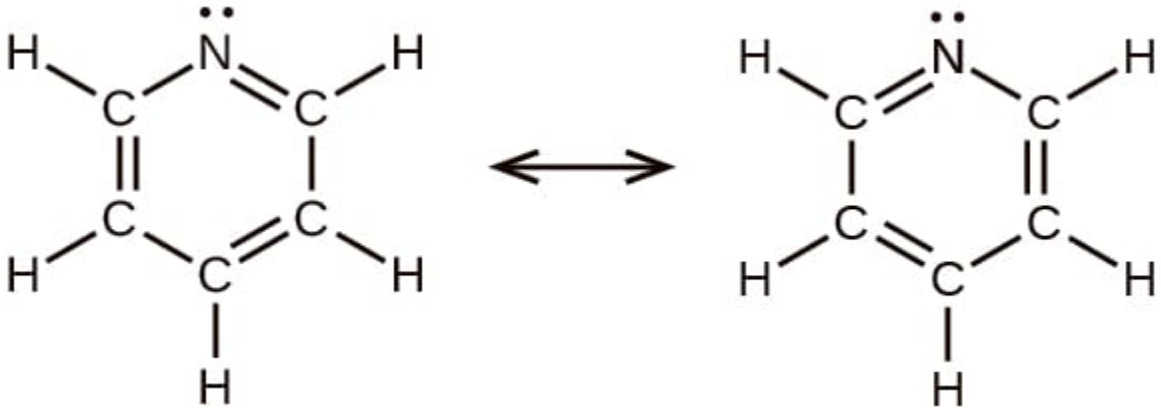
(b)



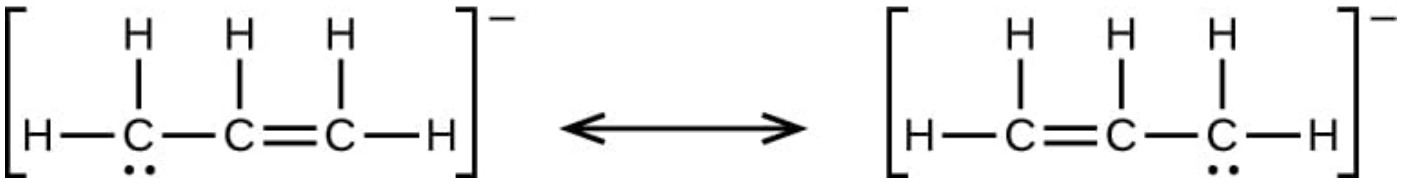
(c)



(d)

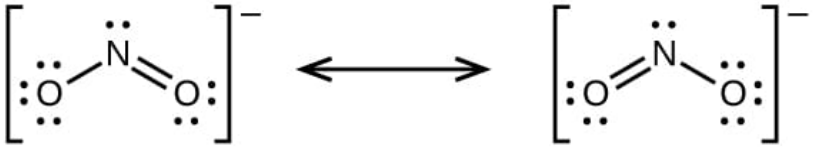


(e)



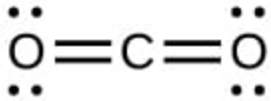
58.

For NO_2^-



60.

(a)



(b)



CO has the strongest carbon-oxygen bond because there is a triple bond joining C and O. CO_2 has double bonds.

62.

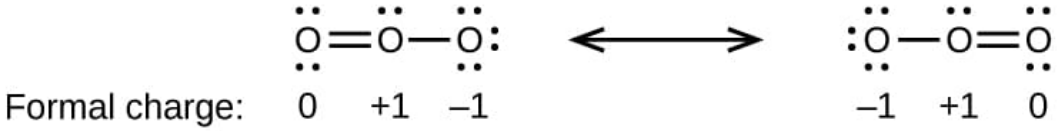
(a) H: 0, Cl: 0; (b) C: 0, F: 0; (c) P: 0, Cl 0; (d) P: 0, F: 0

64.

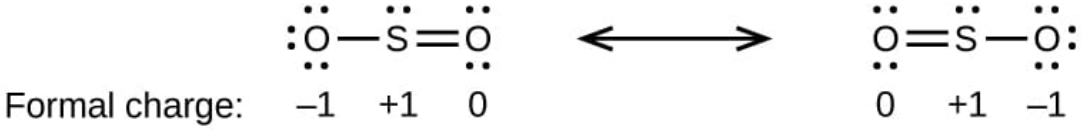
Cl in Cl_2: 0; Cl in $BeCl_2$: 0; Cl in ClF_5: 0

66.

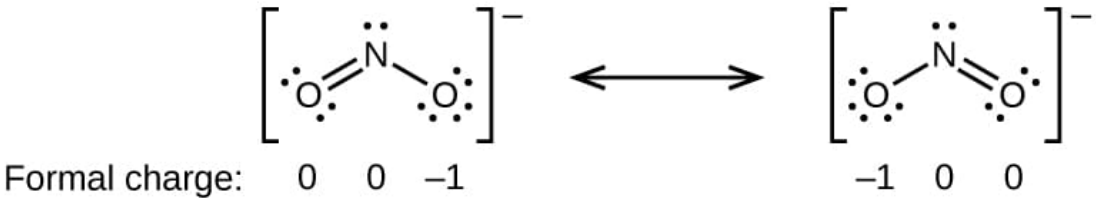
(a)



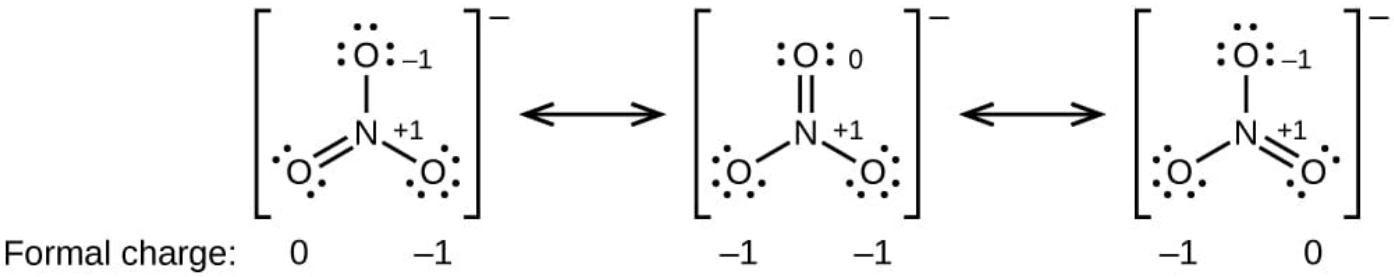
(b)



(c)



(d)

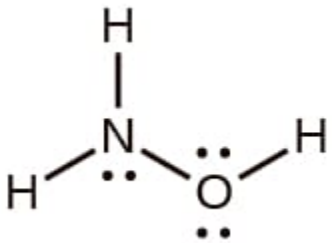


68.

HOCl

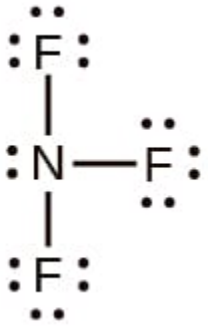
70.

The structure that gives zero formal charges is consistent with the actual structure:

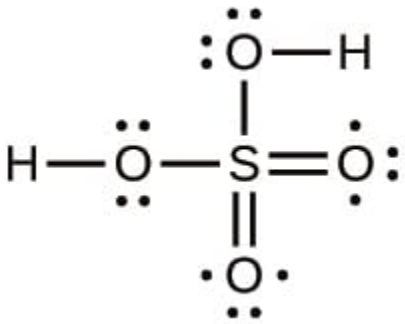


72.

NF_3;



74.



75.

The placement of the two sets of unpaired electrons in water forces the bonds to assume a tetrahedral arrangement, and the resulting HOH molecule is bent. The HBeH molecule (in which Be has only two electrons to bond with the two electrons from the hydrogens) must have the electron pairs as far from one another as possible and is therefore linear.

77.

Space must be provided for each pair of electrons whether they are in a bond or are present as lone pairs. Electron-pair geometry considers the placement of all electrons. Molecular structure considers only the bonding-pair geometry.

79.

As long as the polar bonds are compensated (for example. two identical atoms are found directly across the central atom from

one another), the molecule can be nonpolar.

81.

(a) Both the electron geometry and the molecular structure are octahedral. (b) Both the electron geometry and the molecular structure are trigonal bipyramid. (c) Both the electron geometry and the molecular structure are linear. (d) Both the electron geometry and the molecular structure are trigonal planar.

83.

(a) electron-pair geometry: octahedral, molecular structure: square pyramidal; (b) electron-pair geometry: tetrahedral, molecular structure: bent; (c) electron-pair geometry: octahedral, molecular structure: square planar; (d) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal; (e) electron-pair geometry: trigonal bypyramidal, molecular structure: seesaw; (f) electron-pair geometry: tetrahedral, molecular structure: bent (109°)

85.

(a) electron-pair geometry: trigonal planar, molecular structure: bent (120°); (b) electron-pair geometry: linear, molecular structure: linear; (c) electron-pair geometry: trigonal planar, molecular structure: trigonal planar; (d) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal; (e) electron-pair geometry: tetrahedral, molecular structure: tetrahedral; (f) electron-pair geometry: trigonal bipyramidal, molecular structure: seesaw; (g) electron-pair geometry: tetrahedral, molecular structure: trigonal pyramidal

87.

All of these molecules and ions contain polar bonds. Only ClF_5, ClO_2^-, PCl_3, SeF_4, and PH_2^- have dipole moments.

89.

SeS_2, CCl_2F_2, PCl_3, and ClNO all have dipole moments.

91.

P

93.

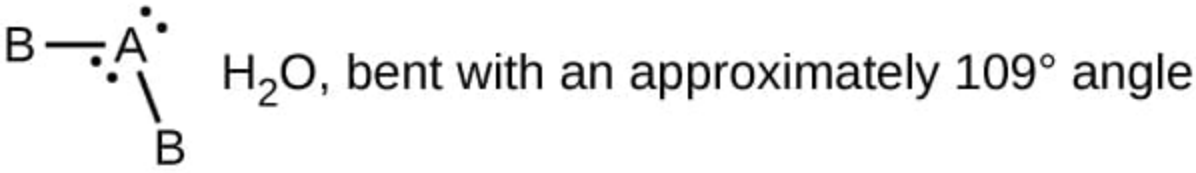
nonpolar

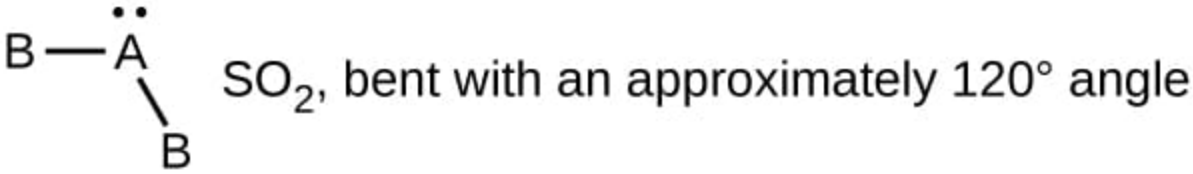
95.

