CHEM 2000: CHEMISTRY FOR ENGINEERS



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CHM 2000 General Chemistry for Engineering

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Licensing

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Preface

This is the first text in a new, coordinated engineering curriculum, integrating Introduction to Engineering, Chemistry, Physics and Calculus. These courses are commonly taken by first and second year engineering students, but except for Introduction to Engineering, they are not designed for engineers.

Particularly in the case of chemistry, the normal courses assume that students do not know many things that engineering students do such as the SI system, emphasize many things that are superfluous to most engineers such as bio-chemistry, and, because most engineers only take the first semester, leave out important topics such as chemical kinetics and equilibrium.

Many things that are customarily taught in General Chemistry, such as the old quantum theory (Bohr atom, Heisenberg Uncertainty Principle), may be mentioned but will not be covered in this course, because you will encounter them in General Physics. The course assumes that engineering students know a number of topics generally covered in General Chemistry such as SI units, significant figures, conversion factors, dimensional analysis, logarithms and exponents, etc.

This textbook is designed for an intensive, one semester, General Chemistry course for Engineers including kinetics, equilibrium and electrochemistry. Biologically oriented topics often found in General Chemistry textbooks are eliminated and replaced by materials centered themes.

The traditional approach of General Chemistry Texts is ad hoc, sequentially introducing any number of models of chemical bonding and reaction without providing a conceptual basis for them. This Atoms First text starts by discussing atomic structure, the periodic table and molecular structure. The ad hoc models are then easily seen to be special applications of the more general atomic structure taught at the beginning of this course. After this chapters describe states of matter and simple chemical reactions, followed by discussion of chemical kinetics, equilibrium, thermodynamics, electrochemistry and nuclear chemistry. The text discusses exciting and relevant aspects of materials science that are usually relegated to the last few chapters,

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The authors acknowledge the help and support of Prof. Delmar Larson at UC Davis who created and runs the LibreText project. Prof. Larson has been a great help and mentor in preparing this text.

Broader impacts of research and teaching are an important part of a scientist's life and are made possible by the freedom to explore new things granted by universities and research agencies. Joshua Halpern (Howard University), Scott Sinex and Scott Johnson (both PGCC) gratefully acknowledge the support of this LibreTexts Book by NSF Award 1205608. Josh Halpern acknowledges the support of NSF Award 1524638.

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So who wrote the book? Well, the underlying text, Principles of General Chemistry, published under a the Creative Commons by-nc-sa 3.0 license, can be found at Lardbucket together with an explanation as to why, at least there, the names of the original authors and the publisher are not to be found.

The ChemWiki project and I naturally will follow the request of the publisher in this matter.

The text of this Atoms First edition has a number of modifications (we hope improvements) that have made which can be identified by comparison with the text at Lardbucket.

Josh Halpern. Scott Sinex and Scott Johnson

January 2016

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Chapter 1.1: The Atom

learning_objectives

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

To date, about 115 different elements have been discovered; each is chemically unique. That means that they behave differently in forming molecules and reacting with other elements and molecules. To understand why they are unique, you need to understand the structure of the atom (the fundamental, individual particle of an element) and the characteristics of these components.

Atoms consist of electrons, a light, subatomic particle with a negative charge that resides around the nucleus of all atoms protons and neutrons.This is an oversimplification that ignores the other subatomic particles that have been discovered, but it is sufficient for our discussion of chemical principles. Some properties of these subatomic particles are summarized in Table 1.1.1 , which illustrates three important points.

1. Electrons and protons have electrical charges that are identical in magnitude but opposite in sign. No particle with any fractional charge has ever been discovered although many have tried. For historical reasons having to do with the earliest studies of electricity we assign charges of −1 and +1 to the electron and proton, respectively.
2. Neutrons have approximately the same mass as protons but no charge. They are electrically neutral.
3. The mass of a proton or a neutron is about 1836 times greater than the mass of an electron. Protons and neutrons constitute by far the bulk of the mass of atoms.

The discovery of the electron and the proton was crucial to the development of the modern model of the atom. This will be discussed in our General Physics course.

Table 1.1.1 Properties of Subatomic Particles*

Particle	Mass (g)	Atomic Mass (amu)	Electrical Charge (coulombs)	Relative Charge
electron	9.109×10^{-28}	0.0005486	-1.602×10^{-19}	−1
proton	1.673×10^{-24}	1.007276	$+1.602 \times 10^{-19}$	+1
neutron	1.675×10^{-24}	1.008665	0	0

The Atomic Model

Ernest Rutherford proved that all of the positive charge and almost all of the mass each atom was found in a small core, called the nucleus. Although Rutherford could not explain why repulsion between the positive charges in nuclei that contained more than one positive charge did not cause the nucleus to disintegrate, he reasoned that repulsion between the positively charged nucleus and the negatively charged electrons would cause the electrons to be distributed throughout the atom's volume.Today we know that *strong nuclear forces*, which are much stronger than electrostatic interactions, hold the protons and the neutrons together in the nucleus. For this and other insights, Rutherford was awarded the Nobel Prize in Chemistry in 1908.

Subsequently, Rutherford established that the nucleus of the hydrogen atom was a positively charged particle, for which he coined the name *proton* in 1920. He also suggested that the nuclei of elements other than hydrogen must contain electrically neutral particles with approximately the same mass as the proton. The neutron, however, was not discovered until 1932, when James Chadwick (1891–1974, a student of Rutherford discovered it. For this he won the Nobel Prize in Physics in 1935.

Rutherford's model of the atom is essentially the same as the modern one, except that we now know that electrons are *not* uniformly distributed throughout an atom's volume. Instead, they are distributed according to a set of principles described in Chapter 2.

A more detailed discussion of how the atomic model was established can be found in the companion textbook at Howard University. In 1913 Nels Bohr created a simple model of Rutherford's hydrogen atom. You can follow his work in this LibreTexts book and read more about it in this other LibreTexts book.

Summary

Atoms, the smallest particles of an element that exhibit the properties of that element, consist of negatively charged **electrons** around a central **nucleus** composed of more massive positively charged **protons** and electrically neutral **neutrons**. **Radioactivity** is the emission of energetic particles and rays (radiation) by some substances.

Key Takeaway

- The atom consists of discrete particles that govern its chemical and physical behavior.

Contributors

- Anonymous

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Chapter 1.2: Isotopes and Atomic Masses

Learning Objectives

- To know the meaning of isotopes and atomic masses.

Rutherford's nuclear model of the atom helped explain why atoms of different elements exhibit different chemical behavior. The identity of an element is defined by its atomic number (*Z*)The number of protons in the nucleus of an atom of an element., the number of protons in the nucleus of an atom of the element. *The atomic number is therefore different for each element*. The known elements are arranged in order of increasing *Z* in the periodic tableA chart of the chemical elements arranged in rows of increasing atomic number so that the elements in each column (group) have similar chemical properties. (Figure 1.2.1). We will explain the rationale for the form of the periodic table in Chapter 3 . In the periodic table each element is assigned a unique one-, two-, or three-letter symbol. The names of the elements are listed in the periodic table, along with their symbols, atomic numbers, and atomic masses. The chemistry of each element is determined by its number of protons and electrons. In a neutral atom, the number of electrons equals the number of protons.

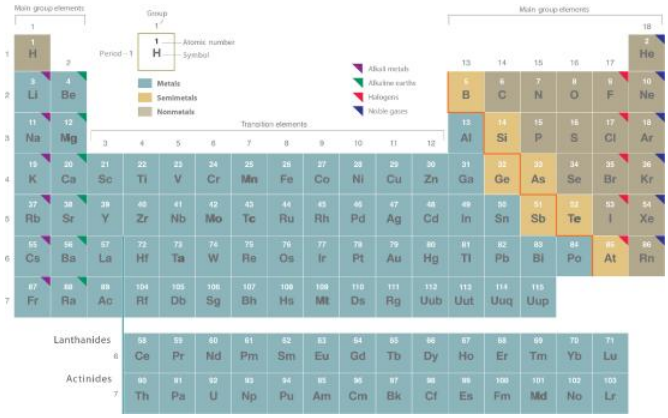


Figure 1.2.1 The Periodic Table Showing the Elements in Order of Increasing *Z* *The metals are shown in blue, and the nonmetals are shown in brown. The semimetals lie along a diagonal line separating the metals and nonmetals. In the third chapter we will discover why the table appears as it does.*

In most cases, the symbols for the elements are derived directly from each element's name, such as C for carbon, U for uranium, Ca for calcium, and Po for polonium. Elements have also been named for their properties [such as radium (Ra) for its radioactivity], for the native country of the scientist(s) who discovered them [polonium (Po) for Poland], for eminent scientists [curium (Cm) for the Curies], for gods and goddesses [selenium (Se) for the Greek goddess of the moon, Selene], and for other poetic or historical reasons. Some of the symbols used for elements that have been known since antiquity are derived from historical names that are no longer in use; only the symbols remain to remind us of their origin. Examples are Fe for iron, from the Latin *ferrum*; Na for sodium, from the Latin *natrium*; and W for tungsten, from the German *wolfram*. Examples are in Table 1.2.1 As you work through this text, you will encounter the names and symbols of the elements repeatedly, and much as you become familiar with characters in a play or a film, their names and symbols will become familiar.

Table 1.2.1 Element Symbols Based on Names No Longer in Use

Element	Symbol	Derivation	Meaning
antimony	Sb	*stibium*	Latin for “mark”
copper	Cu	*cuprum*	from *Cyprium*, Latin name for the island of Cyprus, the major source of copper ore in the Roman Empire
gold	Au	*aurum*	Latin for “gold”
iron	Fe	*ferrum*	Latin for “iron”
lead	Pb	*plumbum*	Latin for “heavy”
mercury	Hg	*hydrargyrum*	Latin for “liquid silver”
potassium	K	*kalium*	from the Arabic *al-qili*, “alkali”
silver	Ag	*argentum*	Latin for “silver”
sodium	Na	*natrium*	Latin for “sodium”
tin	Sn	*stannum*	Latin for “tin”
tungsten	W	*wolfram*	German for “wolf stone” because it interfered with the smelting of tin and was thought to devour the tin

If you want to learn the names of the elements and how to pronounce them, there is nothing better than a song

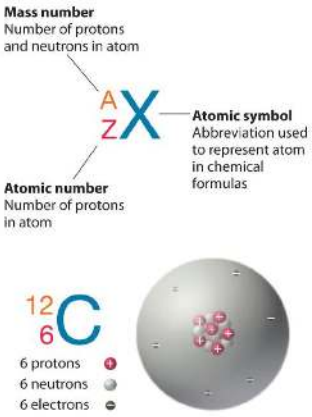




Old timers (perhaps your lecturer is the only one in the class) will recognize this as a cover of Tom Lehrer's Song of the Elements

Recall from Section 1.1 that the nuclei of most atoms contain neutrons as well as protons. Unlike protons, the number of neutrons is not absolutely fixed for most elements. Atoms that have *the same number of protons*, and hence the same atomic number, but *different numbers of neutrons* are called isotopesAtoms that have the same numbers of protons but different numbers of neutrons. All isotopes of an element have the same number of protons and electrons, which means they exhibit the same chemistry. The isotopes of an element differ only in their atomic mass, which is given by the mass number (*A*)The number of protons and neutrons in the nucleus of an atom of an element., the sum of the numbers of protons and neutrons.

The element carbon (C) has an atomic number of 6, which means that all neutral carbon atoms contain 6 protons and 6 electrons. In a typical sample of carbon-containing material, 98.89% of the carbon atoms also contain 6 neutrons, so each has a mass number of 12. An isotope of any element can be uniquely represented as $^{A}_{Z}X$where X is the atomic symbol of the element. The isotope of carbon that has 6 neutrons is therefore $^{12}_{6}C$ The subscript indicating the atomic number is actually redundant because the atomic symbol already uniquely specifies *Z*. Consequently, it is more often written as ^{12}C, which is read as “carbon-12.” Nevertheless, the value of *Z* is commonly included in the notation for *nuclear* reactions because these reactions involve changes in *Z*.



In addition to ^{12}C, a typical sample of carbon contains 1.11% $^{13}_{6}C$ (^{13}C), with 7 neutrons and 6 protons, and a trace of $^{14}_{6}C$ (^{14}C), with 8 neutrons and 6 protons. The nucleus of ^{14}C is not stable, however, but undergoes a slow radioactive decay that is the basis of the carbon-14 dating technique used in archaeology. Many elements other than carbon have more than one stable isotope; tin, for example, has 10 isotopes. The properties of some common isotopes are in Table 1.2.2 .

Table 1.2.2 Properties of Selected Isotopes

Element	Symbol	Atomic Mass (amu)	Isotope Mass Number	Isotope Masses (amu)	Percent Abundances (%)
hydrogen	H	1.0079	1	1.007825	99.9855
			2	2.014102	0.0115
boron	B	10.81	10	10.012937	19.91
			11	11.009305	80.09
carbon	C	12.011	12	12 (defined)	99.89
			13	13.003355	1.11
oxygen	O	15.9994	16	15.994915	99.757
			17	16.999132	0.0378
			18	17.999161	0.205
iron	Fe	55.845	54	53.939611	5.82
			56	55.934938	91.66
			57	56.935394	2.19
			58	57.933276	0.33
uranium	U	238.03	234	234.040952	0.0054
			235	235.043930	0.7204
			238	238.050788	99.274

Sources of isotope data: G. Audi et al., Nuclear Physics A 729 (2003): 337–676; J. C. Kotz and K. F. Purcell, Chemistry and Chemical Reactivity, 2nd ed., 1991.