(a) tetrahedral; (b) trigonal pyramidal; (c) bent (109°); (d) trigonal planar; (e) bent (109°); (f) bent (109°); (g) $\underline{C}H_3CCH$ tetrahedral, $CH_3\underline{C}\underline{C}H$ linear; (h) tetrahedral; (i) $H_2C\underline{C}CH_2$ linear; $H_2\underline{C}C\underline{C}H_2$ trigonal planar

97.

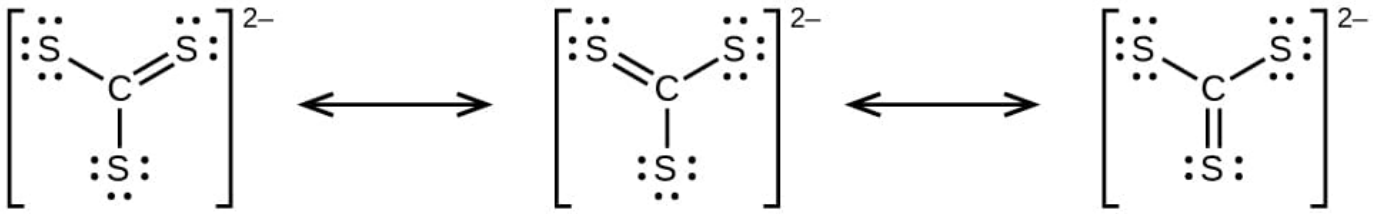




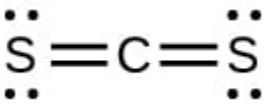


99.

(a)



(b)



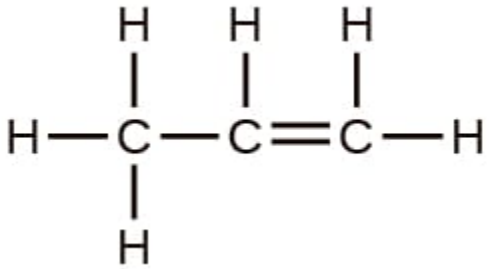
(c)



(d) CS_3^{2-} includes three regions of electron density (all are bonds with no lone pairs); the shape is trigonal planar; CS_2 has only two regions of electron density (all bonds with no lone pairs); the shape is linear

101.

The Lewis structure is made from three units, but the atoms must be rearranged:



103.

The molecular dipole points away from the hydrogen atoms.

105.

The structures are very similar. In the model mode, each electron group occupies the same amount of space, so the bond angle is shown as 109.5°. In the “real” mode, the lone pairs are larger, causing the hydrogens to be compressed. This leads to the smaller angle of 104.5°.

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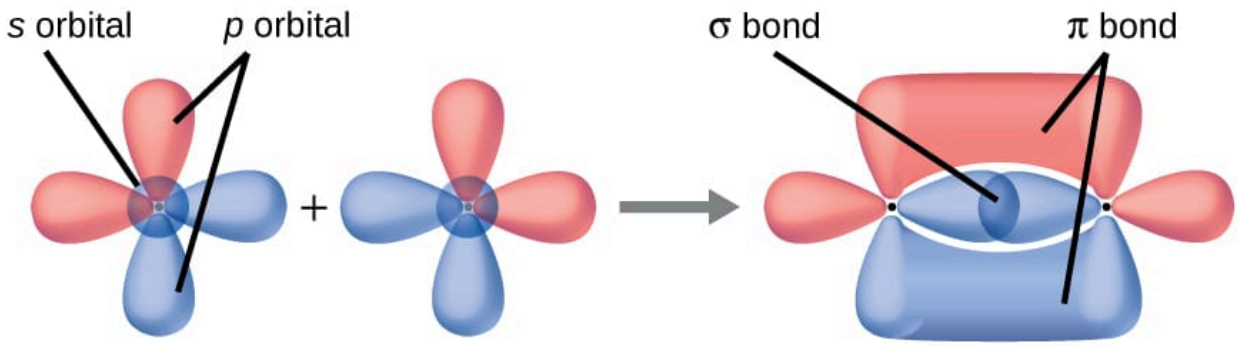
11.14.4: Chapter 4 - Advanced Theories of Bonding

1.

Similarities: Both types of bonds result from overlap of atomic orbitals on adjacent atoms and contain a maximum of two electrons. Differences: σ bonds are stronger and result from end-to-end overlap and all single bonds are σ bonds; π bonds between the same two atoms are weaker because they result from side-by-side overlap, and multiple bonds contain one or more π bonds (in addition to a σ bond).

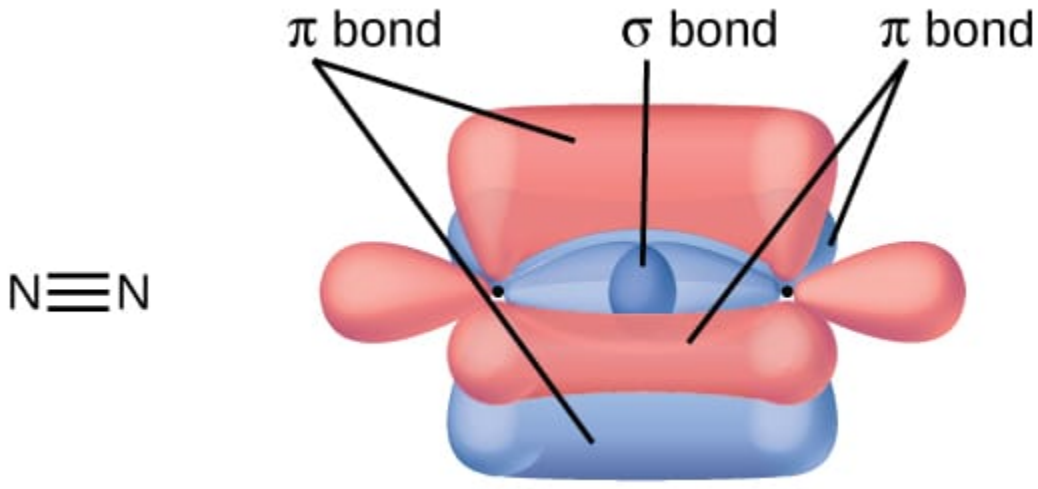
3.

Bonding: One σ bond and one π bond. The *s* orbitals are filled and do not overlap. The *p* orbitals overlap along the axis to form a σ bond and side-by-side to form the π bond.



5.

No, two of the *p* orbitals (one on each N) will be oriented end-to-end and will form a σ bond.



7.

Hybridization is introduced to explain the geometry of bonding orbitals in valance bond theory.

9.

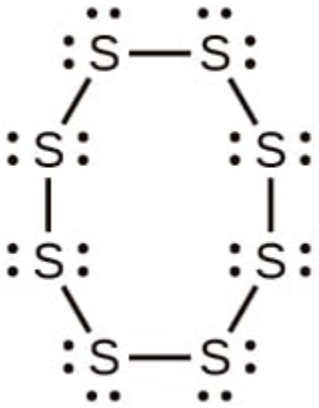
There are no *d* orbitals in the valence shell of carbon.

11.

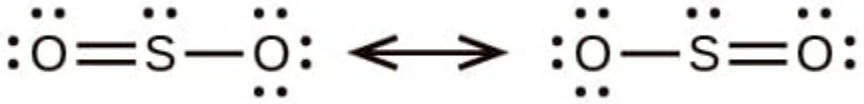
trigonal planar, sp^2; trigonal pyramidal (one lone pair on A) sp^3; T-shaped (two lone pairs on A sp^3d, or (three lone pairs on A) sp^3d^2

13.

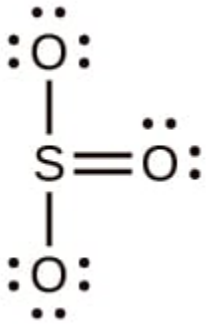
(a) Each S has a bent (109°) geometry, sp^3



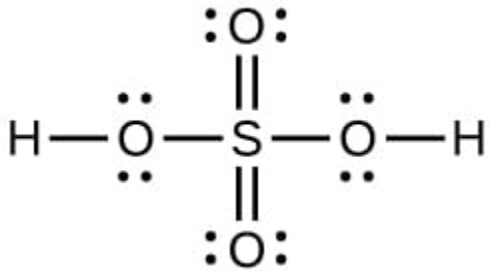
(b) Bent (120°), sp^2



(c) Trigonal planar, sp^2

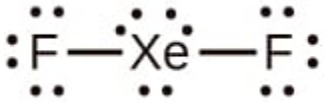


(d) Tetrahedral, sp^3



15.

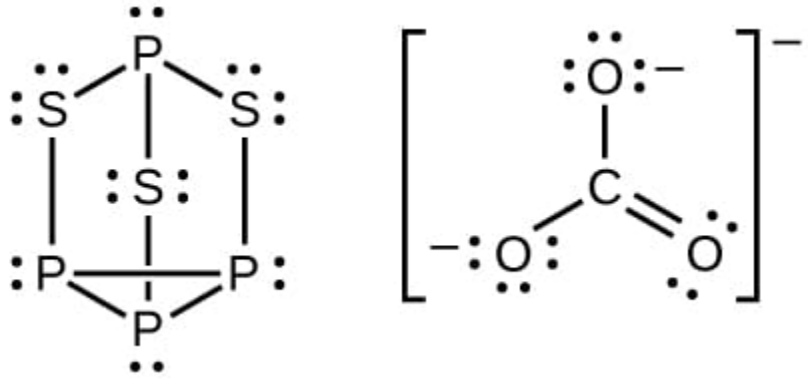
(a) XeF_2
(b)



(c) linear (d) sp^3d

17.

(a)



(b) P atoms, trigonal pyramidal; S atoms, bent, with two lone pairs; Cl atoms, trigonal pyramidal; (c) Hybridization about P, S, and Cl is, in all cases, sp^3; (d) Oxidation states P +1, $S-1\frac{1}{3}$, Cl +5, O –2. Formal charges: P 0; S 0; Cl +2: O –1

19.



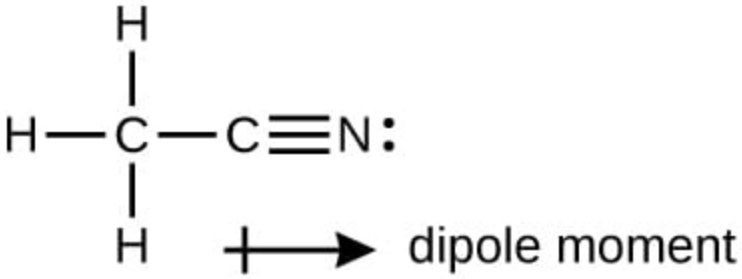
Phosphorus and nitrogen can form sp^3 hybrids to form three bonds and hold one lone pair in PF_3 and NF_3, respectively. However, nitrogen has no valence *d* orbitals, so it cannot form a set of sp^3d hybrid orbitals to bind five fluorine atoms in NF_5. Phosphorus has *d* orbitals and can bind five fluorine atoms with sp^3d hybrid orbitals in PF_5.

21.

A triple bond consists of one σ bond and two π bonds. A σ bond is stronger than a π bond due to greater overlap.

23.

(a)



(b) The terminal carbon atom uses sp^3 hybrid orbitals, while the central carbon atom is *sp* hybridized. (c) Each of the two π bonds is formed by overlap of a *2p* orbital on carbon and a nitrogen *2p* orbital.

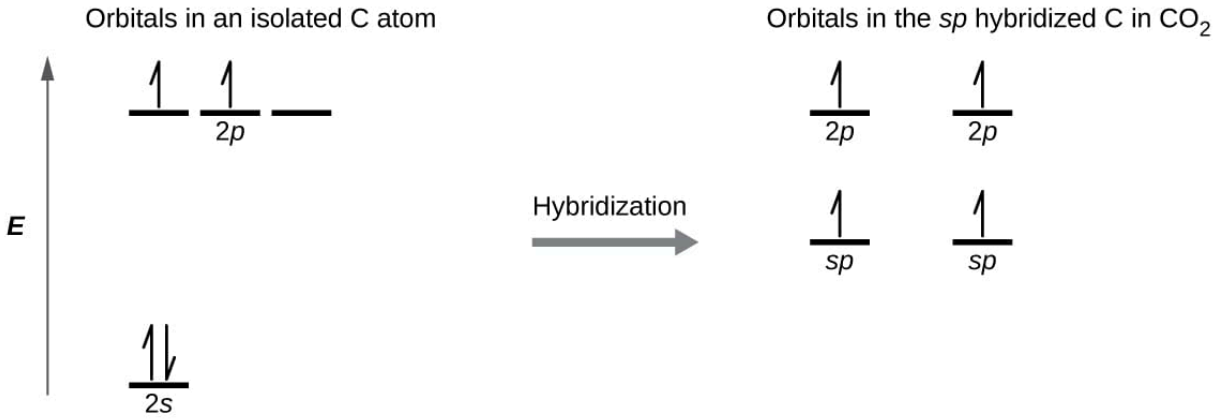
25.

(a) sp^2; (b) *sp*; (c) sp^2; (d) sp^3; (e) sp^3; (f) sp^3d; (g) sp^3

27.

(a) sp^2, delocalized; (b) *sp*, localized; (c) sp^2, delocalized; (d) sp^3, delocalized

29.



Each of the four electrons is in a separate orbital and overlaps with an electron on an oxygen atom.

31.

(a) Similarities: Both are bonding orbitals that can contain a maximum of two electrons. Differences: σ orbitals are end-to-end combinations of atomic orbitals, whereas π orbitals are formed by side-by-side overlap of orbitals. (b) Similarities: Both are quantum-mechanical constructs that represent the probability of finding the electron about the atom or the molecule. Differences: ψ for an atomic orbital describes the behavior of only one electron at a time based on the atom. For a molecule, ψ represents a mathematical combination of atomic orbitals. (c) Similarities: Both are orbitals that can contain two electrons. Differences: Bonding orbitals result in holding two or more atoms together. Antibonding orbitals have the effect of destabilizing any bonding that has occurred.

33.

An odd number of electrons can never be paired, regardless of the arrangement of the molecular orbitals. It will always be paramagnetic.

35.

Bonding orbitals have electron density in close proximity to more than one nucleus. The interaction between the bonding

positively charged nuclei and negatively charged electrons stabilizes the system.

37.

The pairing of the two bonding electrons lowers the energy of the system relative to the energy of the nonbonded electrons.

39. (a) H_2 bond order $= 1, {H_2}^+$bond order $= 0.5, {H_2}^-$bond order $= 0.5$, strongest bond is H_2; (b) O_2 bond order $= 2, {O_2}^{2+}$ bond order = 3; ${O_2}^{2-}$ bond order = 1, strongest bond is ${O_2}^{2+}$; (c) Li_2 bond order = 1, ${Be_2}^+$bond order $= 0.5, Be_2$ bond order $= 0$, strongest bond is Li_2; (d) F_2 bond order $= 1,$ ${F_2}^+$bond order $= 1.5,$ ${F_2}^-$ bond order $= 0.5$, strongest bond is ${F_2}^+$; (e) N_2 bond order $= 3,$ ${N_2}^+$bond order = 2.5, ${N_2}^-$bond order = 2.5, strongest bond is N_2

41.](a) H_2; (b) N_2; (c) O; (d) C_2; (e) B_2

43. Yes, fluorine is a smaller atom than Li, so atoms in the 2s orbital are closer to the nucleus and more stable.

45. 2+

47. N_2 has s-p mixing, so the π orbitals are the last filled in ${N_2}^{2+}.O_2$ does not have s-p mixing, so the σ_p orbital fills before the π orbitals.

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11.14.5: Chapter 5 - Thermochemistry

1. The temperature of 1 gram of burning wood is approximately the same for both a match and a bonfire. This is an intensive property and depends on the material (wood). However, the overall amount of produced heat depends on the amount of material; this is an extensive property. The amount of wood in a bonfire is much greater than that in a match; the total amount of produced heat is also much greater, which is why we can sit around a bonfire to stay warm, but a match would not provide enough heat to keep us from getting cold.

3. Heat capacity refers to the heat required to raise the temperature of the mass of the substance 1 degree; specific heat refers to the heat required to raise the temperature of 1 gram of the substance 1 degree. Thus, heat capacity is an extensive property, and specific heat is an intensive one.

5. (a) 47. 6 J/°C; 11. 38 cal $°C^{-1}$; (b) 407 J/°C; 97. 3 cal $°C^{-1}$

7. 1310 J; 313 cal

9. 7. 15 °C

11. (a) 0. 390 J/g °C; (b) Copper is a likely candidate.

13. We assume that the density of water is 1. 0 g/cm^3(1 g/mL) and that it takes as much energy to keep the water at 85 °F as to heat it from 72 °F to 85 °F. We also assume that only the water is going to be heated. Energy required = 7. 47 kWh

15. lesser; more heat would be lost to the coffee cup and the environment and so ΔT for the water would be lesser and the calculated q would be lesser

17. greater, since taking the calorimeter's heat capacity into account will compensate for the thermal energy transferred to the solution from the calorimeter; this approach includes the calorimeter itself, along with the solution, as "surroundings": $q_{rxn} = -(q_{solution} + q_{calorimeter})$; since both $q_{solution}$ and $q_{calorimeter}$ are negative, including the latter term (q_{rxn}) will yield a greater value for the heat of the dissolution

19. The temperature of the coffee will drop 1 degree.

21. 5.7×10^2 kJ

23. 38. 5 °C

25. –2. 2 kJ; The heat produced shows that the reaction is exothermic.

27. 1. 4 kJ

29. 22. 6. Since the mass and the heat capacity of the solution is approximately equal to that of the water, the two-fold increase in the amount of water leads to a two-fold decrease of the temperature change.

31. 11. 7 kJ

33. 30%

35. 0. 24 g

37. 1.4×10^2 Calories

39. The enthalpy change of the indicated reaction is for exactly 1 mol HCL and 1 mol NaOH; the heat in the example is produced by 0. 0500 mol HCl and 0. 0500 mol NaOH.

41. 25 kJ mol^{-1}

43. 81 kJ mol^{-1}

45. 5204. 4 kJ

47. 1. 83 × 10^{-2} mol

49. −802 kJ mol^{-1}

51. 15. 5 kJ/°C

53. 7. 43 g

55. Yes.

57. 459. 6 kJ

59. −494 kJ/mol

61. 44. 01 kJ/mol

63. −394 kJ

65. 265 kJ

67. 90. 3 kJ/mol

69. (a) −1615. 0 kJ mol^{-1}; (b) −484. 3 kJ mol^{-1}; (c) 164. 2 kJ; (d) −232. 1 kJ

71. −54. 04 kJ mol^{-1}

73. −2660 kJ mol^{-1}

75. −66. 4 kJ

77. −122. 8 kJ

79. 3. 7 kg

81. On the assumption that the best rocket fuel is the one that gives off the most heat, B_2H_6 is the prime candidate.

83. −88. 2 kJ

85. (a) $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O\,(l)$; (b) 330 L air; (c) −104. 5 kJ mol^{-1}; (d) 75. 4 °C

88. (a) −114 kJ; (b) 30 kJ; (c) −1055 kJ

91. The specific average bond distance is the distance with the lowest energy. At distances less than the bond distance, the positive charges on the two nuclei repel each other, and the overall energy increases.