Example 1.2.1

An element with three stable isotopes has 82 protons. The separate isotopes contain 124, 125, and 126 neutrons. Identify the element and write symbols for the isotopes.

Given: number of protons and neutrons

Asked for: element and atomic symbol

Strategy:

A Refer to the periodic table and use the number of protons to identify the element.

B Calculate the mass number of each isotope by adding together the numbers of protons and neutrons.

C Give the symbol of each isotope with the mass number as the superscript and the number of protons as the subscript, both written to the left of the symbol of the element.

Solution:

A The element with 82 protons (atomic number of 82) is lead: Pb.

B For the first isotope, A = 82 protons + 124 neutrons = 206. Similarly, A = 82 + 125 = 207 and A = 82 + 126 = 208 for the second and third isotopes, respectively. The symbols for these isotopes are ${}^{206}_{82}Pb$, ${}^{207}_{82}Pb$ and ${}^{208}_{82}Pb$ which are usually abbreviated as ^{206}Pb, ^{207}Pb, and ^{208}Pb.

Exercise

Identify the element with 35 protons and write the symbols for its isotopes with 44 and 46 neutrons.

Answer: $^{79}_{35}Br$ and $^{81}_{35}Br$ or, more commonly, ^{79}Br and ^{81}Br.

Although the masses of the electron, the proton, and the neutron are known to a high degree of precision (Table 1.2.2), the mass of any given atom is not simply the sum of the masses of its electrons, protons, and neutrons. For example, the ratio of the masses of ^{1}H (hydrogen) and ^{2}H (deuterium) is actually 0.500384, rather than 0.49979 as predicted from the numbers of neutrons and protons present. Although the difference in mass is small, it is extremely important because it is the binding energy of the nucleus. We can easily calculate the binding energy from the mass difference using Einstein's formula $E=mc^2$.

Because atoms are much too small to measure individually and do not have a charge, there is no convenient way to accurately measure *absolute* atomic masses. Scientists can measure *relative* atomic masses very accurately, however, using an instrument called a *mass spectrometer*. The technique is conceptually similar to the one Thomson used to determine the mass-to-charge ratio of the electron. First, electrons are removed from or added to atoms or molecules, thus producing charged particles called ionsA charged particle produced when one or more electrons is removed from or added to an atom or molecule.. When an electric field is applied, the ions are accelerated into a separate chamber where they are deflected from their initial trajectory by a magnetic field, like the electrons in Thomson's experiment. The extent of the deflection depends on the mass-to-charge ratio of the ion. By measuring the relative deflection of ions that have the same charge, scientists can determine their relative masses (Figure 1.2.2). Thus it is not possible to calculate absolute atomic masses accurately by simply adding together the masses of the electrons, the protons, and the neutrons, and *absolute* atomic masses cannot be measured, but *relative* masses can be measured very accurately. It is actually rather common in chemistry to encounter a quantity whose magnitude can be measured only relative to some other quantity, rather than absolutely. We will encounter many other examples later in this text. In such cases, chemists usually define a standard by arbitrarily assigning a numerical value to one of the quantities, which allows them to calculate numerical values for the rest.

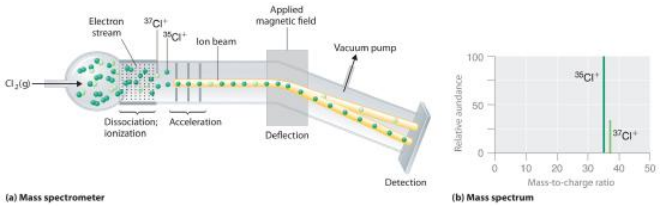
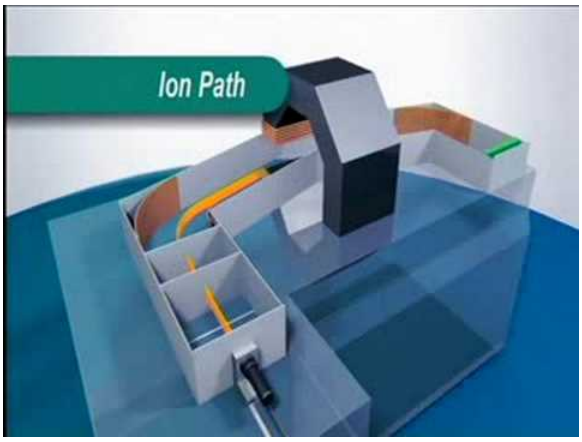


Figure 1.2.2 Determining Relative Atomic Masses Using a Mass Spectrometer *Chlorine consists of two isotopes, ^{35}Cl and ^{37}Cl, in approximately a 3:1 ratio. (a) When a sample of elemental chlorine is injected into the mass spectrometer, electrical energy is used to dissociate the Cl_2 molecules into chlorine atoms and convert the chlorine atoms to Cl^+ ions. The ions are then accelerated into a magnetic field. The extent to which the ions are deflected by the magnetic field depends on their relative mass-to-charge ratios. Note that the lighter $^{35}Cl^+$ ions are deflected more than the heavier $^{37}Cl^+$ ions. By measuring the relative deflections of the ions, chemists can determine their mass-to-charge ratios and thus their masses. (b) Each peak in the mass spectrum corresponds to an ion with a particular mass-to-charge ratio. The abundance of the two isotopes can be determined from the heights of the peaks.*

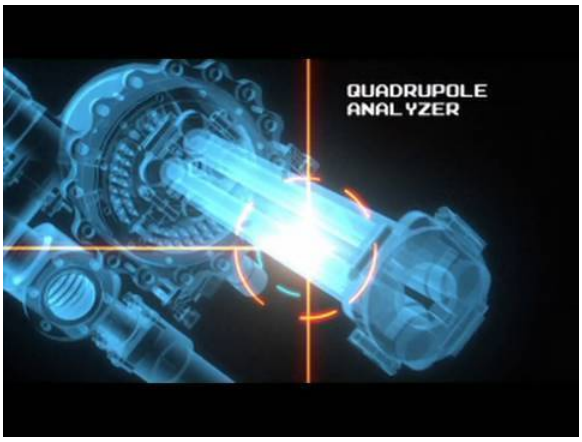
This video from the Royal Society of Chemistry describes how one type of mass spectrometer works





NASA has flown a different type of mass spectrometer to Mars to search for molecules and life





The arbitrary standard that has been established for describing atomic mass is the atomic mass unit (amu) One-twelfth of the mass of one atom of $\mathbf{1\ amu = 1.66 \times 10^{-24} g}$, defined as one-twelfth of the mass of one atom of ^{12}C. Because the masses of all other atoms are calculated relative to the ^{12}C standard, ^{12}C is the only atom listed in Table 1.2.2 whose exact atomic mass is equal to the mass number. Experiments have shown that 1 amu = 1.66×10^{-24} g.

Mass spectrometric experiments give a value of 0.167842 for the ratio of the mass of ^{2}H to the mass of ^{12}C, so the absolute mass of ^{2}H is

$$\frac{mass\ of\ ^{2}H}{mass\ of\ ^{12}C} \times mass\ of\ ^{12}C = 0.167842\ \times\ 12\ amu\ =\ 2.104104\ amu$$

The masses of the other elements are determined in a similar way.

The periodic table lists the atomic masses of all the elements. If you compare these values with those given for some of the isotopes in Table 1.2,2, you can see that the atomic masses given in the periodic table never correspond exactly to those of any of the isotopes. Because most elements exist as mixtures of several stable isotopes, the **atomic mass** of an element is defined as the weighted average of the masses of the isotopes. For example, naturally occurring carbon is largely a mixture of two isotopes: 98.89% ^{12}C (mass = 12 amu by definition) and 1.11% ^{13}C (mass = 13.003355 amu). The percent abundance of ^{14}C is so low that it can be ignored in this calculation. The *average* atomic mass of carbon is then calculated as

(0.9889 × 12 amu) + (0.0111 × 13.003355 amu) = 12.01 amu

Carbon is predominantly ^{12}C, so its average atomic mass should be close to 12 amu, which is in agreement with our calculation.

The value of 12.01 is shown under the symbol for C in the periodic table although without the abbreviation *amu*, which is customarily omitted. Thus the tabulated *atomic mass* of carbon or any other element is the weighted average of the masses of the naturally occurring isotopes.

Example 1.2.2

Naturally occurring bromine consists of the two isotopes listed in the following table:

Isotope	Exact Mass (amu)	Percent Abundance (%)
^{79}Br	78.9183	50.69
^{81}Br	80.9163	49.31

Calculate the atomic mass of bromine.

Given: exact mass and percent abundance

Asked for: atomic mass

Strategy:

A Convert the percent abundences to decimal form to obtain the mass fraction of each isotope.

B Multiply the exact mass of each isotope by its corresponding mass fraction (percent abundance ÷ 100) to obtain its weighted mass.

C Add together the weighted masses to obtain the atomic mass of the element.

D Check to make sure that your answer makes sense.

Solution:

A The atomic mass is the weighted average of the masses of the isotopes. In general, we can write

atomic mass of element = [(mass of isotope 1 in amu) (mass fraction of isotope 1)] + [(mass of isotope 2) (mass fraction of isotope 2)] + …

Bromine has only two isotopes. Converting the percent abundances to mass fractions gives

$$\mathbf{^{79}Br: 79.9183\ amu \times 0.5069 = 40.00\ amu}$$

B Multiplying the exact mass of each isotope by the corresponding mass fraction gives the isotope's weighted mass:

$$\mathbf{^{79}Br: 79.9183\ amu \times 0.5069 = 40.00\ amu}$$

$$\mathbf{^{81}Br: 80.9163\ amu \times 0.4931 = 39.90\ amu}$$

C The sum of the weighted masses is the atomic mass of bromine is

$$\mathbf{40.00\ amu + 39.90\ amu = 79.90\ amu}$$

D This value is about halfway between the masses of the two isotopes, which is expected because the percent abundance of each is approximately 50%.

Exercise

Magnesium has the three isotopes listed in the following table:

Isotope	Exact Mass (amu)	Percent Abundance (%)
^{24}Mg	23.98504	78.70
^{25}Mg	24.98584	10.13
^{26}Mg	25.98259	11.17

Use these data to calculate the atomic mass of magnesium.

Answer: 24.31 amu

Summary

Each atom of an element contains the same number of protons, which is the **atomic number** (*Z*). Neutral atoms have the same number of electrons and protons. Atoms of an element that contain different numbers of neutrons are called **isotopes**. Each isotope of a given element has the same atomic number but a different **mass number** (*A*), which is the sum of the numbers of protons and neutrons. The relative masses of atoms are reported using the **atomic mass unit** (**amu**), which is defined as one-twelfth of the mass of one atom of carbon-12, with 6 protons, 6 neutrons, and 6 electrons. The **atomic mass** of an element is the weighted average of the masses of the naturally occurring isotopes. When one or more electrons are added to or removed from an atom or molecule, a charged particle called an **ion** is produced, whose charge is indicated by a superscript after the symbol.

Key Takeaway

- The mass of an atom is a weighted average that is largely determined by the number of its protons and neutrons, whereas the number of protons and electrons determines its charge.

Conceptual Problems

1. Complete the following table for the missing elements, symbols, and numbers of electrons.

Element	Symbol	Number of Electrons
molybdenum		
		19
titanium		
	B	
		53
	Sm	
helium		
		14

2. Complete the following table for the missing elements, symbols, and numbers of electrons.

Element	Symbol	Number of Electrons
lanthanum		
	Ir	
aluminum		
		80
sodium		
	Si	
		9
	Be	

3. Is the mass of an ion the same as the mass of its parent atom? Explain your answer.

4. What isotopic standard is used for determining the mass of an atom?

5. Give the symbol ${}^{A}_{Z}X$ for these elements, all of which exist as a single isotope.

    1. beryllium
    2. ruthenium
    3. phosphorus
    4. aluminum
    5. cesium
    6. praseodymium
    7. cobalt
    8. yttrium
    9. arsenic

6. Give the symbol $^{A}_{Z}X$ for these elements, all of which exist as a single isotope.
    1. fluorine
    2. helium
    3. terbium
    4. iodine
    5. gold
    6. scandium
    7. sodium
    8. niobium
    9. manganese
7. Identify each element, represented by X, that have the given symbols.
    1. $^{55}_{26}X$
    2. $^{74}_{33}X$
    3. $^{24}_{12}X$
    4. $^{127}_{53}X$
    5. $^{40}_{18}X$
    6. $^{152}_{63}X$

Numerical Problems

1. The isotopes ^{131}I and ^{60}Co are commonly used in medicine. Determine the number of neutrons, protons, and electrons in a neutral atom of each.
2. Determine the number of protons, neutrons, and electrons in a neutral atom of each isotope:
    1. ^{97}Tc
    2. ^{113}In
    3. ^{63}Ni
    4. ^{55}Fe
3. Both technetium-97 and americium-240 are produced in nuclear reactors. Determine the number of protons, neutrons, and electrons in the neutral atoms of each.
4. The following isotopes are important in archaeological research. How many protons, neutrons, and electrons does a neutral atom of each contain?
    1. ^{207}Pb
    2. ^{16}O
    3. ^{40}K
    4. ^{137}Cs
    5. ^{40}Ar
5. Copper, an excellent conductor of heat, has two isotopes: ^{63}Cu and ^{65}Cu. Use the following information to calculate the average atomic mass of copper:

Isotope	Percent Abundance (%)	Atomic Mass (amu)
^{63}Cu	69.09	62.9298
^{65}Cu	30.92	64.9278

6. Silicon consists of three isotopes with the following percent abundances:

Isotope	Percent Abundance (%)	Atomic Mass (amu)
^{28}Si	92.18	27.976926
^{29}Si	4.71	28.976495
^{30}Si	3.12	29.973770

Calculate the average atomic mass of silicon.

7. Complete the following table for neon. The average atomic mass of neon is 20.1797 amu.

Isotope	Percent Abundance (%)	Atomic Mass (amu)
^{20}Ne	90.92	19.99244
^{21}Ne	0.257	20.99395
^{22}Ne		

8. Are $^{63}_{28}\mathrm{X}$ and $^{62}_{29}\mathrm{X}$ isotopes of the same element? Explain your answer.
9. Complete the following table:

Isotope	Number of Protons	Number of Neutrons	Number of Electrons
^{238}X			95
^{238}U			
	75	112	

10. Complete the following table:

Isotope	Number of Protons	Number of Neutrons	Number of Electrons
^{57}Fe			
^{40}X		20	
^{36}S			

11. Using a mass spectrometer, a scientist determined the percent abundances of the isotopes of sulfur to be 95.27% for ^{32}S, 0.51% for ^{33}S, and 4.22% for ^{34}S. Use the atomic mass of sulfur from the periodic table and the following atomic masses to determine whether these data are accurate, assuming that these are the only isotopes of sulfur: 31.972071 amu for ^{32}S, 32.971459 amu for ^{33}S, and 33.967867 amu for ^{34}S.
12. The percent abundances of two of the three isotopes of oxygen are 99.76% for ^{16}O, and 0.204% for ^{18}O. Use the atomic mass of oxygen given in the periodic table and the following data to determine the mass of ^{17}O: 15.994915 amu for ^{16}O and 17.999160 amu for ^{18}O.
13. Which element has the higher proportion by mass in NaI?

    Which element has the higher proportion by mass in KBr?

Contributors

- Anonymous

Modified by Joshua Halpern, Scott Sinex and Scott Johnson

Periodic Table Song from AsapScience on YouTube

Mass spectrometer explanation from the Royal Society of Chemistry on YouTube

NASA Mass Spectrometer Video from NASA on YouTube

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Chapter 1.3: The Nucleus and Radioactivity

Learning Objective

- To know the meaning of isotopes and atomic masses.

We know about four forces in the universe. Gravity is a very weak force that functions on the scale of galaxies as well as apples falling. Gravitational effects are only obvious for very large objects, such as the Earth, the Sun, galaxies and the universe. There is little to nothing in chemistry where we have to include gravity in our analysis, well other than in how we weigh chemicals.

Most chemical phenomina are controlled by electromagnetic forces. The typical distances involved in the interactions of these charged particles are a billionth of a meter.

The weak and strong forces are forces holding nuclei together. These forces are studied by nuclear and high energy physicists. Their range is much smaller than the electromagnetic force, in the case of the weak interaction 10^{-17} m, roughly the size of the atomic nucleus.

The strong force, is short range, but also very strong. It is what holds atomic nuclei together and confines quarks in nuclear particles such as protons and neutrons. Again, like gravitation, there is very little in chemistry where we need to consider the strong and weak forces in our analysis except for nuclear reactions.

Nuclear reactions differ from chemical processes in one critical way: in a nuclear reaction, the identities of the elements change. In addition, nuclear reactions are often accompanied by the release of enormous amounts of energy, as much as a *billion* times more than the energy released by chemical reactions. Moreover, the yields and rates of a nuclear reaction are generally unaffected by changes in temperature, pressure, because the energy associated with a change in temperature or pressure is miniscule compared to the energies of nuclear reaction

We all know about $E=mc^{2.}$ Einstein discovered that mass and energy are related. However the amount of energy released in conversion of even the tiniest amount of mass to energy is far beyond normal chemistry. For practical purposes atoms (mass) are not transmuted either into other types of atoms or to pure energy. We can and do do this in nuclear reactors, atom smashers and atomic weapons, however, these are not normal, everyday chemistry, and the energy range involved in nuclear chemistry and such processes is well beyond common experience and this course.

The amount of mass converted into binding energy varies across the periodic table. As shown in Figure 1.3.1 the binding energy per nucleon increases rapidly with increasing atomic number until about Z = 26, where it levels off to about 8–9 MeV per nucleon and then decreases slowly. The initial increase in binding energy is not a smooth curve but exhibits sharp peaks corresponding to the light nuclei that have equal numbers of protons and neutrons (e.g., ^{4}He, ^{12}C, and ^{16}O). As mentioned earlier, these are particularly stable combinations.

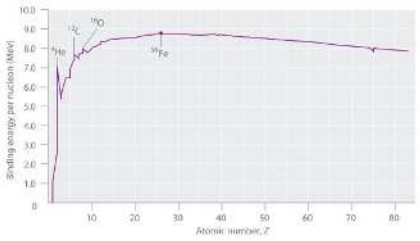


Figure 1.3.1 The Curve of Nuclear Binding Energy *This plot of the average binding energy per nucleon as a function of atomic number shows that the binding energy per nucleon increases with increasing atomic number until about Z = 26, levels off, and then decreases. The sharp peaks correspond to light nuclei that have equal numbers of protons and neutrons.*

Because the maximum binding energy per nucleon is reached at ^{56}Fe, all other nuclei are thermodynamically unstable with regard to the formation of ^{56}Fe. Most elements have a number of isotopes but only a few that are stable. The rest decay spontaneously

either by spitting out an electron, called a β particle, a helium nucleus, called an α particle, a neutron or a high energy photon, also called a γ. Heavier nuclei (toward the right in Figure 1.3.1) could spontaneously undergo reactions that decrease their atomic number by emitting an α particle which consists of two protons and four neutrons. If this happens the atomic number of the nucleus decreases by two, equivalent to moving to the left in Figure 1.3.1. Conversely, lighter elements (on the left in Figure 1.3.1) should spontaneously undergo reactions that result in an increase in atomic number by converting a neutron to a proton and an electron an emitting the electron. When this happens to conserve momentum a neutrino (don't ask in this class) is also emitted. If a neutron is emitted /absorbed then the atomic number stays the same, but the resulting isotope has one less or more neutron.

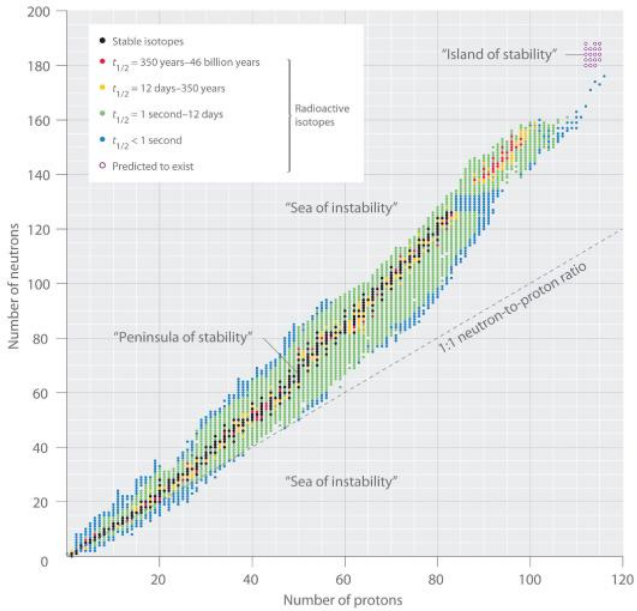


Figure 1.3.2 The Relationship between Nuclear Stability and the Neutron-to-Proton Ratio *In this plot of the number of neutrons versus the number of protons, each black point corresponds to a stable nucleus. In this classification, a stable nucleus is arbitrarily defined as one with a half-life longer than 46 billion years (10 times the age of Earth). As the number of protons (the atomic number) increases, the number of neutrons required for a stable nucleus increases even more rapidly. Isotopes shown in red, yellow, green, and blue are progressively less stable and more radioactive; the farther an isotope is from the diagonal band of stable isotopes, the shorter its half-life. The purple dots indicate superheavy nuclei that are predicted to be relatively stable, meaning that they are expected to be radioactive but to have relatively long half-lives. In most cases, these elements have not yet been observed or synthesized.*

Data source: National Nuclear Data Center, Brookhaven National Laboratory, Evaluated Nuclear Structure Data File (ENSDF), Chart of Nuclides, http://www.nndc.bnl.gov/chart. This is an interactive chart

Looking at Figure 1.3.2 we see how the number of neutrons increases faster than the number of protons in stable and even in unstable (radioactive) isotopes. No isotopes in the sea of instability have been observed. If they could be made, they would simply decay too quickly to be seen. Figure 1.3.3 shows the lower part of the table with the various elements and their isotopes identified. The times listed at the bottom of the box for unstable isotopes is the time in which half of any sample undergo nuclear reaction. This is called the half life and we will discuss it in the chapter on kinetics.

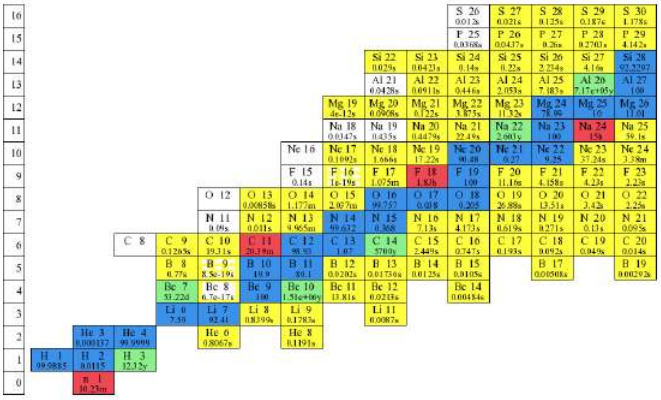


Figure 1.3.3 Observed isotopes of the elements from Hydrogen to Sulfur(partial). *Stable isotopes are shown in blue. Lifetimes of unstable isotopes shown in green, yellow, pink and white are indicated at the bottom of each box. Note that naked neutrons decay to a proton and an electron in about 10 minutes.*

Contributors ▶

- Anonymous

Modified by Joshua Halpern, Scott Sinex and Scott Johnson

Interactive table of nuclides from National Nuclear Data Center, Brookhaven National Laboratory, Evaluated Nuclear Structure Data File (ENSDF)

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Chapter 1.4: The Mole and Molar Mass

Learning Objective

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

Chemistry is the study of how atoms and molecules interact with each other which occurs on the atomic scale. Chemists need a way of simply determining how many molecules they have in a beaker. The mole concept, which we will introduce here, bridges that gap by relating the mass of a single atom or molecule in amu to the mass of a collection of a large number of such molecules in grams.

As you learned, the **mass number** is the sum of the numbers of protons and neutrons present in the nucleus of an atom. The mass number is an integer that is approximately equal to the numerical value of the atomic mass. Although the atomic mass is unitless, it is assigned units called **atomic mass units (amu) measured relative to the mass of a single atom of ^{12}C**. Because a molecule or a polyatomic ion is an assembly of atoms whose identities are given in its molecular or ionic formula, we can calculate the average atomic mass of any molecule or polyatomic ion from its composition by adding together the masses of the constituent atoms. The average mass of a monatomic ion is the same as the average mass of an atom of the element because the mass of electrons is so small that it is insignificant in most calculations. This is not much help in the laboratory for the typical chemist who only has a balance to weight out chemicals but needs to know how the number of atoms or molecules. Clearly something clever is needed but first let us briefly review how to calculate molecular masses.

Molecular

The molecular mass The sum of the average masses of the atoms in one molecule of a substance, each multiplied by its subscript. of a substance is the sum of the average masses of the atoms in one molecule of a substance. It is calculated by adding together the atomic masses of the elements in the substance, each multiplied by its subscript (written or implied) in the molecular formula. Because the units of atomic mass are atomic mass units, the units of molecular mass are also atomic mass units. The procedure for calculating molecular masses is illustrated in Example 1.

Example 1.4.1

Calculate the molecular mass of ethanol, whose condensed structural formula is CH_3CH_2OH. Among its many uses, ethanol is a fuel for internal combustion engines.

Given: molecule

Asked for: molecular mass

Strategy:

A Determine the number of atoms of each element in the molecule.

B Obtain the atomic masses of each element from the periodic table and multiply the atomic mass of each element by the number of atoms of that element.

C Add together the masses to give the molecular mass.

Solution:

A The molecular formula of ethanol may be written in three different ways: CH_3CH_2OH (which illustrates the presence of an ethyl group, CH_3CH_2-, and an $-OH$ group), C_2H_5OH, and C_2H_6O; all show that ethanol has two carbon atoms, six hydrogen atoms, and one oxygen atom.