92. The greater bond energy is in the figure on the left. It is the more stable form.

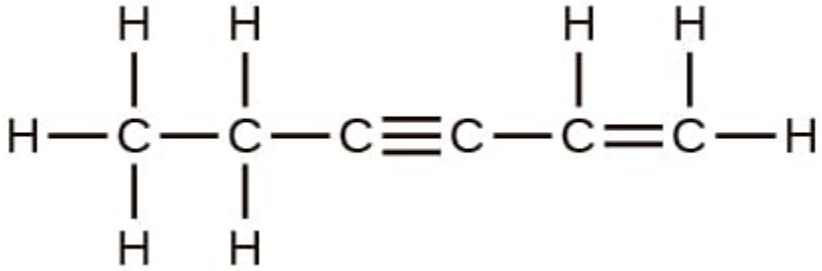
94.

$$\begin{array}{ll} HCl(g) \longrightarrow \frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) & \Delta H_1^\circ = -\Delta H_{f[HCl(g)]}^\circ \\ \frac{1}{2}H_2(g) \longrightarrow H(g) & \Delta H_2^\circ = \Delta H_{f[H(g)]}^\circ \\ \frac{1}{2}Cl_2(g) \longrightarrow Cl(g) & \Delta H_3^\circ = \Delta H_{f[Cl(g)]}^\circ \end{array}$$

$$\begin{aligned} \mathrm{HCl}(g) \longrightarrow \mathrm{H}(g) + \mathrm{Cl}(g) \quad \Delta H^\circ_{298} &= \Delta H^\circ_1 + \Delta H^\circ_2 + \Delta H^\circ_3 \\ D_{\mathrm{HCl}} = \Delta H^\circ_{298} &= \Delta H^\circ_{\mathrm{f}[\mathrm{HCl}(g)]} + \Delta H^\circ_{\mathrm{f}[\mathrm{H}(g)]} + \Delta H^\circ_{\mathrm{f}[\mathrm{Cl}(g)]} \\ &= -(-92.307\ \mathrm{kJ}) + 217.97\ \mathrm{kJ} + 121.3\ \mathrm{kJ} \\ &= 431.6\ \mathrm{kJ} \end{aligned}$$

96. The S–F bond in SF_4 is stronger.

98.



The C–C single bonds are longest.

100. (a) When two electrons are removed from the valence shell, the Ca radius loses the outermost energy level and reverts to the lower *n* = 3 level, which is much smaller in radius. (b) The +2 charge on calcium pulls the oxygen much closer compared with K, thereby increasing the lattice energy relative to a less charged ion. (c) Removal of the 4*s* electron in Ca requires more energy than removal of the 4*s* electron in K because of the stronger attraction of the nucleus and the extra energy required to break the pairing of the electrons. The second ionization energy for K requires that an electron be removed from a lower energy level, where the attraction is much stronger from the nucleus for the electron. In addition, energy is required to unpair two electrons in a full orbital. For Ca, the second ionization potential requires removing only a lone electron in the exposed outer energy level. (d) In Al, the removed electron is relatively unprotected and unpaired in a *p* orbital. The higher energy for Mg mainly reflects the unpairing of the 2*s* electron.

102. (d)

104. 4008 kJ/mol; both ions in MgO have twice the charge of the ions in LiF; the bond length is very similar and both have the same structure; a quadrupling of the energy is expected based on the equation for lattice energy

106. (a) Na_2O; Na^+ has a smaller radius than K^+; (b) BaS; Ba has a larger charge than K; (c) BaS; Ba and S have larger charges; (d) BaS; S has a larger charge

108. (e)

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11.14.6: Chapter 6 - Thermodynamics

1. A reaction has a natural tendency to occur and takes place without the continual input of energy from an external source.

3. (a) spontaneous; (b) nonspontaneous; (c) spontaneous; (d) nonspontaneous; (e) spontaneous; (f) spontaneous

5. 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.

7. There are four initial microstates and four final microstates.

$\Delta S = k \ln \frac{W_f}{W_i} = 1.38 \times 10^{-23}\ \text{J/K} \times \ln \frac{4}{4} = 0$

9. The probability for all the particles to be on one side is 1/32. This probability is noticeably lower than the 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.

11. There is only one initial state. For the final state, the energy can be contained in pairs A-C, A-D, B-C, or B-D. Thus, there are four final possible states.

$\Delta S = k \ln \left(\frac{W_f}{W_i}\right) = 1.38 \times 10^{-23}\ \text{J/K} \times \ln \left(\frac{4}{1}\right) = 1.91 \times 10^{-23}\ \text{J/K}$

13. 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.

15. (a) $C_3H_7OH(l)$ as it is a larger molecule (more complex and more massive), and so more microstates describing its motions are available at any given temperature. (b) $C_2H_5OH(g)$ as it is in the gaseous state. (c) $2H(g)$, 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).

17. (a) Negative. The relatively ordered solid precipitating decreases the number of mobile ions in solution. (b) Negative. There is a net loss of three moles of gas from reactants to products. (c) Positive. There is a net increase of seven moles of gas from reactants to products.

19. $\text{C}_6\text{H}_6(l) + 7.5\text{O}_2(g) \longrightarrow 3\text{H}_2\text{O}(g) + 6\text{CO}_2(g)$

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.

21. (a) 107 J/K; (b) –86.4 J/K; (c) 133.2 J/K; (d) 118.8 J/K; (e) –326.6 J/K; (f) –171.9 J/K; (g) –7.2 J/K

23. 100.6 J/K

25. (a) –198.1 J/K; (b) –348.9 J/K

27. 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.

29. (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

31. The reaction is nonspontaneous at room temperature. Above 400 K, ΔG will become negative, and the reaction will become spontaneous.

33. (a) 465.1 kJ nonspontaneous; (b) –106.86 kJ spontaneous; (c) –291.9 kJ spontaneous; (d) –83.4 kJ spontaneous; (e) –406.7 kJ spontaneous; (f) –154.3 kJ spontaneous

35. (a) The standard free energy of formation is –1124.3 kJ/mol. (b) 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.

37. (a) The reaction is nonspontaneous; (b) Above 566 °C the process is spontaneous.

39. (a) 1.5×10^2 kJ; (b) -21.9 kJ; (c) -5.34 kJ; (d) -0.383 kJ; (e) 18 kJ; (f) 71 kJ

41. (a) K = 41; (b) K = 0.053; (c) K = 6.9 × 10^{13}; (d) K = 1.9; (e) K = 0.04

42. (a) 22.1 kJ; (b) 98.9 kJ/mol

44. 90 kJ/mol

46. (a) Under standard thermodynamic conditions, the evaporation is nonspontaneous; (b) $K_p = 0.031$; (c) The evaporation of water is spontaneous; (d) $P_{\mathrm{H_2O}}$ must always be less than K_p or less than 0.031 atm. 0.031 atm represents air saturated with water vapor at $25^{\circ}\mathrm{C}$, or 100% humidity.

48. (a) Nonspontaneous as $\Delta G^{\circ} > 0$; (b) $\Delta G^{\circ} = \Delta G^{\circ} + RT \ln Q$,
$\Delta G = 1.7 \times 10^3 + \left(8.314 \times 310 \times \ln \frac{28}{120}\right) = -2.1$ kJ. The forward reaction to produce F6P is spontaneous under these conditions.

50. 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.

52.

(a) Increasing $P_{\mathrm{O_2}}$ will shift the equilibrium toward the products, which increases the value of K. ΔG° therefore becomes more negative.
(b) Increasing $P_{\mathrm{O_2}}$ will shift the equilibrium toward the products, which increases the value of K. ΔG° therefore becomes more negative.
(c) Increasing $P_{\mathrm{O_2}}$ will shift the equilibrium the reactants, which decreases the value of K. ΔG° therefore becomes more positive.

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11.14.7: Chapter 7 - Fundamental Equilibrium Concepts

1. The reaction can proceed in both the forward and reverse directions.

3. When a system has reached equilibrium, no further changes in the reactant and product concentrations occur; the forward and reverse reactions continue to proceed, but at equal rates.

5. Not necessarily. A system at equilibrium is characterized by *constant* reactant and product concentrations, but the values of the reactant and product concentrations themselves need not be equal.

7. 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.

9. (a) $K_c = \left[\mathrm{Ag}^+\right]\left[\mathrm{Cl}^-\right] < 1$. AgCl is insoluble; thus, the concentrations of ions are much less than $1M$;
(b) $K_c = \dfrac{1}{\left[\mathrm{Pb}^{2+}\right]\left[\mathrm{Cl}^-\right]^2} > 1$ because $\mathrm{PbCl_2}$ is insoluble and formation of the solid will reduce the concentration of ions to a low level (<1 M).

11. Since $K_c = \dfrac{[\mathrm{C_6H_6}]}{[\mathrm{C_2H_2}]^3}$, a value of $K_c \approx 10$ means that $\mathrm{C_6H_6}$ predominates over $\mathrm{C_2H_2}$. In such a case, the reaction would be commercially feasible if the rate to equilibrium is suitable.

13. $K_c > 1$

15.

(a) $Q_c = \dfrac{[\mathrm{CH_3Cl}]\,[\mathrm{HCl}]}{[\mathrm{CH_4}]\,[\mathrm{Cl_2}]}$;

(b) $Q_c = \dfrac{[\mathrm{NO}]^2}{[\mathrm{N_2}]\,[\mathrm{O_2}]}$;

(c) $Q_c = \dfrac{[\mathrm{SO_3}]^2}{[\mathrm{SO_2}]^2\,[\mathrm{O_2}]}$;

(d) $Q_c = [\mathrm{SO_2}]$;

(e) $Q_c = \dfrac{1}{[\mathrm{P_4}]\,[\mathrm{O_2}]^5}$;

(f) $Q_c = \dfrac{[\mathrm{Br}]^2}{[\mathrm{Br_2}]}$;

(g) $Q_c = \dfrac{[\mathrm{CO_2}]}{[\mathrm{CH_4}]\,[\mathrm{O_2}]^2}$; (h) $Q_c = [\mathrm{H_2O}]^5$

Since $K_c = \dfrac{[\mathrm{C_6H_6}]}{[\mathrm{C_2H_2}]^3}$, a value of $K_c \approx 10$ means that $\mathrm{C_6H_6}$ predominates over $\mathrm{C_2H_2}$. In such a case, the reaction would be commercially feasible if the rate to equilibrium is suitable.

17. (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

19. The system will shift toward the reactants to reach equilibrium.

21. (a) homogenous; (b) homogenous; (c) homogenous; (d) heterogeneous; (e) heterogeneous; (f) homogenous; (g) heterogeneous; (h) heterogeneous

23. This situation occurs in (a) and (b).

25. (a) $K_P = 1.6 \times 10^{-4}$; (b) $K_P = 50.2$; (c) $K_c = 5.31 \times 10^{-39}$; (d) $K_c = 4.60 \times 10^{-3}$

27. $K_P = P_{\mathrm{H_2O}} = 0.042$.

29. $Q_c = \dfrac{[\mathrm{NH_4^+}]\,[\mathrm{OH^-}]}{[\mathrm{NH_3}]}$

31. The amount of $CaCO_3$ must be so small that PCO2 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 PCO2 required for equilibrium.

33. 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.

34. 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.