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

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

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

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

C Adding together the masses gives the molecular mass:

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

Alternatively, we could have used unit conversions to reach the result in one step, as described in Essential Skills 2

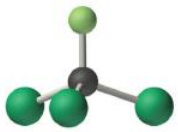
$$\left[2\ atoms\ \left(\frac{12.011\ amu}{1\ atom\ C}\right)\right] + \left[6\ atoms\ H\ \left(\frac{1.0079\ amu}{1\ atom\ H}\right)\right] + \left[1\ atoms\ O\ \left(\frac{15.9994\ amu}{1\ atom\ O}\right)\right]$$

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

2C	(2 atoms)(12.011 amu/atom) = 24.022 amu
6H	(6 atoms)(1.0079 amu/atom) = 6.0474 amu
1O	(1 atoms)(15.9994 amu/atom) = 15.9994 amu
C_2H_6O	molecular mass of ethanol = 46.069 amu

Exercise

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



Freon-11, CCl_3F

Answer: 137.368 amu

Note the Pattern

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

The Mole

Each chemical compound has a particular combination of atoms and the ratios of the *numbers* of atoms of the elements present are usually small whole numbers. The problem for early chemists was to discover the quantitative relationship between the number of atoms in a chemical substance and its mass. Because the masses of individual atoms are so minuscule (on the order of 10^{-23} g/atom), chemists do not measure the mass of individual atoms or molecules. In the laboratory, for example, the masses of compounds and elements used by chemists typically range from milligrams to grams, while in industry, chemicals are bought and sold in kilograms and tons. To analyze the transformations that occur between individual atoms or molecules in a chemical reaction. A process in which a substance is converted to one or more other substances with different compositions and properties, it is therefore absolutely essential for chemists to know how many atoms or molecules are contained in a measurable quantity in the laboratory—a given mass of sample. The unit that provides this link is the mole (mol). The quantity of a substance that contains the same number of units (e.g., atoms or molecules) as the number of carbon atoms in exactly 12 g of isotopically pure carbon-12., from the Latin *moles*, meaning “pile” or “heap” (*not* from the small subterranean animal!).

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

A **mole** is defined as the amount of a substance that contains the number of carbon atoms in exactly 12 g of isotopically pure carbon-12. According to the most recent experimental measurements, this mass of carbon-12 contains 6.022142×10^{23} atoms, but

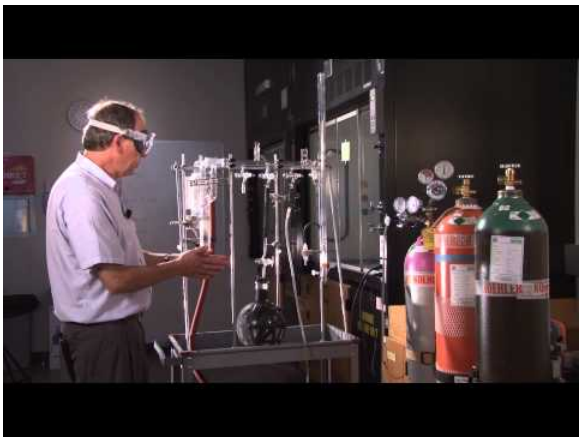
for most purposes 6.022×10^{23} provides an adequate number of significant figures. Just as 1 mol of atoms contains 6.022×10^{23} atoms, 1 mol of eggs contains 6.022×10^{23} eggs. The number in a mole is called Avogadro's numberThe number of units (e.g., atoms, molecules, or formula units) in 1 mol: 6.022142 x 10^{23}, after the 19th-century Italian scientist who first proposed how to measure the number of molecules in a gas. Since the mass of the gas can also be measured on a sensitive balance, knowing both the number of molecules and their total mass allows us to simply determine the mass of a single molecule in grams.

The mole provides a bridge between the atomic world (amu) and the laboratory (grams). It allows determination of the number of molecules or atoms by weighing them. The numerical value of Avogadro's number, usually written as ***No***, is a consequence of the arbitrary value of one kilogram, a block of Pt-Ir metal called the International Prototype Kilogram, and the choice of reference for the atomic mass unit scale, one atom of carbon-12. A mole of C-12 by definition weighs exactly 12 g and Avogadro's number is determined by counting the number of atoms. It is not so easy. Avogadro's number is the fundamental constant that is least accurately determined.

The definition of a mole—that is, the decision to base it on 12 g of carbon-12—is arbitrary but one arrived at after some discussion between chemists and physicists debating about whether to use naturally occurring carbon, a mixture of C-12 and C-13, or hydrogen. The important point is that *1 mol of carbon—or of anything else, whether atoms, compact discs, or houses—always has the same number of objects: 6.022×10^{23}.*

In the following video, Prof. Steve Boon shows how Avogadro's hypothesis can be used to measure the molecular masses of He, N_2 and CO2. Follow along and record the measurements to get the relative masses. When we consider the behavior of gases in Unit 4, we can use the data to calculate the molecular weight of each gas. This method was, until the invention of the mass spectrometer, the best way of measuring molecular weights of gas molecules





Note the Pattern

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

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

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

Molar Mass

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

Note the Pattern

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

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

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

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

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

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

$$\text{(moles)(molar mass)} \rightarrow \text{mass} \quad (1.4.1)$$

or, more specifically,

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

$$\left(\frac{mass}{molar\ mass}\right) \rightarrow moles$$

$$\left(\frac{grams}{grams/mole}\right) = grams\left(\frac{mole}{grams}\right) = moles$$

Be sure to pay attention to the units when converting between mass and moles.

Figure 1.4.2 is a flowchart for converting between mass; the number of moles; and the number of atoms, molecules, or formula units. The use of these conversions is illustrated in Example 3 and Example 4.

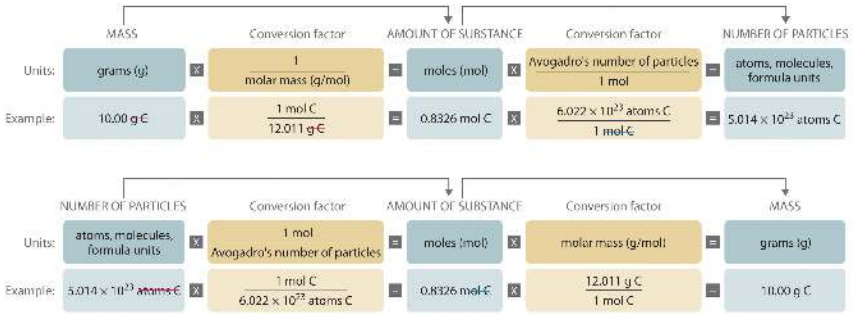


Figure 1.4.2 A Flowchart for Converting between Mass; the Number of Moles; and the Number of Atoms, Molecules, or Formula Units

Example 1.4.2

For 35.00 g of ethylene glycol ($HOCH_2CH_2OH$), which is used in inks for ballpoint pens, calculate the number of

1. moles.
2. molecules.

Given: mass and molecular formula

Asked for: number of moles and number of molecules

Strategy:

A Use the molecular formula of the compound to calculate its molecular mass in grams per mole.

B Convert from mass to moles by dividing the mass given by the compound's molar mass.

C Convert from moles to molecules by multiplying the number of moles by Avogadro's number.

Solution:

A The molecular mass of ethylene glycol can be calculated from its molecular formula using the method illustrated in Example 1:

2C	(2 atoms)(12.011 amu/atom) = 24.022 amu
6H	(6 atoms)(1.0079 amu/atom) = 6.0474 amu
2O	(2 atoms)(15.9994 amu/atom) = 31.9988 amu
C_2H_6O	molecular mass of ethanol = 62.068 amu

The molar mass of ethylene glycol is 62.068 g/mol

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

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

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

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

$$molecules\ of\ ethylene\ glycol = 0.5639\ mol\left(\frac{6.022 \times 10^{23}}{1\ mol}\right)$$

$$= 3.396 \times 10^{23}\ molecules$$

Exercise

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

1. moles.
2. molecules.

Answer:

1. 0.546 mol
2. 3.29×10^{23} molecules

Example 1.4.3

Calculate the mass of 1.75 mol of each compound.

1. S_2Cl_2 (common name: sulfur monochloride; systematic name: disulfur dichloride)
2. $Ca(ClO)_2$ (calcium hypochlorite)

Given: number of moles and molecular or empirical formula

Asked for: mass

Strategy:

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

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

Solution:

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

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

2S	(2 atoms)(32.065 amu/atom) = 64.130 amu
2Cl	(2 atoms)(35.353 amu/atom) = 70.906 amu
S_2Cl_2	molecular mass of S_2Cl_2 = 135.036 amu

The molar mass of S_2Cl_2 is 135.036 g/mol.

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

$$moles\ S_2Cl_2 \left[molar\ mass \frac{g}{mol}\right] = mass\ S_2Cl_2$$

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

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

1Ca	(1 atom)(40.078 amu/atom) = 40.078 amu
2Cl	(2 atoms)(35.453 amu/atom) = 70.906 amu
2O	(2 atoms)(15.9994 amu/atom) = 31.9988 amu
$Ca(ClO)_2$	**formula** mass of $Ca(ClO)_2$ = 142.983 amu

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

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

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

Exercise

Calculate the mass of 0.0122 mol of each compound.

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

Answer:

1. 1.71 g
2. 0.721 g

Summary

The **molecular mass** and the **formula mass** of a compound are obtained by adding together the atomic masses of the atoms present in the molecular formula or empirical formula, respectively; the units of both are atomic mass units (amu). The **mole** is a unit used to measure the number of atoms, molecules, or (in the case of ionic compounds) formula units in a given mass of a substance. The

mole is defined as the amount of substance that contains the number of carbon atoms in exactly 12 g of carbon-12 and consists of **Avogadro's number** (6.022×10^{23}) of atoms of carbon-12. The **molar mass** of a substance is defined as the mass of 1 mol of that substance, expressed in grams per mole, and is equal to the mass of 6.022×10^{23} atoms, molecules, or formula units of that substance.

Key Takeaway

- To analyze chemical transformations, it is essential to use a standardized unit of measure called the mole.

Conceptual Problems

1. Describe the relationship between an atomic mass unit and a gram.
2. Construct a flowchart to show how you would calculate the number of moles of silicon in a 37.0 g sample of orthoclase ($KAlSi_3O_8$), a mineral used in the manufacture of porcelain.
3. Construct a flowchart to show how you would calculate the number of moles of nitrogen in a 22.4 g sample of nitroglycerin that contains 18.5% nitrogen by mass.

Numerical Problems

1. Derive an expression that relates the number of molecules in a sample of a substance to its mass and molecular mass.
2. Calculate the molecular mass or formula mass of each compound.
    1. KCl (potassium chloride)
    2. NaCN (sodium cyanide)
    3. H_2S (hydrogen sulfide)
    4. NaN_3 (sodium azide)
    5. H_2CO_3 (carbonic acid)
    6. K_2O (potassium oxide)
    7. $Al(NO_3)_3$ (aluminum nitrate)
    8. $Cu(ClO_4)_2$ [copper(II) perchlorate]
3. Calculate the molecular mass or formula mass of each compound.
    1. V_2O_4 (vanadium(IV) oxide)
    2. $CaSiO_3$ (calcium silicate)
    3. BiOCl (bismuth oxychloride)
    4. CH_3COOH (acetic acid)
    5. Ag_2SO_4 (silver sulfate)
    6. Na_2CO_3 (sodium carbonate)
    7. $(CH_3)_2CHOH$ (isopropyl alcohol)
4. Calculate the mass in grams of each sample.
    1. 0.520 mol of N_2O_4
    2. 1.63 mol of $C_6H_4Br_2$
    3. 4.62 mol of $(NH_4)_2SO_3$
5. Give the number of molecules or formula units in each sample.
    1. 1.30×10^{-2} mol of SCl_2
    2. 1.03 mol of N_2O_5
    3. 0.265 mol of $Ag_2Cr_2O_7$
6. Give the number of moles in each sample.
    1. 9.58×10^{26} molecules of Cl_2
    2. 3.62×10^{27} formula units of KCl
    3. 6.94×10^{28} formula units of $Fe(OH)_2$

7. What is the total number of atoms in each sample?
    1. 0.431 mol of Li
    2. 2.783 mol of methanol (CH_3OH)
    3. 0.0361 mol of $CoCO_3$
    4. 1.002 mol of $SeBr_2O$
8. What is the total number of atoms in each sample?
    1. 0.980 mol of Na
    2. 2.35 mol of O_2
    3. 1.83 mol of Ag_2S
    4. 1.23 mol of propane (C_3H_8)
9. What is the total number of atoms in each sample?
    1. 2.48 g of HBr
    2. 4.77 g of CS_2
    3. 1.89 g of NaOH
    4. 1.46 g of SrC_2O_4
10. Decide whether each statement is true or false and explain your reasoning.
    1. There are more molecules in 0.5 mol of Cl_2 than in 0.5 mol of H_2.
    2. One mole of H_2 has 6.022×10^{23} hydrogen atoms.
    3. The molecular mass of H_2O is 18.0 amu.
    4. The formula mass of benzene is 78 amu.
11. Complete the following table.