36. Add N_2; add H_2; decrease the container volume; heat the mixture.

38. (a) *T* increase = shift right, *V* decrease = shift left; (b) *T* increase = shift right, *V* = no effect; (c) *T* increase = shift left, *V* decrease = shift left; (d) *T* increase = shift left, *V* decrease = shift right.

40. (a) $K_c = \dfrac{[\mathrm{CH_3OH}]}{[\mathrm{H_2}]^2\,[\mathrm{CO}]}$; (b) $[\mathrm{H_2}]$ increases, $[\mathrm{CO}]$ decreases, $[\mathrm{CH_3OH}]$ increases; (c), $[\mathrm{H_2}]$ increases, $[\mathrm{CO}]$ decreases, $[\mathrm{CH_3OH}]$ decreases; (d), $[\mathrm{H_2}]$ increases, $[\mathrm{CO}]$ increases, $[\mathrm{CH_3OH}]$ increases; (e), $[\mathrm{H_2}]$ increases, $[\mathrm{CO}]$ increases, $[\mathrm{CH_3OH}]$ decreases; (f), no changes.

42. (a) $K_c = \dfrac{[\mathrm{CO}]\,[\mathrm{H_2}]}{[\mathrm{H_2O}]}$; (b) $[\mathrm{H_2O}]$ no change, $[\mathrm{CO}]$ no change, $[\mathrm{H_2}]$ no change; (c) $[\mathrm{H_2O}]$ decreases, $[\mathrm{CO}]$ decreases, $[\mathrm{H_2}]$ decreases; (d) $[\mathrm{H_2O}]$ increases, $[\mathrm{CO}]$ increases, $[\mathrm{H_2}]$ decreases; (f) $[\mathrm{H_2O}]$ decreases, $[\mathrm{CO}]$ increases, $[\mathrm{H_2}]$ increases. In (b), (c), (d), and (e), the mass of carbon will change, but its concentration (activity) will not change.

44. Only (b)

46. 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).

48. Though the solution is saturated, the dynamic nature of the solubility equilibrium means the opposing processes of solid dissolution and precipitation continue to occur (just at equal rates, meaning the dissolved ion concentrations and the amount of undissolved solid remain constant). The radioactive Ag^+ ions detected in the solution phase come from dissolution of the added solid, and their presence is countered by precipitation of nonradioactive Ag^+.

50. $K_c = \dfrac{[\mathrm{C}]^2}{[\mathrm{A}][\mathrm{B}]^2}$. $[\mathrm{A}] = 0.1M, [\mathrm{B}] = 0.1M, [\mathrm{C}] = 1M$; and $[\mathrm{A}] = 0.01, [\mathrm{B}] = 0.250, [\mathrm{C}] = 0.791$.

52. $K_C = 6.00 \times 10^{-2}$

54. $K_C = 0.50$

56. $K_P = 1.9 \times 10^3$

58. $K_P = 3.06$

60. (a) –2*x*, +2*x*; (b) +43x+43x, –23x–23x, –2*x*; (c) –2*x*, 3*x*; (d) +*x*, –*x*, –3*x*; (e) +*x*; (f) –14x–14x.

62. Activities of pure crystalline solids equal 1 and are constant; however, the mass of Ni does change.

64. $[NH_3] = 9.1 \times 10^{-2}$ *M*

66. $P_{BrCl} = 4.9 \times 10^{-2}$ atm

68. $[CO] = 2.04 \times 10^{-4}$ *M*

70. P_{\mathrm{H}_2 \mathrm{O}}=3.64 \times 10^{-3} \mathrm{~atm}

72. 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.

74.

(a) $[NO_2] = 1.17 \times 10^{-3}$ *M*
$[N_2O_4] = 0.128$ *M*
(b) The assumption that *x* is negligibly small compared to 0.129 is confirmed by comparing the initial concentration of the N_2O_4 to its concentration at equilibrium (they differ by just 1 in the least significant digit's place).

76. (a) $[H_2S] = 0.810$ atm

$[H_2] = 0.014$ atm
$[S_2] = 0.0072$ atm

(b) The assumption that 2*x* is negligibly small compared to 0.824 is confirmed by comparing the initial concentration of the H_2S to its concentration at equilibrium (0.824 atm versus 0.810 atm, a difference of less than 2%).

78. 507 g

80. 330 g

83. (a) 0.33 mol. (b) $[CO]_2 = 0.50$ *M*. Added H_2 forms some water as a result of a shift to the left after H_2 is added.

85. (a) $K_c = \frac{[NH_3]^4 [O_2]^7}{[NO_2]^4 [H_2O]^6}$. (b) $[NH_3]$ must increase for Q_c to reach K_c. (c) The increase in system volume would lower the partial pressures of all reactants (including NO_2). (d) $P_{O_2} = 49$ torr

87. $P_{N_2O_3} = 1.90$ atm and $P_{NO} = P_{NO_2} = 1.90$ atm

90. 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 Δ*G* = Δ*H*° – *T*Δ*S*°.

(a) $K = 1.07 \times 10^{-13}$;
(b) $K = 2.42 \times 10^{-3}$;
(c) $K = 2.73 \times 10^{4}$;
(d) $K = 0.229$;
(e) $K = 16.1$

92. 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 $\Delta G = 0$.

94. The reaction will be spontaneous at temperatures greater than 287 K.

96. $K = 5.35 \times 10^{15}$ The process is exothermic.

98. 1.0×10^{-8} atm. This is the maximum pressure of the gases under the stated conditions

100. $x = 1.29 \times 10^{-5}$ atm $= P_{O_2}$

102. -0.16 kJ

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11.14.8: Chapter 8 - Acid-Base Equilibria

1. One example for NH_3 as a conjugate acid: $NH_2^- + H^+ \longrightarrow NH_3$; as a conjugate base:

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

3. (a) $H_3O^+(aq) \longrightarrow H^+(aq) + H_2O(l)$; (b) $HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$; (c)

$$NH_3(aq) \longrightarrow H^+(aq) + NH_2^-(aq);\ \text{(d)}\ CH_3CO_2H(aq) \longrightarrow H^+(aq) + CH_3CO_2^-(aq);\ \text{(e)}$$
$$NH_4 + (aq) \longrightarrow H^+(aq) + NH_3(aq);\ \text{(f)}\ HSO_4^-(aq) \longrightarrow H^+(aq) + SO_4^{2-}(aq)$$

5. (a) $H_2O(l) + H^+(aq) \longrightarrow H_3O^+(aq)$; (b) $OH^-(aq) + H^+(aq) \longrightarrow H_2O(l)$; (c)

$$NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq);\ \text{(d)}\ CN^-(aq) + H^+(aq) \longrightarrow HCN(aq);\text{(e)}$$
$$S^{2-}(aq) + H^+(aq) \longrightarrow HS^-(aq);\ \text{(f)}\ H_2PO_4^-(aq) + H^+(aq) \longrightarrow H_3PO_4(aq)$$

7. (a) H_2O, O^{2-}; (b) H_3O^+, OH^-; (c) $H_2CO_3, {CO_3}^{2-}$; (d) ${NH_4}^+, {NH_2}^-$; (e) $H_2SO_4, {SO_4}^{2-}$; (f) ${H_3O_2}^+, {HO_2}^-$;

$$\text{(g)}\ H_2\ S; S^{2-};\ \text{(h)}\ {H_6\ N_2}^{2+}, H_4\ N_2$$

9. 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) $[Cu\,(H_2O)_3\,(OH)]^+\,(BB), [Al\,(H_2O)_6]^{3+}\,(BA), [Cu\,(H_2O)_4]^{2+}\,(CA), [Al\,(H_2O)_5\,(OH)]^{2+}\,(CB)$; (g) $H_2\ S(BA), {NH_2}^-(BB), HS^-(CB), NH_3(CA)$

11. 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: $H_2O(aq) + NH_3(aq) \rightleftharpoons {NH_4}^+(aq) + OH^-(aq)$. As a base:

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

13. amphiprotic: (a) $NH_3 + {H_3O}^+ \longrightarrow NH_4OH + H_2O, NH_3 + {OCH_3}^- \longrightarrow {NH_2}^- + CH_3OH$; (b) ${HPO_4}^{2-} + OH^- \longrightarrow {PO_4}^{3-} + H_2O, {HPO_4}^{2-} + HClO_4 \longrightarrow {H_2PO_4}^- + {ClO_4}^-$; not amphiprotic:
(c) Br^-; (d) ${NH_4}^+$; (e) ${AsO_4}^{3-}$

15. In a neutral solution [H_3O^+] = [OH^-]. At 40 °C, [H_3O^+] = [OH^-] = $(2.910 \times 10^{-14})^{1/2} = 1.7 \times 10^{-7}$.

17. x=3.051 \times 10^{-7} M=\left[\mathrm{H}_3 \mathrm{O}^{+}\right]=\left[\mathrm{OH}^{-}\right] ; \mathrm{pH}=-\log 3.051 \times 10^{-7}=-(-6.5156)=6.5156 ; \mathrm{pOH}=\mathrm{pH}=6.5156

19. (a) pH = 3.587; pOH = 10.413; (b) pOH = 0.68; pH = 13.32; (c) pOH = 3.85; pH = 10.15; (d) pOH = –0.40; pH = 14.4

21.

[H_3O^+] = 3.0×10^{-7} *M*; [OH^-] = 3.3×10^{-8} *M*

23.

[H_3O^+] = 1×10^{-2} *M*; [OH^-] = 1×10^{-12} *M*

25.

[OH^-] = 3.1×10^{-12} *M*

27.

The salt ionizes in solution, but the anion slightly reacts with water to form the weak acid. This reaction also forms OH^-, which causes the solution to be basic.

29. $[H_2O] > [CH_3CO_2H] > [H_3O^+] \approx [CH_3CO_2^-] > [OH^-]$

31. The oxidation state of the sulfur in H_2SO_4 is greater than the oxidation state of the sulfur in H_2SO_3.

33. $\underset{\text{BB}}{\text{Mg(OH)}_2(s)} + \underset{\text{BA}}{2\text{HCl}(aq)} \Rightarrow \text{Mg}^{2+}(aq) + \underset{\text{CB}}{2\text{Cl}^-(aq)} + \underset{\text{CA}}{2\text{H}_2\text{O}(l)}$

35. $K_a = 2.3 \times 10^{-11}$

37. The stronger base or stronger acid is the one with the larger K_b or K_a, respectively. In these two examples, they are $(CH_3)_2NH$ and $CH_3NH_3^+$.

39. triethylamine

41. (a) HSO_4^-; higher electronegativity of the central ion. (b) $H_2O; NH_3$ is a base and water is neutral, or decide on the basis of K_a values. (c) $HI; PH_3$ is weaker than $HCl; HCl$ is weaker than HI . Thus, PH_3 is weaker than HI . (d) PH_3; in binary compounds of hydrogen with nonmetals, the acidity increases for the element lower in a group. (e) HBr; in a period, the acidity increases from left to right; in a group, it increases from top to bottom. Br is to the left and below S , so HBr is the stronger acid.

43. (a) $NaHSeO_3 < NaHSO_3 < NaHSO_4$; in polyoxy acids, the more electronegative central element- S , in this case-forms the stronger acid. The larger number of oxygen atoms on the central atom (giving it a higher oxidation state) also creates a greater release of hydrogen atoms, resulting in a stronger acid. As a salt, the acidity increases in the same manner.

(b) $ClO_2^- < BrO_2^- < IO_2^-$; the basicity of the anions in a series of acids will be the opposite of the acidity in their oxyacids. The acidity increases as the electronegativity of the central atom increases. CI is more electronegative than Br, and I is the least electronegative of the three.

(c) $HOI < HOBr < HOCl$; in a series of the same form of oxyacids, the acidity increases as the electronegativity of the central atom increases. CI is more electronegative than Br, and I is the least electronegative of the three.

(d) $HOCl < HOClO < HOClO_2 < HOClO_3$; in a series of oxyacids of the same central element, the acidity increases as the number of oxygen atoms increases (or as the oxidation state of the central atom increases).

(e) $HTe^- < HS^- \ll PH_2^- < NH_2^-; PH_2^-$and $NH_2^-$are anions of weak bases, so they act as strong bases toward $H^+.HTe^-$and HS^- are anions of weak acids, so they have less basic character. In a periodic group, the more electronegative element has the more basic anion.

(f) $BrO_4^- < BrO_3^- < BrO_2^- < BrO^-$; with a larger number of oxygen atoms (that is, as the oxidation state of the central ion increases), the corresponding acid becomes more acidic and the anion consequently less basic.

45. $[H_2O] > [C_6H_4OH(CO_2H)] > [H^+]\,0 > [C_6H_4OH(CO_2)^-] \gg [C_6H_4O(CO_2H)^-] > [OH^-]$

47. 1. 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. 2. Assume we can neglect the contribution of water to the equilibrium concentration of H_3O^+.

48. (b) The addition of HCl

50. (a) 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. (b) 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. (c) 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. (d) Adding NaCl has no effect on the concentrations of the ions. (e) Adding KNO_2 adds NO_2^-ions and shifts the equilibrium to the right, increasing the HNO_2 and OH^-ion concentrations.

52. This is a case in which the solution contains a mixture of acids of different ionization strengths. In solution, the $\mathrm{HCO_2H}$ exists primarily as $\mathrm{HCO_2H}$ molecules because the ionization of the weak acid is suppressed by the strong acid. Therefore, the $\mathrm{HCO_2H}$ 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 $[\mathrm{H_3O^+}]$produced by the stronger acid.

54. (a) $K_\mathrm{b} = 1.8 \times 10^{-5}$; (b) $K_\mathrm{a} = 4.5 \times 10^{-4}$; (c) $K_\mathrm{b} = 6.4 \times 10^{-5}$; (d) $K_\mathrm{a} = 5.6 \times 10^{-10}$

56. $K_\mathrm{a} = 1.2 \times 10^{-2}$

58. (a) $K_\mathrm{b} = 4.3 \times 10^{-12}$ (b) $K_\mathrm{a} = 1.6 \times 10^{-10}$ (c) $K_\mathrm{b} = 5.9 \times 10^{-8}$ (d) $K_\mathrm{b} = 4.2 \times 10^{-3}$(e) $K_\mathrm{b} = 2.3 \times 10^{-5}$ (f) $K_\mathrm{b} = 6.3 \times 10^{-13}$

60. (a) $\dfrac{[\mathrm{H_3O^+}]\,[\mathrm{ClO^-}]}{[\mathrm{HClO}]} = \dfrac{(x)(x)}{(0.0092 - x)} \approx \dfrac{(x)(x)}{0.0092} = 2.9 \times 10^{-8}$

Solving for x gives $1.63 \times 10^{-5} M$. 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:

$[\mathrm{H_3O^+}] = [\mathrm{ClO^-}] = 1.6 \times 10^{-5}\mathrm{M}$
$[\mathrm{HClO^-}] = 0.0092\mathrm{M}$
$[\mathrm{OH^-}] = 6.1 \times 10^{-10}\mathrm{M}$

(b) $\dfrac{[\mathrm{C_6H_5NH_3{}^+}]\,[\mathrm{OH^-}]}{[\mathrm{C_6H_5NH_2}]} = \dfrac{(x)(x)}{(0.0784 - x)} \approx \dfrac{(x)(x)}{0.0784} = 4.3 \times 10^{-10}$

Solving for x gives $5.81 \times 10^{-6} M$. 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:

$[\mathrm{C_6H_5NH_3{}^+}] = [\mathrm{OH^-}] = 5.8 \times 10^{-6}\mathrm{M}$
$[\mathrm{C_6H_5NH_2}] = 0.0784\mathrm{M}$
$[\mathrm{H_3O^+}] = 1.7 \times 10^{-9}\mathrm{M};$

(c) $\dfrac{[\mathrm{H_3O^+}]\,[\mathrm{CN^-}]}{[\mathrm{HCN}]} = \dfrac{(x)(x)}{(0.0810 - x)} \approx \dfrac{(x)(x)}{0.0810} = 4.9 \times 10^{-10}$

Solving for x gives $6.30 \times 10^{-6} M$. 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:

$[\mathrm{H_3O^+}] = [\mathrm{CN^-}] = 6.3 \times 10^{-6}\mathrm{M}$
$[\mathrm{HCN^-}] = 0.0810\mathrm{M}$
$[\mathrm{OH^-}] = 1.6 \times 10^{-9}\mathrm{M};$

(d) $\dfrac{[(\mathrm{CH_3})_3\,\mathrm{NH^+}]\,[\mathrm{OH^-}]}{[(\mathrm{CH_3})_3\ \mathrm{N}]} = \dfrac{(x)(x)}{(0.11 - x)} \approx \dfrac{(x)(x)}{0.11} = 6.3 \times 10^{-5}$

Solving for x gives $2.63 \times 10^{-3} M$. 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:

$[(\mathrm{CH_3})_3\,\mathrm{NH^+}] = [\mathrm{OH^-}] = 2.6 \times 10^{-3}\mathrm{M}$
$[(\mathrm{CH_3})_3\ \mathrm{N}] = 0.11\mathrm{M}$
$[\mathrm{H_3O^+}] = 3.8 \times 10^{-12}\mathrm{M}$

(e) $\dfrac{[\mathrm{Fe\,(H_2O)_5\,(OH)^+}]\,[\mathrm{H_3O^+}]}{[\mathrm{Fe\,(H_2O)_6{}^{2+}}]} = \dfrac{(x)(x)}{(0.120 - x)} \approx \dfrac{(x)(x)}{0.120} = 1.6 \times 10^{-7}$

Solving for x gives $1.39 \times 10^{-4} M$. 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:

$[\mathrm{Fe(H_2O)_5(OH)^+}] = [\mathrm{H_3O^+}] = 1.4 \times 10^{-4}\mathrm{M}$
$[\mathrm{Fe(H_2O)_6}^{2+}] = 0.120\mathrm{M}$
$[\mathrm{OH^-}] = 7.2 \times 10^{-11}\mathrm{M}$

62. pH = 2.41

64. $[\mathrm{C_{10}H_{14}\ N_2}] = 0.049M; [\mathrm{C_{10}H_{14}\ N_2H^+}] = 1.9 \times 10^{-4}M; [\mathrm{C_{10}H_{14}\ N_2H_2}^{2+}] = 1.4 \times 10^{-11}M; [\mathrm{OH^-}] = 1.9 \times 10^{-4}M; [\mathrm{H_3O^+}] = 5.3 \times 10^{-11}M$

66. $K_\mathrm{a} = 1.2 \times 10^{-2}$

68. $K_\mathrm{b} = 1.77 \times 10^{-5}$

70. (a) acidic; (b) basic; (c) acidic; (d) neutral

72. $[\mathrm{H_3O^+}]$and $[\mathrm{HCO_3^-}]$are practically equal

74. $[\mathrm{C_6H_4(CO_2H)_2}]\ 7.2 \times 10^{-3}M$, $[\mathrm{C_6H_4(CO_2H)(CO_2)^-}] = [\mathrm{H_3O^+}]\ 2.8 \times 10^{-3}M$, $[\mathrm{C_6H_4(CO_2)_2}^{2-}]\ 3.9 \times 10^{-6}M$, $[\mathrm{OH^-}]\ 3.6 \times 10^{-12}M$

76. (a) $K_{\mathrm{a}2} = 1.5 \times 10^{-11}$;

(b) $K_\mathrm{b} = 4.3 \times 10^{-12}$;

(c) $\dfrac{[\mathrm{Te^{2-}}]\,[\mathrm{H_3O^+}]}{[\mathrm{HTe^-}]} = \dfrac{(x)(0.0141+x)}{(0.0141-x)} \approx \dfrac{(x)(0.0141)}{0.0141} = 1.5 \times 10^{-11}$

Solving for x gives $1.5 \times 10^{-11}M$. Therefore, compared with $0.014M$, this value is negligible ($1.1 \times 10^{-7}\%$).