Substance	Mass (g)	Number of Moles	Number of Molecules or Formula Units	Number of Atoms or Ions
$MgCl_2$	37.62			
$AgNO_3$		2.84		
BH_4Cl			8.93×10^{25}	
K_2S				7.69×10^{26}
H_2SO_4		1.29		
C_6H_{14}	11.84			
$HClO_3$			2.45×10^{26}	

Contributors

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Verifying Avogadro's Hypothesis Video from HC Communications on YouTube

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CHAPTER OVERVIEW

Chapter 2: Atomic Structure

Learning Objective

To learn about the electronic structure of atoms

Chemistry, the interaction of atoms and molecules with each other, is principally governed by the electrons which are bound most weakly to the nucleus. In this chapter we learn about the electronic structure of atoms and how this is related to the properties of the atoms

Chapter 2.1: Wave - Particle Duality
Chapter 2.2: Atomic Orbitals and Their Energies
Chapter 2.3: Building Up The Periodic Table
Chapter 2.4: Electronic Structure of the Transition Metals
Chapter 2.5: Atomic Spectra and Models of the Atom
Chapter 2.6: End of Chapter Material

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Chapter 2.1: Wave - Particle Duality

Learning Objective

- To understand the wave–particle duality of matter.

Sitting at your computer, moving the mouse you can see the cursor move. In a similar way if someone tosses you a ball you can anticipate where it will be and catch it. If you catch the ball you can feel the shape in your hands. We could use a ruler or a caliper to measure the size of the ball. This is all obvious.

When we move to the atomic scale things are not obvious, in fact, since we have no experience on that scale, things will be quite confusing. For example, think about how you see the ball. Light whose wavelength is between 400 nm (blue) and 700 nm (red) bounces off the ball into your eye. The size of an atom is only about 0.1 nm. Using visible light, you would never be able to locate a single atom because the wavelength of the light would be thousands of times larger. Some might bounce off the atom into your eye but locating where it bounced could only narrow the location of the atom to ~500 nm or so.

Well, what if we used light with a 0.1 nm wavelength. You should remember from Introduction to Engineering that the wavelength of light is related to its frequency by

$$c = \lambda\nu$$

where c is the velocity of light in a vacuum, 3 x 10^{8} cm/sec. Thus the frequency of 0.1nm light is 3.00 x 10^{18} Hz. At this point we will introduce a basic foundation of quantum mechanics, that the energy of a light particle, called a photon, is related to it's frequency by

$$E = h\nu$$

where h = 6.626 x 10^{-34} J-s, is Planck's constant. The energy of the photon we need to locate the atom is 2.00 x 10^{-15} J.

The simplest atom is Hydrogen, which consists of an electron bound to a proton. The energy holding the electron is 2.18 x 10^{-18} J. Another basic principle of quantum mechanics is that the photon can act like a particle and when it hits the electron can cause it to move. Our 0.1 nm photon would simply blow the electron in the Hydrogen atom away. So we might know where the hydrogen atom was when the photon hit it, but we would have no idea where it would be blasted to after the photon hit it.

Measurement of the size of the atom poses similar issues, what can be used as a ruler? Does the atom have a sharp, well defined edge that we could measure?

The answer is no. What quantum mechanics teaches us is that every object has properties that are particle like and properties that are wave like. Massive objects (remember the ball) are more particle like. This includes atomic nucleii, which compared to the electrons are very heavy. Light electrons, on the other hand, have significant wavelike properties.

Although we still usually think of electrons as particles, the wave nature of electrons is employed in an *electron microscope*, which has revealed most of what we know about the microscopic structure of living organisms and materials. Because the size of electrons is much smaller than the wavelength of a beam of visible light, this instrument can resolve smaller details than a light microscope can (Figure 2.4.1).

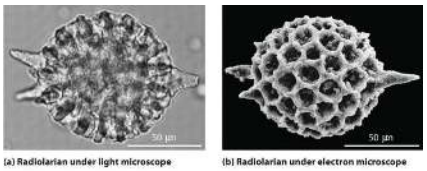


Figure 2.4.1 A Comparison of Images Obtained Using a Light Microscope and an Electron Microscope *Because of their shorter wavelength, high-energy electrons have a higher resolving power than visible light. Consequently, an electron microscope (b) is able to resolve finer details than a light microscope (a). (Radiolaria, which are shown here, are unicellular planktonic organisms.)*

Our approach to quantum mechanics will be to present a few simple facts about the properties of electrons in atoms from which we can build up the properties of the atoms. A more complete discussion will occur in General Physics. The goal is to provide you with

enough information about the properties of atoms (and then molecules) that you can understand their chemistry, without getting bogged down in the historical and mathematical background.

What can we say about the properties of an electron in an atom. Surprisingly we can say exactly what the energy of the electron is. While we cannot say where the electron is or will be, we can find the probability of finding the electron at any point in space. This information is contained in what we call the wave function which will be discussed in the next section.

Summary

The modern model for the electronic structure of the atom is based on recognizing that an electron possesses particle and wave properties, the so-called **wave–particle duality**.

Key Takeaway

- An electron possesses both particle and wave properties.

Contributors

- Anonymous

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Chapter 2.2: Atomic Orbitals and Their Energies

Learning Objective

- To apply the results of quantum mechanics to chemistry.

The problem of measurement at the quantum scale and the wavelike nature of subatomic particles such as the electron made it impossible to use the equations of classical physics to describe the motion of electrons in atoms. Scientists needed a new approach that took the wave behavior of the electron into account. In 1926, an Austrian physicist, Erwin Schrödinger (1887–1961; Nobel Prize in Physics, 1933), developed *wave mechanics*, a mathematical technique that describes the relationship between the motion of a particle that exhibits wavelike properties (such as an electron) and its allowed energies. Schrödinger's theory today is called quantum mechanicsA theory developed by Erwin Schrödinger that describes the energies and spatial distributions of electrons in atoms and molecules.. It successfully describes the energies and spatial distributions of electrons in atoms and molecules.

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Erwin Schrödinger (1887–1961)

Schrödinger’s unconventional approach to atomic theory was typical of his unconventional approach to life. He was notorious for his intense dislike of memorizing data and learning from books. When Hitler came to power in Germany, Schrödinger escaped to Italy. He then worked at Princeton University in the United States but eventually moved to the Institute for Advanced Studies in Dublin, Ireland, where he remained until his retirement in 1955.

Although quantum mechanics uses sophisticated mathematics, you do not need to understand the mathematical details to follow our discussion of its general conclusions. We focus on the properties of the *wave functions* that are the solutions of Schrödinger’s equations. The Schrödinger equation is similar in form to equations for the propagation of waves, which is why originally quantum mechanics was called wave mechanics, but there are significant differences between quantum wave functions and those that describe real waves. Therefore, at this point it would be best to lean only lightly on the standing wave analogy.

Wave Functions

A wavefunction (Ψ)A mathematical function that relates the location of an electron at a given point in space to the amplitude of its wave, which corresponds to its energy., Ψ is the uppercase Greek letter psi, is a mathematical expression that can be used to calculate any property of an atom. In general, wavefunctions depend on both time and position. For atoms, solutions to the Schrödinger equation correspond to arrangements of the electrons, which, if left alone, remain unchanged. To indicate time independence we use lower case ψ

Wavefunctions for each atom have some properties that are exact, for example each wavefunction describes an electron in quantum state with a specific energy. Each of these exact properties is associated with an integer. The energy of an electron in an atom is associated with the integer *n*. These integers are called quantum numbers and different wavefunctions have different sets of quantum numbers. The important point about quantum numbers is that they are countable integers, not continuous variables like the number of points on a line. In the case of atoms, each electron has four quantum numbers which determine its wavefunction.

For other properties, there is a mathematical procedure by which the wavefunctions can be used to calculate average values and probabilities for anything, for example the probability of finding the electron at any point in space. The calculation of probabilities is the best we can do for properties not associated directly with quantum numbers.

The properties of wave functions derived from quantum mechanics are summarized here. Although there are no equations there are a number of advanced concepts. Try to understand the key concepts.:

- **A time independent wavefunction uses three variables to describe the position of an electron.** Three coordinates specify the position in space (as with the Cartesian coordinates *x*, *y*, and *z*, or spherical coordinates *r*, *θ*, *φ*). Figure 2.21 shows both Cartesian and spherical coordinates. For the motion of an electron about the massive nucleus, spherical coordinates can be more natural than Cartesian.

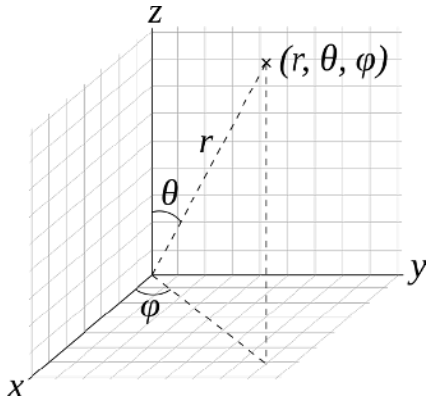


Figure 2.2.1 Cartesian (x, y, z) and spherical coordinates (r, θ, φ)

- **Wave functions have both real and imaginary parts. They are complex functions**, which is a mathematical term indicating that they contain $\sqrt{-1}$., represented as *i*. Imaginary and complex numbers have no physical significance.

Imaginary Numbers

If you need an introduction to imaginary number, here is one. To see it you will have to be attached to the INTERNET



- **The probability of finding an electron at a point is given by the product of the wave function ψ and its complex conjugate ψ* in which all terms that contain *i* are replaced by −*i*.** This product is called the modulus square and for wave functions it always must be a real positive number or zero. Negative, impaginary or complex probabilities of finding an electron at a point would be meaningless. This interpretation was discovered by Max Born, for which he won the Nobel prize. We use probabilities because of its wavelike properties we cannot precisely specify the position of an electron.

Mathematically expressed this means that the integral over all space of ψ*ψ is unity

$$\int \psi^* \psi d\tau = 1$$

The probability of finding an electron at any point in space depends on the quantum numbers specifying the wavefunction and the three coordinates specifying the position in space we are interested in. As one way of graphically representing the probability distribution, the probability of finding an electron is indicated by the density of colored dots, shown for the ground state of the hydrogen atom in Figure 2.2.2

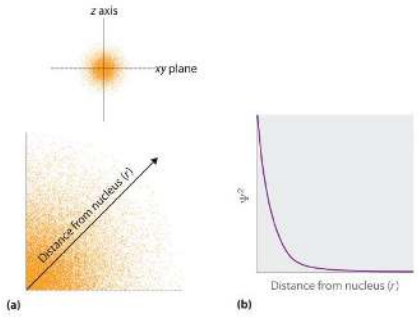


Figure 2.2.2 Probability of Finding the Electron in the Ground State of the Hydrogen Atom at Different Points in Space *(a) The density of the dots shows electron probability. (b) In this plot of Ψ^2 versus r for the ground state of the hydrogen atom, the electron probability density is greatest at r = 0 (the nucleus) and falls off with increasing r. Because the line never actually reaches the horizontal axis, the probability of finding the electron at very large values of r is very small but not zero.*

- **The total probability of finding the electron anywhere must be 100%**. It has to be somewhere. On the other hand, since there is a lot more space far away from a nucleus than near it, the probability of finding the electron at any one point as one moves away from the nucleus must eventually go to zero.
- **The relative phases of wave function for electrons in different atoms** determines bonding. This will be important in our discussion of chemical bonding in Chapter 5. Wavefunctions like waves, can positively reinforce each other or destructively interfere. When they reinforce they are said to be in phase, and when they interfere they are said to be out of phase. The phases are indicated as positive, +, or negative, -. Do not confuse the sign of the phase with a positive or negative electrical charge.

An Important Wave Property - Phase

A wave is a disturbance that travels in space. The magnitude of the wave at any point in space and time varies sinusoidally. While the absolute value of the magnitude of one wave at any point is not very important, the **relative** displacement of two waves called the phase difference, is vitally important because it determines whether the waves reinforce or interfere with each other. Figure 2.4.2a, shows an arbitrary phase difference between two wave. Figure 2.4.2b shows what happens when the two waves are 180 degrees out of phase. The green line is their sum. Figure 2.4.2c shows what happens when the two lines are in phase, exactly superimposed on each other. Again, the green line is the sum of the intensities.

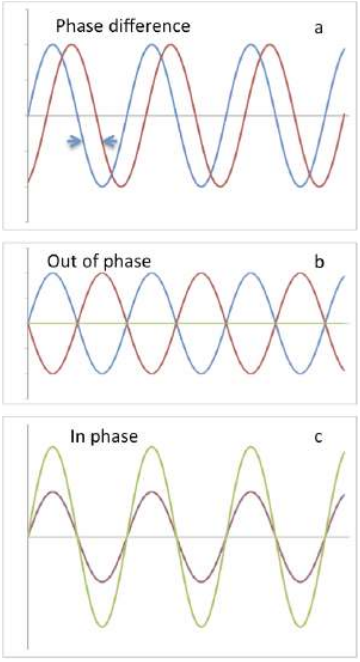


Figure 2.4.2 Phase *Two waves traveling together are displaced by a phase difference. If the phase difference is 0 then they lay on top of each other and reinforce. If the phase diffence is 180 they completely cancel each other out.*

A more detailed explanation can be seen in the video below.