78. Excess $\mathrm{H_3O^+}$is removed primarily by the reaction:

$\mathrm{H_3O^+}(aq) + \mathrm{H_2PO_4^-}(aq) \longrightarrow \mathrm{H_3PO_4}(aq) + \mathrm{H_2O}(l)$

Excess base is removed by the reaction: $\mathrm{OH^-}(aq) + \mathrm{H_3PO_4}(aq) \longrightarrow \mathrm{H_2PO_4}^-(aq) + \mathrm{H_2O}(l)$

80. \left[\mathrm{H}_3 \mathrm{O}^{+}\right]=1.5 \times 10^{-4} M

82. \left[\mathrm{OH}^{-}\right]=4.2 \times 10^{-4} \mathrm{M}

84. (a) The added HCl will increase the concentration of $\mathrm{H_3O^+}$slightly, which will react with $\mathrm{CH_3CO_2^-}$and produce $\mathrm{CH_3CO_2H}$ in the process. Thus, $[\mathrm{CH_3CO_2^-}]$decreases and $[\mathrm{CH_3CO_2H}]$ increases. (b) The added $\mathrm{KCH_3CO_2}$ will increase the concentration of $[\mathrm{CH_3CO_2^-}]$which will react with $\mathrm{H_3O^+}$and produce $\mathrm{CH_3CO_2H}$ in the process. Thus, $[\mathrm{H_3O^+}]$decreases slightly and $[\mathrm{CH_3CO_2H}]$ increases. (c) The added NaCl will have no effect on the concentration of the ions. (d) The added KOH will produce $\mathrm{OH^-}$ions, which will react with the $\mathrm{H_3O^+}$, thus reducing [$\mathrm{H_3O^+}$]. Some additional $\mathrm{CH_3CO_2H}$ will dissociate, producing [$\mathrm{CH_3CO_2^-}$] ions in the process. Thus, $[\mathrm{CH_3CO_2H}]$ decreases slightly and $[\mathrm{CH_3CO_2^-}]$increases. (e) The added $\mathrm{CH_3CO_2H}$ will increase its concentration, causing more of it to dissociate and producing more [$\mathrm{CH_3CO_2^-}$] and $\mathrm{H_3O^+}$in the process. Thus, $[\mathrm{H_3O^+}]$increases slightly and $[\mathrm{CH_3CO_2^-}]$increases.

86. pH = 8.95

88. 37 g (0.27 mol)

90. (a) pH = 5.222; (b) The solution is acidic. (c) pH = 5.220

92. At the equivalence point in the titration of a weak base with a strong acid, the resulting solution is slightly acidic due to the presence of the conjugate acid. Thus, pick an indicator that changes color in the acidic range and brackets the pH at the equivalence point. Methyl orange is a good example.

94. (a) pH = 2.50; (b) pH = 4.01; (c) pH = 5.60; (d) pH = 8.35; (e) pH = 11.08

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11.14.9: Chapter 9 - Electrochemistry

1. (a) reduction; (b) oxidation; (c) oxidation; (d) reduction

3. (a) $\mathrm{F_2 + Ca \longrightarrow 2\ F^- + Ca^{2+}}$; (b) $\mathrm{Cl_2 + 2Li \longrightarrow 2Li^+ + 2Cl^-}$; (c) $\mathrm{3Br_2 + 2Fe \longrightarrow 2Fe^{3+} + 6Br^-}$; (d) $\mathrm{MnO_4^- + 4H^+ + 3Ag \longrightarrow 3Ag^+ + MnO_2 + 2H_2O}$

5. Oxidized: (a) $\mathrm{Sn^{2+}}$; (b) Hg ; (c) Al ; reduced: (a) $\mathrm{H_2O_2}$; (b) $\mathrm{PbO_2}$; (c) $\mathrm{Cr_2O_7^{2-}}$; oxidizing agent: (a) $\mathrm{H_2O_2}$; (b) $\mathrm{PbO_2}$; (c) $\mathrm{Cr_2O_7^{2-}}$; reducing agent: (a) $\mathrm{Sn^{2+}}$; (b) Hg; (c) Al

7. Oxidized = reducing agent: (a) $\mathrm{SO_3^{2-}}$; (b) $\mathrm{Mn(OH)_2}$; (c) $\mathrm{H_2}$; (d) Al; reduced = oxidizing agent: (a) $\mathrm{Cu(OH)_2}$; (b) $\mathrm{O_2}$; (c) $\mathrm{NO_3^-}$; (d) $\mathrm{CrO_4^{2-}}$

9. In basic solution, $\mathrm{[OH^-] > 1 \times 10^{-7} \mathit{M} > [H^+]}$. Hydrogen ion cannot appear as a reactant because its concentration is essentially zero. If it were produced, it would instantly react with the excess hydroxide ion to produce water. Thus, hydrogen ion should not appear as a reactant or product in basic solution.

11. (a) $\mathrm{Mg(\mathit{s})\left|Mg^{2+}(\mathit{aq})\right\|Ni^{2+}(\mathit{aq})\left|Ni(\mathit{s})\right.}$; (b) $\mathrm{Cu(\mathit{s})\left|Cu^{2+}(\mathit{aq})\right\|Ag^{+}(\mathit{aq})\left|Ag(\mathit{s})\right.}$; (c) $\mathrm{Mn(\mathit{s})\left|Mn^{2+}(\mathit{aq})\right\|Sn^{2+}(\mathit{aq})|Sn(\mathit{s})}$; (d) $\mathrm{Pt(\mathit{s})|Cu^{+}(\mathit{aq}), Cu^{2+}(\mathit{aq})\left\|Au^{3+}(\mathit{aq})\right|Au(\mathit{s})}$

13. (a) $\mathrm{Mg(\mathit{s}) + Cu^{2+}(\mathit{aq}) \longrightarrow Mg^{2+}(\mathit{aq}) + Cu(\mathit{s})}$; (b) $\mathrm{2Ag^{+}(\mathit{aq}) + Ni(\mathit{s}) \longrightarrow Ni^{2+}(\mathit{aq}) + 2Ag(\mathit{s})}$

15. Species oxidized = reducing agent: (a) Al(s); (b) NO(g); (c) $\mathrm{Mg(\mathit{s})}$; and (d) $\mathrm{MnO_2(\mathit{s})}$; Species reduced = oxidizing agent: (a) $\mathrm{Zr^{4+}(\mathit{aq})}$; (b) $\mathrm{Ag^{+}(\mathit{aq})}$; (c) $\mathrm{SiO_3^{2-}(\mathit{aq})}$; and (d) $\mathrm{ClO_3^{-}(\mathit{aq})}$

17. 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.

19. 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.

21. (a) +2.115 V (spontaneous); (b) +0.4626 V (spontaneous); (c) +1.048 V (spontaneous); (d) +0.727 V (spontaneous)

23. $\mathrm{3Cu(\mathit{s}) + 2Au^{3+}(\mathit{aq}) \longrightarrow 3Cu^{2+}(\mathit{aq}) + 2Au(\mathit{s})}$; $+1.16\ \mathrm{V}$; spontaneous

25. $\mathrm{3Cd(\mathit{s}) + 2Al^{3+}(\mathit{aq}) \longrightarrow 3Cd^{2+}(\mathit{aq}) + 2Al(\mathit{s})}$; $-1.259\ \mathrm{V}$; nonspontaneous

27. (a) 0 kJ/mol; (b) $-83.7\ \mathrm{kJ/mol}$; (c) $+235.3\ \mathrm{kJ/mol}$

29. (a) standard cell potential: 1.50 V, spontaneous; cell potential under stated conditions: 1.43 V, spontaneous; (b) standard cell potential: 1.405 V, spontaneous; cell potential under stated conditions: 1.423 V, spontaneous; (c) standard cell potential: -2.749 V, nonspontaneous; cell potential under stated conditions: -2.733 V, nonspontaneous

31. (a) 1.7×10^{-10}; (b) 2.6×10^{-21}; (c) 4.693×10^{21}; (d) 1.0×10^{-14}

[33. (a) anode: $\mathrm{Cu(\mathit{s}) \longrightarrow Cu^{2+}(\mathit{aq}) + 2e^-}$ cathode: $\mathrm{2 \times (Ag^{+}(\mathit{aq}) + e^- \longrightarrow Ag(\mathit{s}))}$ $E^\circ_{\mathrm{cathode}} = 0.7996\ \mathrm{V}'$; (b) 3.5×10^{15}; (c) $5.6 \times 10^{-9} \mathit{M}$

34. Batteries are self-contained and have a limited supply of reagents to expend before going dead. Alternatively, battery reaction byproducts accumulate and interfere with the reaction. Because a fuel cell is constantly resupplied with reactants and products are expelled, it can continue to function as long as reagents are supplied.

36. According to kinetic theory, chemical reactions occur more slowly at lower temperatures due to the decreased rate of collisions between reactant molecules. The rates of the redox reactions taking place within batteries decrease with temperature, resulting in a decreased production of electrical current.

38. Mg and Zn

40. Both examples involve cathodic protection. The (sacrificial) anode is the metal that corrodes (oxidizes or reacts). In the case of iron (-0.447 V) and zinc (-0.7618 V), zinc has a more negative standard reduction potential and so serves as the anode. In the case of iron and copper (0.34 V), iron has the smaller standard reduction potential and so corrodes (serves as the anode).

42. While the reduction potential of lithium would make it capable of protecting the other metals, this high potential is also indicative of how reactive lithium is; it would have a spontaneous reaction with most substances. This means that the lithium would react quickly with other substances, even those that would not oxidize the metal it is attempting to protect. Reactivity like this means the sacrificial anode would be depleted rapidly and need to be replaced frequently. (Optional additional reason: fire hazard in the presence of water.)

46. (a) $\begin{matrix}\text{mass Ca} = 69.1\text{ g}\\ \text{mass Cl}_2 = 122\text{ g}\end{matrix}$; (b) $\begin{matrix}\text{mass Li} = 23.9\text{ g}\\ \text{mass H}_2 = 3.48\text{ g}\end{matrix}$; (c) $\begin{matrix}\text{mass Al} = 31.0\text{ g}\\ \text{mass Cl}_2 = 122\text{ g}\end{matrix}$; (d) $\begin{matrix}\text{mass Cr} = 59.8\text{ g}\\ \text{mass Br}_2 = 276\text{ g}\end{matrix}$

48. 0.79 L

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11.14.10: Chapter 10 - Kinetics

1.

The instantaneous rate is the rate of a reaction at any particular point in time, a period of time that is so short that the concentrations of reactants and products change by a negligible amount. The initial rate is the instantaneous rate of reaction as it starts (as product just begins to form). Average rate is the average of the instantaneous rates over a time period.

3.

$\text{rate} = +\frac{1}{2}\,\frac{\Delta[\text{ClF}_3]}{\Delta t} = -\frac{\Delta[\text{Cl}_2]}{\Delta t} = -\frac{1}{3}\,\frac{\Delta[\text{F}_2]}{\Delta t}$

5.

(a) average rate, 0 – 10 s = 0.0375 mol L^{-1} s^{-1}; average rate, 10 – 20 s = 0.0265 mol L^{-1} s^{-1}; (b) instantaneous rate, 15 s = 0.023 mol L^{-1} s^{-1}; (c) average rate for B formation = 0.0188 mol L^{-1} s^{-1}; instantaneous rate for B formation = 0.012 mol L^{-1} s^{-1}

7.

Higher molarity increases the rate of the reaction. Higher temperature increases the rate of the reaction. Smaller pieces of magnesium metal will react more rapidly than larger pieces because more reactive surface exists.

9.

(a) 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. (b) Particles of reactant must come into contact with each other before they can react.

11.

(a) very slow; (b) As the temperature is increased, the reaction proceeds at a faster rate. The amount of reactants decreases, and the amount of products increases. After a while, there is a roughly equal amount of *BC*, *AB*, and *C* in the mixture and a slight excess of *A*.

13.

(a) 2; (b) 1

15.

(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.

17.

4.3×10^{-5} mol/L/s

19.

7.9×10^{-13} mol/L/year

21.

rate = *k*; $k = 2.0 \times 10^{-2}$ mol L^{-1} h^{-1} (about 0.9 g L^{-1} h^{-1} for the average male); The reaction is zero order.

23.

rate = $k[\text{NOCl}]^2$; $k = 8.0 \times 10^{-8}$ L/mol/h; second order

25.

rate = $k[NO]^2[Cl_2]$; k = 9.1 L^2 mol^{-2} h^{-1}; second order in NO; first order in Cl_2

27.

(a) The rate law is second order in A and is written as rate = $k[A]^2$. (b) $k = 7.88 \times 10^{-3}$ L mol^{-1} s^{-1}

29.

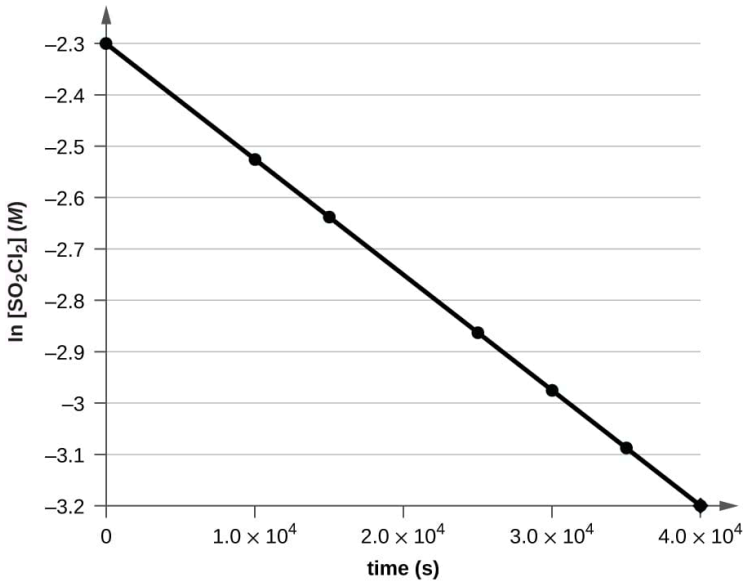
(a) 2.5×10^{-4} mol/L/min

31.

rate = $k[I^-][OCl^-]$; $k = 6.1 \times 10^{-2}$ L mol^{-1} s^{-1}

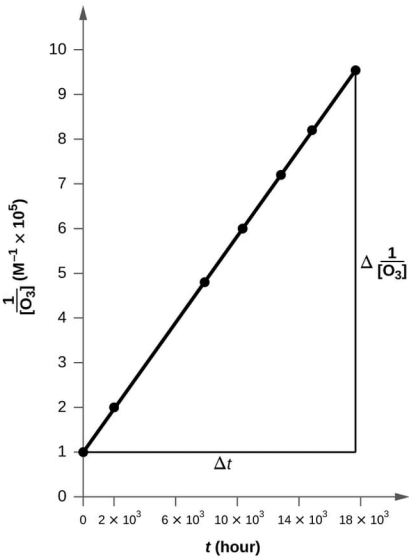
33.

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}

34.



The plot is nicely linear, so the reaction is second order. k = 50.1 L mol^{-1} h^{-1}

36.

14.3 d

38.

8.3×10^7 s

40.

0.826 s

42.

The reaction is first order. $k = 1.0 \times 10^7$ L mol^{-1} min^{-1}

44.

1.16×10^3 s ; 20% remains

46.

252 days

48.

$[A]_0$ (M)	$k \times 10^3$ (s^{-1})
4.88	2.45
3.52	2.51
2.29	2.53
1.81	2.58
5.33	2.36
4.05	2.47

$[A]_0$ (M)	$k \times 10^3$ (s^{-1})
2.95	2.48
1.72	2.43

50.

The reactants either may be moving too slowly to have enough kinetic energy to exceed the activation energy for the reaction, or the orientation of the molecules when they collide may prevent the reaction from occurring.

52.

The activation energy is the minimum amount of energy necessary to form the activated complex in a reaction. It is usually expressed as the energy necessary to form one mole of activated complex.

54.

After finding k at several different temperatures, a plot of ln k versus $\frac{1}{T}$, gives a straight line with the slope [redacted] from which E_a may be determined.

56.

(a) 4-times faster (b) 128-times faster

58.

$3.9 \times 10^{15}\,\mathrm{s}^{-1}$

60.

43.0 kJ/mol

62.

177 kJ/mol

64.

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.

66.

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.

68.

No. In general, for the overall reaction, we cannot predict the effect of changing the concentration without knowing the rate law. Yes. If the reaction is an elementary reaction, then doubling the concentration of *A* doubles the rate.

70.

Rate = $k[A][B]^2$; Rate = $k[A]^3$

72.

(a) Rate$_1$ = k[O_3]; (b) Rate$_2$ = k[O_3][Cl]; (c) Rate$_3$ = k[ClO][O]; (d) Rate$_2$ = k[O_3][NO]; (e) Rate$_3$ = k[NO_2][O]

74.

(a) Doubling [H_2] doubles the rate. [H_2] must enter the rate law to the first power. Doubling [NO] increases the rate by a factor of 4. [NO] must enter the rate law to the second power. (b) Rate = k [NO]^2[H_2]; (c) k = 5.0 $\times$ 10^3 mol^{-2} L^{-2} min^{-1}; (d) 0.0050 mol/L; (e) Step II is the rate-determining step. If step I gives N_2O_2 in adequate amount, steps 1 and 2 combine to give $2\mathrm{NO} + \mathrm{H_2} \longrightarrow \mathrm{H_2O} + \mathrm{N_2O}$. This reaction corresponds to the observed rate law. Combine steps 1 and 2 with step 3, which occurs by supposition in a rapid fashion, to give the appropriate stoichiometry.

76.

The general mode of action for a catalyst is to provide a mechanism by which the reactants can unite more readily by taking a path with a lower reaction energy. The rates of both the forward and the reverse reactions are increased, leading to a faster achievement of equilibrium.

78.

(a) Chlorine atoms are a catalyst because they react in the second step but are regenerated in the third step. Thus, they are not used up, which is a characteristic of catalysts. (b) NO is a catalyst for the same reason as in part (a).

79.

no changes.

82.

The lowering of the transition state energy indicates the effect of a catalyst. (a) B; (b) B

84.

The energy needed to go from the initial state to the transition state is (a) 10 kJ; (b) 10 kJ

86.

Both diagrams describe two-step, exothermic reactions, but with different changes in enthalpy, suggesting the diagrams depict two different overall reactions.

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GLOSSARY

A

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 $[H_3O^+]>[OH^-]$

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 | 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

Amphiphilic | molecules possessing both hydrophobic (nonpolar) and a hydrophilic (polar) parts

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 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 6.022×10^{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

B

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 $[H_3O^+] < [OH^-]$

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

Bicarbonate anion | salt of the hydrogen carbonate ion, HCO_3^-

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

Born-Haber cycle | thermochemical cycle relating the various energetic steps involved in the formation of an ionic solid from the relevant elements

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

C

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 CO_3^{2-}; 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

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)

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 number | number of atoms closest to any given atom in a crystal or to the central metal atom in a complex

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 | bond formed when electrons are shared between atoms

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

Covalent radius | one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond

Critical point | temperature and pressure above which a gas cannot be condensed into a liquid

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

D

***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

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

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

Dispersion force | (also, London dispersion force) attraction between two rapidly fluctuating, temporary dipoles; significant only when particles are very close together

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

E

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 (1 V = 1 J/C)

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

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 (ΔH) | 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

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

F

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

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)

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 (ν) | number of wave cycles (peaks or troughs) that pass a specified point in space per unit time

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 $e = 1.602\ 10^{-19}$ C

Fusion | combination of very light nuclei into heavier nuclei, accompanied by the conversion of mass into large amounts of energy

G

Galvanic cell | electrochemical cell that involves a spontaneous oxidation-reduction reaction; electrochemical cells with positive cell potentials; also called a voltaic cell

Gas | state in which matter has neither definite volume nor shape

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

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

H

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^-)

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

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

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 halide | binary compound formed between hydrogen and the halogens: HF, HCl, HBr, and HI

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

I

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

J

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

K_c | equilibrium constant for reactions based on concentrations of reactants and products

Kelvin (K) | SI unit of temperature; 273.15 K = 0 °C

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

Kinetic energy | energy of a moving body, in joules, equal to 1/2 mv^2 (where m = mass and v = velocity

K_P | equilibrium constant for gas-phase reactions based on partial pressures of reactants and products

L

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 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

Lewis structure | diagram showing lone pairs and bonding pairs of electrons in a molecule o

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

M

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

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, 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

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 | 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

N

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_3^- 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, 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

Nucleon | collective term for protons and neutrons in a nucleus

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

Nutritional calorie (Calorie) | unit used for quantifying energy provided by digestion of foods, defined as 1000 cal or 1 kcal

O

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), 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

***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, O_2^{2-}

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

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 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

Q

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

R

Radiation absorbed dose (rad) | SI unit for measuring radiation dose, frequently used in medical applications; 1 rad = 0.01 Gy

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

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

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 reactantsr

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 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

S

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

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

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 +1/2 or - 1/2

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 ($E°_{cell}$) | 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 ($\Delta H°_c$) | heat released when one mole of a compound undergoes complete combustion under standard conditions

Standard enthalpy of formation ($\Delta H°_f$) | 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 $S°_{298}$

Standard entropy change (ΔS°) | change in entropy for a reaction calculated using the standard entropies, usually at room temperature and denoted $S°_{298}$

Standard free energy change (ΔG°) | 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 ($\Delta G°_f$) | 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 | SO_4^{2-}

Sulfite | SO_3^{2-}

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_2^-

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

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; 1 torr = 1/760 atm

***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

U

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

V

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

W

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

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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