- **Each wavefunction has a unique sets of** quantum numbersA unique set of numbers that specifies a wave function (a solution to the Schrödinger equation), which provides important information about the energy and spatial distribution of an electron.**.** The spacial patterns of the three-dimensional wave functions are complex. Fortunately, however, in the 18th century, a French mathematician, Adrien Legendre (1752–1783), developed a set of equations to describe the motion of tidal waves on the surface of a water world, which turn out to be solutions of the Schrödinger equation for a spherically symmetric atom.
- **Each wave function is associated with a particular energy.** The energy of an electron in an atom is quantized; it can have only certain allowed values. The major difference between a simpler early model of Bohr's which assumed that the electrons moved in perfect circles about the nucleus and Schrödinger's approach is that Bohr had to impose the idea of quantization arbitrarily, whereas in Schrödinger's approach, quantization emerges from the wave equation.

Quantum Numbers

Schrödinger's approach requires three quantum numbers (n, l, and m_l) to specify a wave function for each electron. The quantum numbers provide information about the spatial distribution of an electron. Although n can be any positive integer (NOT zero), only

certain values of l and m_l are allowed for a given value of n. This is a consequence of the mathematical details of the Schrödinger equation

The Principal Quantum Number

The principal quantum number (n)One of three quantum numbers that tells the average relative distance of an electron from the nucleus. indicates the energy of the electron and the average distance of an electron from the nucleus:

$$n = 1,\ 2,\ 3,\ 4,\ \ldots \tag{2.2.2}$$

As n increases for a given atom, so does the average distance of an electron from the nucleus. A negatively charged electron that is, on average, closer to the positively charged nucleus is attracted to the nucleus more strongly than an electron that is farther out in space. This means that electrons with higher values of n are easier to remove from an atom. All wave functions that have the same value of n are said to constitute a principal shellAll the wave functions that have the same value of n because those electrons have similar average distances from the nucleus. because those electrons have similar average distances from the nucleus. As you will see, the principal quantum number n corresponds to the n used by Bohr to describe electron orbits and by Rydberg to describe atomic energy levels.

The Azimuthal Quantum Number

The second quantum number is often called the azimuthal quantum number (l)One of three quantum numbers that describes the shape of the region of space occupied by an electron.. It is also called the orbital angular momentum quantum number. The value of l describes the *shape* of the region of space occupied by the electron. The allowed values of l depend on the value of n and can range from 0 to n − 1:

$$l = 0,\ 1,.,2,\ 3,\ ..\ (n-1)$$

For example, if n = 1, l can be only 0; if n = 2, l can be 0 or 1; and so forth. For a given atom, all wave functions that have the same values of both n and l form a subshellA group of wave functions that have the same values of n and l. The regions of space occupied by electrons in the same subshell usually have the same shape, but they are oriented differently in space.

The Magnetic Quantum Number

The third quantum number is the magnetic quantum number (m_l)One of three quantum numbers that describes the orientation of the region of space occupied by an electron with respect to an applied magnetic field.. The reason that this is called the magnetic quantum number is that when the atom is in a magnetic field the energy level varies proportionall to m. The value of m_l describes the *orientation* of the region in space occupied by an electron with respect to an applied magnetic field. The allowed values of m_l depend on the value of l: m_l can range from $-l$ to l in integral steps:

$$m = -l,\ -l+1,\ \ldots 0,\ \ \ldots l-1, l$$

For example, if l = 0, m_l can be only 0; if l = 1, m_l can be −1, 0, or +1; and if l = 2, m_l can be −2, −1, 0, +1, or +2.

Each wave function with an allowed combination of n, l, and m_l values describes an atomic orbital A wave function with an allowed combination of n, l and m_l quantum numbers., a particular spatial distribution for an electron. For a given set of quantum numbers, each principal shell has a fixed number of subshells, and each subshell has a fixed number of orbitals.

Example 2.2.1

How many subshells and orbitals are contained within the principal shell with n = 4?

Given: value of n

Asked for: number of subshells and orbitals in the principal shell

Strategy:

A Given n = 4, calculate the allowed values of l. From these allowed values, count the number of subshells.

B For each allowed value of l, calculate the allowed values of m_l. The sum of the number of orbitals in each subshell is the number of orbitals in the principal shell.

Solution:

A We know that l can have all integral values from 0 to $n - 1$. If $n = 4$, then l can equal 0, 1, 2, or 3. Because the shell has four values of l, it has four subshells, each of which will contain a different number of orbitals, depending on the allowed values of m_l.

B For $l = 0$, m_l can be only 0, and thus the $l = 0$ subshell has only one orbital. For $l = 1$, m_l can be 0 or ±1; thus the $l = 1$ subshell has three orbitals. For $l = 2$, m_l can be 0, ±1, or ±2, so there are five orbitals in the $l = 2$ subshell. The last allowed value of l is $l = 3$, for which m_l can be 0, ±1, ±2, or ±3, resulting in seven orbitals in the $l = 3$ subshell. The total number of orbitals in the $n = 4$ principal shell is the sum of the number of orbitals in each subshell and is equal to n^2:

$$\underset{(l=0)}{1} + \underset{(l=1)}{3} + \underset{(l=2)}{5} + \underset{(l=3)}{7} = 16 \text{ orbitals} = (4 \text{ principal shells})^2$$

Exercise

How many subshells and orbitals are in the principal shell with $n = 3$?

Answer: three subshells; nine orbitals

Rather than specifying all the values of n and l every time we refer to a subshell or an orbital, chemists use an abbreviated system with lowercase letters to denote the value of l for a particular subshell or orbital:

l =	0	1	2	3
Designation	*s*	*p*	*d*	*f*

The principal quantum number is named first, followed by the letter *s*, *p*, *d*, or *f* as appropriate. These orbital designations are derived from corresponding spectroscopic characteristics of lines involving them: *s*harp, *p*rinciple, *d*iffuse, and *f*undamental. A 1*s* orbital has $n = 1$ and $l = 0$; a 2*p* subshell has $n = 2$ and $l = 1$ (and has three 2*p* orbitals, corresponding to $m_l = -1$, 0, and +1); a 3*d* subshell has $n = 3$ and $l = 2$ (and has five 3*d* orbitals, corresponding to $m_l = -2$, −1, 0, +1, and +2); and so forth.

We can summarize the relationships between the quantum numbers and the number of subshells and orbitals as follows (Table 2.2.1):

- Each principal shell has n subshells. For $n = 1$, only a single subshell is possible (1*s*); for $n = 2$, there are two subshells (2*s* and 2*p*); for $n = 3$, there are three subshells (3*s*, 3*p*, and 3*d*); and so forth. Every shell has an *ns* subshell, any shell with $n \geq 2$ also has an *np* subshell, and any shell with $n \geq 3$ also has an *nd* subshell. Because a 2*d* subshell would require both $n = 2$ and $l = 2$, which is not an allowed value of l for $n = 2$, a 2*d* subshell does not exist.
- Each subshell has $2l + 1$ orbitals. This means that all *ns* subshells contain a single *s* orbital, all *np* subshells contain three *p* orbitals, all *nd* subshells contain five *d* orbitals, and all *nf* subshells contain seven *f* orbitals.

Note the Pattern

Each principal shell has n subshells, and each subshell has $2l + 1$ orbitals.

Table 2.2.1 Allowed values of *n*, *l*, and m_l through *n* = 4

n	l	Subshell Designation	m_l	Number of Orbitals in Subshell	Number of Orbitals in Shell
1	0	1*s*	0	1	1
2	0	2*s*	0	1	4
	1	2*p*	−1, 0, 1	3	
3	0	3*s*	0	1	9
	1	3*p*	−1, 0, 1	3	
	2	3*d*	−2, −1, 0, 1, 2	5	
4	0	4*s*	0	1	16
	1	4*p*	−1, 0, 1	3	
	2	4*d*	−2, −1, 0, 1, 2	5	
	3	4*f*	−3, −2, −1, 0, 1, 2, 3	7	

Videos

- Quantum numbers - ChemDo

Examples

- Quantum Numbers and Electron Configurations - Purdue - tutorial
- Quantum Chemistry - Ohio State
- Quantum Chemistry Quizzes - mhe education
- AP Chemistry Chapter 7 Review - Science Geek

Answers for these quizzes are included. There are also questions covering more topics in Chapter 2.

Orbital Shapes

An orbital is the quantum mechanical generalization of Bohr's orbit. In contrast to his concept of a simple circular orbit with a fixed radius, orbitals are mathematically derived regions of space with different *probabilities* of having an electron in them.

One way of representing electron probability distributions was illustrated in Figure 2.2.2 for the 1*s* orbital of hydrogen. The probability of finding an electron in a region of space with volume V (such as a cubic picometer) is the product of the volume with $\psi\psi^*$(we can write this as $|\psi|^2$). From our consideration of the properties of the wavefunction, we know that adding up the probability from every such small volume over all space will sum to unity, or a 100% probability that the electron is somewhere. A plot of $|\psi|^2$ versus distance from the nucleus (r) is a plot of the *probability density*. The 1*s* orbital is spherically symmetrical, so the probability of finding a 1*s* electron at any given point depends *only* on its distance from the nucleus. The probability density is greatest at $r = 0$ (at the nucleus) and decreases steadily with increasing distance. At very large values of r, the electron probability density is tiny but *not* exactly zero.

In contrast to the probability density, we can calculate the *radial probability* (the probability of finding a 1*s* electron at a distance r from the nucleus) by adding together the probabilities of an electron being at all points on a series of x spherical shells of radius r_1, r_2, r_3,…, r_{x-1}, r_x. In effect, we are dividing the atom into very thin concentric shells, much like the layers of an onion (part (a) in Figure 2.2.2), and calculating the probability of finding an electron on each spherical shell. Recall that the electron probability density is greatest at $r = 0$ (part (b) in Figure 2.2.3), so the density of dots is greatest for the smallest spherical shells in part (a) in Figure 2.2.3

The surface area of each spherical shell is equal to $4\pi r^2$, which increases rapidly with increasing r (part (c) in Figure 2.2.3). Because the surface area of the spherical shells increases at first more rapidly with increasing r than the electron probability density decreases, the plot of radial probability has a maximum at a particular distance (part (d) in Figure 2.2.3). As important, when r is

very small, the surface area of a spherical shell is so small that the *total* probability of finding an electron close to the nucleus is very low; at the nucleus, the electron probability vanishes because the surface area of the shell is zero (part (d) in Figure 2.2.2).

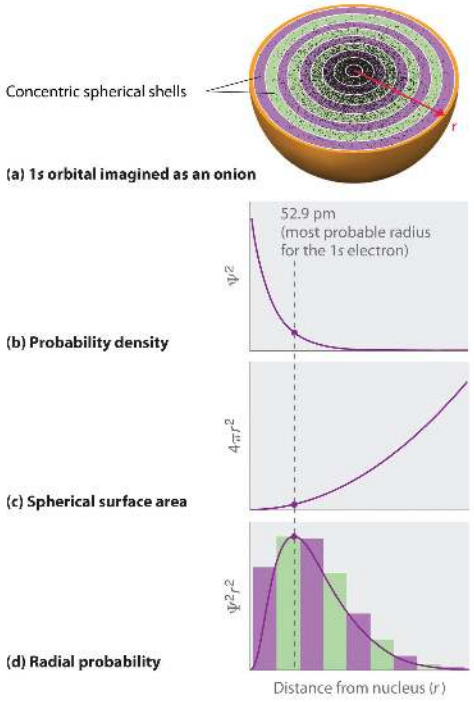


Figure 2.2.3 Most Probable Radius for the Electron in the Ground State of the Hydrogen Atom *(a) Imagine dividing the atom's total volume into very thin concentric shells as shown in the onion drawing. (b) A plot of electron probability density Ψ^2 versus r shows that the electron probability density is greatest at r = 0 and falls off smoothly with increasing r. The density of the dots is therefore greatest in the innermost shells of the onion. (c) The surface area of each shell, given by $4\pi r^2$, increases rapidly with increasing r. (d) If we count the number of dots in each spherical shell, we obtain the total probability of finding the electron at a given value of r. Because the surface area of each shell increases more rapidly with increasing r than the electron probability density decreases, a plot of electron probability versus r (the radial probability) shows a peak. This peak corresponds to the most probable radius for the electron, 52.9 pm, which is exactly the radius predicted by Bohr's model of the hydrogen atom.*

For the hydrogen atom, the peak in the radial probability plot occurs at r = 0.529 Å (52.9 pm), which is exactly the radius calculated by Bohr for the n = 1 orbit. Thus the *most probable radius* obtained from quantum mechanics is identical to the radius calculated by classical mechanics. In Bohr's model, however, the electron was assumed to be at this distance 100% of the time, whereas in the Schrödinger model, it is at this distance only some of the time. The difference between the two models is attributable to the wavelike behavior of the electron.

Figure 2.2,4 compares the electron probability densities for the hydrogen 1*s*, 2*s*, and 3*s* orbitals. Note that all three are spherically symmetrical. For the 2*s* and 3*s* orbitals, however (and for all other *s* orbitals as well), the electron probability density does not fall off smoothly with increasing *r*. Instead, a series of minima and maxima are observed in the radial probability plots (part (c) in Figure 2.2.4). The minima correspond to spherical nodes (regions of zero electron probability), which alternate with spherical regions of nonzero electron probability.

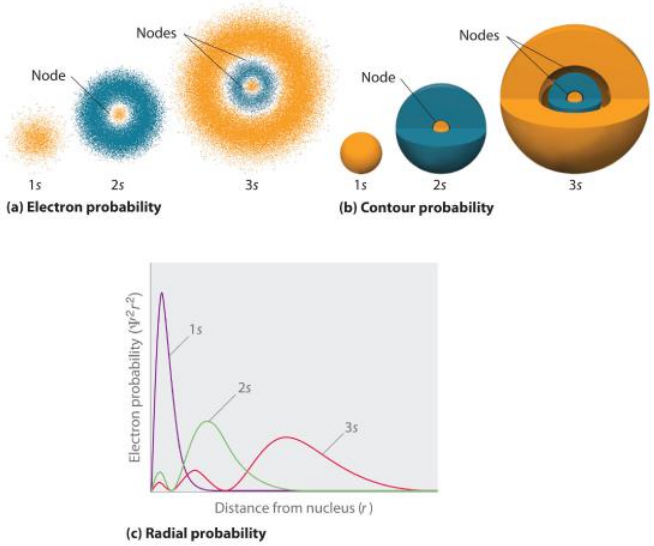


Figure 2.2.4 Probability Densities for the 1*s*, 2*s*, and 3*s* Orbitals of the Hydrogen Atom *(a) The electron probability density in any plane that contains the nucleus is shown. Note the presence of circular regions, or nodes, where the probability density is zero. (b) Contour surfaces enclose 90% of the electron probability, which illustrates the different sizes of the 1s, 2s, and 3s orbitals. The cutaway drawings give partial views of the internal spherical nodes. The orange color corresponds to regions of space where the phase of the wave function is positive, and the blue color corresponds to regions of space where the phase of the wave function is negative. (c) In these plots of electron probability as a function of distance from the nucleus (r) in all directions (radial probability), the most probable radius increases as n increases, but the 2s and 3s orbitals have regions of significant electron probability at small values of r.*

s Orbitals

Three things happen to *s* orbitals as *n* increases (Figure 2.2.4):

1. They become larger, extending farther from the nucleus.
2. They contain more nodes. This is similar to a standing wave that has regions of significant amplitude separated by nodes, points with zero amplitude.
3. For a given atom, the *s* orbitals also become higher in energy as *n* increases because of their increased distance from the nucleus.

Orbitals are generally drawn as three-dimensional surfaces that enclose 90% of the electron densityElectron distributions that are represented as standing waves., as was shown for the hydrogen 1*s*, 2*s*, and 3*s* orbitals in part (b) in Figure 2.2.4 Although such drawings show the relative sizes of the orbitals, they do not normally show the spherical nodes in the 2*s* and 3*s* orbitals because the spherical nodes lie inside the 90% surface. Fortunately, the positions of the spherical nodes are not important for chemical bonding. This makes sense because bonding is an interaction of electrons from two atoms which will be most sensitive to forces at the edges of the orbitals.

p Orbitals

Only *s* orbitals are spherically symmetrical. As the value of *l* increases, the number of orbitals in a given subshell increases, and the shapes of the orbitals become more complex. Because the 2*p* subshell has $l = 1$, with three values of m_l (−1, 0, and +1), there are three 2*p* orbitals.

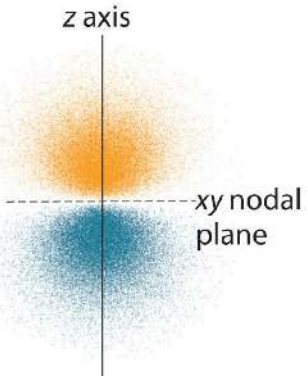


Figure 2.2.5 Electron Probability Distribution for a Hydrogen 2*p* Orbital *The nodal plane of zero electron density separates the two lobes of the 2p orbital. As in Figure 2.2.4 , the colors correspond to regions of space where the phase of the wave function is positive (orange) and negative (blue).*

The electron probability distribution for one of the hydrogen 2*p* orbitals is shown in Figure 2.2.5 . Because this orbital has two lobes of electron density arranged along the *z* axis, with an electron density of zero in the *xy* plane (i.e., the *xy* plane is a nodal plane), it is a $2p_z$ orbital. As shown in Figure 2.2.6 , the other two 2*p* orbitals have identical shapes, but they lie along the *x* axis ($2p_x$) and *y* axis ($2p_y$), respectively. Note that each 2*p* orbital has just one nodal plane. In each case, the phase of the wave function for each of the 2*p* orbitals is positive for the lobe that points along the positive axis and negative for the lobe that points along the negative axis. It is important to emphasize that these signs correspond to the *phase* of the wave that describes the electron motion, *not* to positive or negative charges.

In the next section when we consider the electron configuration of multielectron atoms, the geometric shapes provide an important clue about which orbitals will be occupied by different electrons. Because electrons in different *p* orbitals are geometrically distant from each other, there is less repulsion between them than would be found if two electrons were in the same *p* orbital. Thus, when the *p* orbitals are filled, it will be energetically favorable to first place one electron into each *p* orbital, rather than two into one orbital.

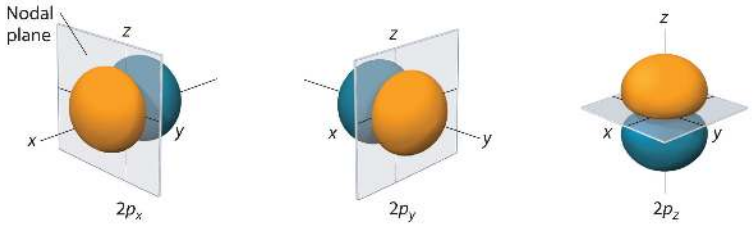


Figure 2.2.6 The Three Equivalent 2*p* Orbitals of the Hydrogen Atom *The surfaces shown enclose 90% of the total electron probability for the $2p_x$, $2p_y$, and $2p_z$ orbitals. Each orbital is oriented along the axis indicated by the subscript and a nodal plane that is perpendicular to that axis bisects each 2p orbital. The phase of the wave function is positive (orange) in the region of space where x, y, or z is positive and negative (blue) where x, y, or z is negative.*

Just as with the *s* orbitals, the size and complexity of the *p* orbitals for any atom increase as the principal quantum number *n* increases. The shapes of the 90% probability surfaces of the 3*p*, 4*p*, and higher-energy *p* orbitals are, however, essentially the same as those shown in Figure 2.2.6. The shapes of *p* orbitals for n > 2 look like strings of beads oriented along the x, y and z axis with two additional nodes per unit increases in n. Visualizations of the orbitals can be found at http://www.winter.group.shef.ac.uk/orbitron/AOs/3p/index.html at the University of Sheffield in Britain.

d Orbitals

Subshells with $l = 2$ have five *d* orbitals; the first principal shell to have a *d* subshell corresponds to $n = 3$. The five *d* orbitals have m_l values of −2, −1, 0, +1, and +2.

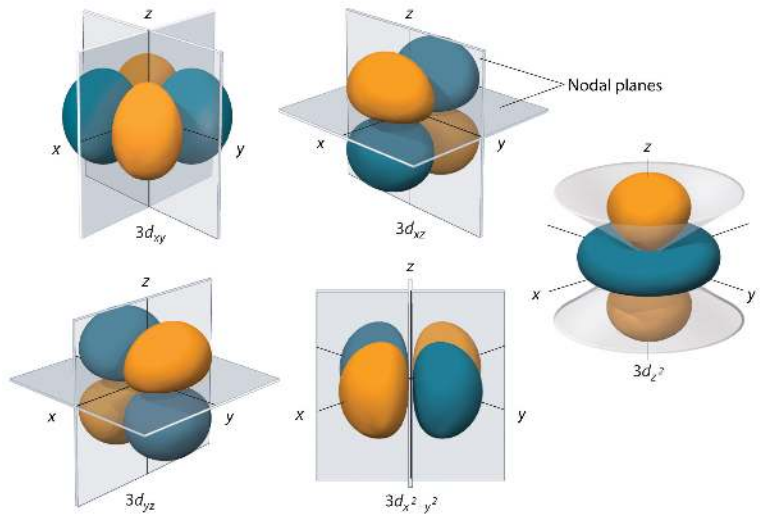


Figure 2.2.7 The Five Equivalent 3*d* Orbitals of the Hydrogen Atom *The surfaces shown enclose 90% of the total electron probability for the five hydrogen 3d orbitals. Four of the five 3d orbitals consist of four lobes arranged in a plane that is intersected by two perpendicular nodal planes. These four orbitals have the same shape but different orientations. The fifth 3d orbital,* $\mathbf{3}d_{z^2}$ *, has a distinct shape even though it is mathematically equivalent to the others. The phase of the wave function for the different lobes is indicated by color: orange for positive and blue for negative.*

The hydrogen 3*d* orbitals, shown in Figure 2.2.7 , have more complex shapes than the 2*p* orbitals. All five 3*d* orbitals contain two nodal surfaces, as compared to one for each *p* orbital and zero for each *s* orbital. In three of the *d* orbitals, the lobes of electron density are oriented between the *x* and *y*, *x* and *z*, and *y* and *z* planes; these orbitals are referred to as the $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$ orbitals, respectively. A fourth *d* orbital has lobes lying along the *x* and *y* axes; this is the $\mathbf{3}d_{x^2-y^2}$ orbital. The fifth 3*d* orbital, called the $\mathbf{3}d_{z^2}$ orbital, has a unique shape: it looks like a $2p_z$ orbital combined with an additional doughnut of electron probability lying in the *xy* plane. Despite its peculiar shape, the $\mathbf{3}d_{z^2}$ orbital is mathematically equivalent to the other four and has the same energy. In contrast to *p* orbitals, the phase of the wave function for *d* orbitals is the same for opposite pairs of lobes. As shown in Figure 2.2.7 , the phase of the wave function is positive for the two lobes of the $\mathbf{3}d_{z^2}$ orbital that lie along the *z* axis, whereas the phase of the wave function is negative for the doughnut of electron density in the *xy* plane. Like the *s* and *p* orbitals, as *n* increases, the size of the *d* orbitals increases, but the overall shapes remain similar to those depicted in Figure 2.2.7 .

f Orbitals

Principal shells with $n = 4$ can have subshells with $l = 3$ and m_l values of −3, −2, −1, 0, +1, +2, and +3. These subshells consist of seven *f* orbitals. Each *f* orbital has three nodal surfaces, so their shapes are complex. Because *f* orbitals are not particularly important for our purposes, we do not discuss them further, and orbitals with higher values of *l* are not discussed at all. Equivalent illustrations of the shapes of the f orbitals are available

Orbital Energies

Although we have discussed the shapes of orbitals, we have said little about their comparative energies. We begin our discussion of orbital energiesA particular energy associated with a given set of quantum numbers. by considering atoms or ions with only a single electron (such as H or He^+). This is the simplest case.

The relative energies of the atomic orbitals with $n \le 4$ for a hydrogen atom are plotted in Figure 2.2.8 note that the orbital energies depend on *only* the principal quantum number *n*. Consequently, the energies of the 2*s* and 2*p* orbitals of hydrogen are the same; the energies of the 3*s*, 3*p*, and 3*d* orbitals are the same; and so forth. The orbital energies obtained for hydrogen using quantum mechanics are exactly the same as the allowed energies calculated by Bohr. In contrast to Bohr's model, however, which allowed only one orbit for each energy level, quantum mechanics predicts that there are *4* orbitals with different electron density distributions in the $n = 2$ principal shell (one 2*s* and three 2*p* orbitals), *9* in the $n = 3$ principal shell, and *16* in the $n = 4$ principal shell.The different values of *l* and m_l for the individual orbitals within a given principal shell are not important for understanding

the emission or absorption spectra of the hydrogen atom under most conditions, but they do explain the splittings of the main lines that are observed when hydrogen atoms are placed in a magnetic field. As we have just seen, however, quantum mechanics also predicts that in the hydrogen atom, all orbitals with the same value of n (e.g., the three 2p orbitals) are degenerateHaving the same energy., meaning that they have the same energy. Figure 2.2.8 shows that the energy levels become closer and closer together as the value of n increases, as expected because of the $1/n^2$ dependence of orbital energies.

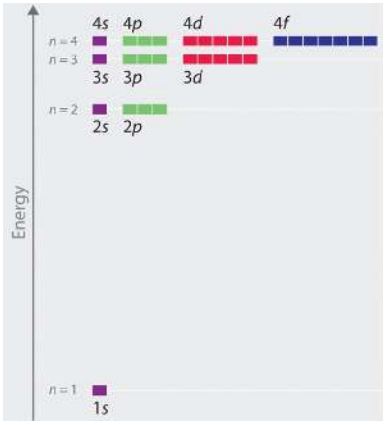


Figure 2.2.8 Orbital Energy Level Diagram for the Hydrogen Atom *Each box corresponds to one orbital. Note that the difference in energy between orbitals decreases rapidly with increasing values of n.*

The energies of the orbitals in any species with only one electron can be calculated by Bohr's equation (Equation 2.2.5.), which can be extended to other single-electron species such as He^+ by incorporating the nuclear charge Z (the number of protons in the nucleus):

$$E = -\frac{Z^2}{n^2}\mathcal{R}hc$$

Here the zero of energy is taken as the ionized electron limit, where the electron is separated an infinite distance from the nucleus and thus the binding energy holding the electron and nucleus together is zero. In general, the binding energy increases and the radius decreases as the nuclear charge increases. As a result of the Z^2 dependence of energy in Equation 2.2.4, electrons in the 1s orbital of carbon, which has a nuclear charge of +6, lie roughly 36 times lower in energy (the 1s electron is held 36 times more strongly) than those in the hydrogen 1s orbital, and the 1s orbital of tin, with an atomic number of 50 is roughly 2500 times lower still. The most stable and tightly bound electrons are in orbitals (those with the lowest energy) closest to the nucleus.

For example, in the ground state of the hydrogen atom, the single electron is in the 1s orbital, whereas in the first excited state, the atom has absorbed energy and the electron has been promoted to one of the n = 2 orbitals. In ions with only a single electron, the energy of a given orbital depends on only n, and all subshells within a principal shell, such as the p_x, p_y, and p_z orbitals, are degenerate.

Videos

- Quantum Mechanics 6a- Hydrogen - via science (don't bother with the first 3 minutes which are advanced math heavy, but the stunning illustrations of orbital shapes afterwards are great)
- Electron Spin and the Pauli Principle - via science.(does an excellent job explaining why electron spin is not a spinning electron)
- Electron Orbitals - Anna Tanczos - more visualizations

Examples

- Quantum Chemistry - Ohio State
- Quantum Chemistry Quizzes - mhe education
- AP Chemistry Chapter 7 Review - Science Geek

Answers for these quizzes are included. There are also questions covering more topics in Chapter 2.

Effective Nuclear Charges

For an atom or an ion with only a single electron, we can calculate the potential energy by considering only the electrostatic attraction between the positively charged nucleus and the negatively charged electron. When more than one electron is present, however, the total energy of the atom or the ion depends not only on attractive electron-nucleus interactions but also on repulsive electron-electron interactions. When there are two electrons, the repulsive interactions depend on the positions of *both* electrons at a given instant, but because we cannot specify the exact positions of the electrons, it is impossible to exactly calculate the repulsive interactions. Consequently, we must use approximate methods to deal with the effect of electron-electron repulsions on orbital energies.

If an electron is far from the nucleus (i.e., if the distance r between the nucleus and the electron is large), then at any given moment, most of the other electrons will be *between* that electron and the nucleus. Hence the electrons will cancel a portion of the positive charge of the nucleus and thereby decrease the attractive interaction between it and the electron farther away. As a result, the electron farther away experiences an effective nuclear charge (Z_{eff})The nuclear charge an electron actually experiences because of shielding from other electrons closer to the nucleus. that is *less* than the actual nuclear charge Z. This effect is called electron shieldingThe effect by which electrons closer to the nucleus neutralize a portion of the positive charge of the nucleus and thereby decrease the attractive interaction between the nucleus and an electron father away.. As the distance between an electron and the nucleus approaches infinity, Z_{eff} approaches a value of 1 because all the other $(Z - 1)$ electrons in the neutral atom are, on the average, between it and the nucleus. If, on the other hand, an electron is very close to the nucleus, then at any given moment most of the other electrons are farther from the nucleus and do not shield the nuclear charge. At $r \approx 0$, the positive charge experienced by an electron is approximately the full nuclear charge, or $Z_{eff} \approx Z$. At intermediate values of r, the effective nuclear charge is somewhere between 1 and Z: $1 \le Z_{eff} \le Z$. Thus the actual Z_{eff} experienced by an electron in a given orbital depends not only on the spatial distribution of the electron in that orbital but also on the distribution of all the other electrons present. This leads to large differences in Z_{eff} for different elements, as shown in Figure 2.2.9 for the elements of the first three rows of the periodic table. Notice that only for hydrogen does $Z_{eff} = Z$, and only for helium are Z_{eff} and Z comparable in magnitude.

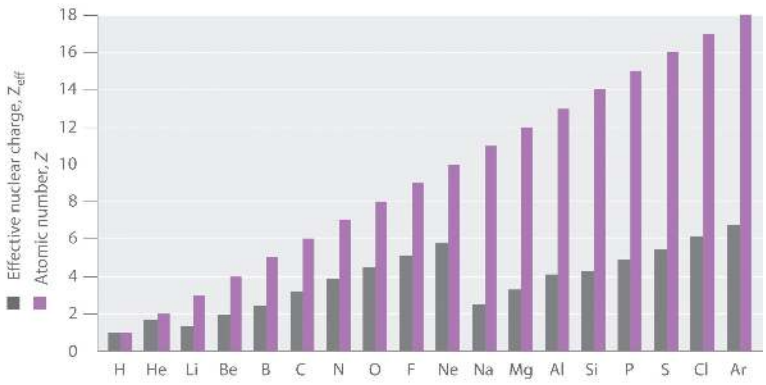


Figure 2.2.9 Relationship between the Effective Nuclear Charge Z_{eff} and the Atomic Number Z for the Outer Electrons of the Elements of the First Three Rows of the Periodic Table *Except for hydrogen, Z_{eff} is always less than Z, and Z_{eff} increases from left to right as you go across a row.*

The trend that you see in Figure 2.2.9 for the first three principal shells corresponding to n = 1, 2, and 3, continues in the further shells. The atomic number and thus the nuclear charge increase linearly, but the sawtooth pattern for Z_{eff} repeats itself, resetting as the quantum number n changes. Chemical bonding and reactivity involves the sharing or exchange of electrons between atoms. Those electrons which can participate are those held least strongly by the atom, the outermost electrons, which, no matter what the atomic number, and nuclear charge, are bound to their atom by roughly the same energy range because of the shielding effect.

In multielectron atoms this shifts the energies of the different orbitals for a typical multielectron atom as shown in Figure 2.2.10 . Within a given principal shell of a multielectron atom, the orbital energies increase with increasing l. An *ns* orbital always lies below the corresponding *np* orbital, which in turn lies below the *nd* orbital. These energy differences are caused by the effects of shielding and *penetration*, the extent to which a given orbital lies inside other filled orbitals. As shown in Figure 2.2.10 for example, an electron in the 2*s* orbital penetrates inside a filled 1*s* orbital more than an electron in a 2*p* orbital does. Hence in an

atom with a filled 1*s* orbital, the Z_{eff} experienced by a 2*s* electron is greater than the Z_{eff} experienced by a 2*p* electron. Consequently, the 2*s* electron is more tightly bound to the nucleus and has a lower energy, consistent with the order of energies shown in Figure 2.2.10

Note the Pattern

Due to electron shielding, Z_{eff} increases more rapidly going across a row of the periodic table than going down a column.

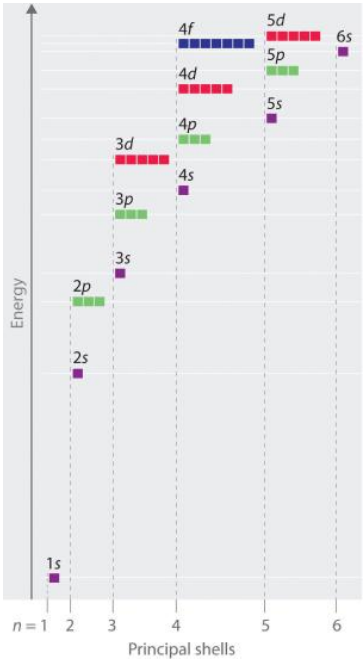


Figure 2.2.10 Orbital Energy Level Diagram for a Typical Multielectron Atom

Because of the effects of shielding and the different radial distributions of orbitals with the same value of *n* but different values of *l*, the different subshells are not degenerate in a multielectron atom. (Compare this with Figure 2.2.8 For a given value of *n*, the *ns* orbital is always lower in energy than the *np* orbitals, which are lower in energy than the *nd* orbitals, and so forth. As a result, some subshells with higher principal quantum numbers are actually lower in energy than subshells with a lower value of *n*; for example, the 4*s* orbital is lower in energy than the 3*d* orbitals for most atoms.

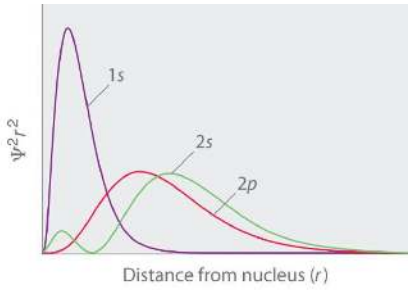


Figure 2.2.11 Orbital Penetration *A comparison of the radial probability distribution of the 2s and 2p orbitals for various states of the hydrogen atom shows that the 2s orbital penetrates inside the 1s orbital more than the 2p orbital does. Consequently, when an electron is in the small inner lobe of the 2s orbital, it experiences a relatively large value of Z_{eff}, which causes the energy of the 2s orbital to be lower than the energy of the 2p orbital.*

Notice in Figure 2.2.10 that the difference in energies between subshells can be so large that the energies of orbitals from different principal shells can become approximately equal. For example, the energy of the 3*d* orbitals in most atoms is actually *between* the energies of the 4*s* and the 4*p* orbitals.

Key Equation

energy of hydrogen-like orbitals

Equation 2.2.5: $E = -\frac{Z^2}{n^2}\mathcal{R}hc$

Summary

Because of wave–particle duality, we can only determine the probability of an electron being at a particular point in space. To do so requires the development of **quantum mechanics**, which uses **wave functions (Ψ)** to describe the mathematical relationship between the motion of electrons in atoms and molecules and their energies. Wave functions have five important properties: (1) the wave function uses three variables (Cartesian axes *x*, *y*, and *z*) to describe the position of an electron; (2) the magnitude of the wave function is proportional to the intensity of the wave; (3) the probability of finding an electron at a given point is proportional to the square of the wave function at that point, leading to a distribution of probabilities in space that is often portrayed as an **electron density** plot; (4) describing electron distributions as standing waves leads naturally to the existence of sets of **quantum numbers** characteristic of each wave function; and (5) each spatial distribution of the electron described by a wave function with a given set of quantum numbers has a particular energy.

Quantum numbers provide important information about the energy and spatial distribution of an electron. The **principal quantum number** n can be any positive integer; as n increases for an atom, the average distance of the electron from the nucleus also increases. All wave functions with the same value of n constitute a **principal shell** in which the electrons have similar average distances from the nucleus. The **azimuthal quantum number** l can have integral values between 0 and $n − 1$; it describes the shape of the electron distribution. Wave functions that have the same values of both n and l constitute a **subshell**, corresponding to electron distributions that usually differ in orientation rather than in shape or average distance from the nucleus. The **magnetic quantum number** m_l can have $2l + 1$ integral values, ranging from $−l$ to $+l$, and describes the orientation of the electron distribution. Each wave function with a given set of values of n, l, and m_l describes a particular spatial distribution of an electron in an atom, an **atomic orbital**.

The four chemically important types of atomic orbital correspond to values of $l = 0$, 1, 2, and 3. Orbitals with $l = 0$ are *s* orbitals and are spherically symmetrical, with the greatest probability of finding the electron occurring at the nucleus. All orbitals with values of $n > 1$ and $l = 0$ contain one or more nodes. Orbitals with $l = 1$ are *p* orbitals and contain a nodal plane that includes the nucleus, giving rise to a dumbbell shape. Orbitals with $l = 2$ are *d* orbitals and have more complex shapes with at least two nodal surfaces. Orbitals with $l = 3$ are *f* orbitals, which are still more complex.

Because its average distance from the nucleus determines the energy of an electron, each atomic orbital with a given set of quantum numbers has a particular energy associated with it, the **orbital energy**. In atoms or ions with only a single electron, all orbitals with the same value of n have the same energy (they are **degenerate**), and the energies of the principal shells increase smoothly as n increases. An atom or ion with the electron(s) in the lowest-energy orbital(s) is said to be in its ground state, whereas an atom or ion in which one or more electrons occupy higher-energy orbitals is said to be in an excited state.

The calculation of orbital energies in atoms or ions with more than one electron (multielectron atoms or ions) is complicated by repulsive interactions between the electrons. The concept of **electron shielding**, in which intervening electrons act to reduce the positive nuclear charge experienced by an electron, allows the use of hydrogen-like orbitals and an **effective nuclear charge** (Z_{eff}) to describe electron distributions in more complex atoms or ions. The degree to which orbitals with different values of l and the same value of n overlap or penetrate filled inner shells results in slightly different energies for different subshells in the same principal shell in most atoms.

Key Takeaway

- There is a relationship between the motions of electrons in atoms and molecules and their energies that is described by quantum mechanics.

Conceptual Problems

1. Why does an electron in an orbital with $n = 1$ in a hydrogen atom have a lower energy than a free electron ($n = \infty$)?
2. What four variables are required to fully describe the position of any object in space? In quantum mechanics, one of these variables is not explicitly considered. Which one and why?

3. Chemists generally refer to the square of the wave function rather than to the wave function itself. Why?
4. Orbital energies of species with only one electron are defined by only one quantum number. Which one? In such a species, is the energy of an orbital with $n = 2$ greater than, less than, or equal to the energy of an orbital with $n = 4$? Justify your answer.
5. In each pair of subshells for a hydrogen atom, which has the higher energy? Give the principal and the azimuthal quantum number for each pair.
    1. 1*s*, 2*p*
    2. 2*p*, 2*s*
    3. 2*s*, 3*s*
    4. 3*d*, 4*s*
6. What is the relationship between the energy of an orbital and its average radius? If an electron made a transition from an orbital with an average radius of 846.4 pm to an orbital with an average radius of 476.1 pm, would an emission spectrum or an absorption spectrum be produced? Why?
7. In making a transition from an orbital with a principal quantum number of 4 to an orbital with a principal quantum number of 7, does the electron of a hydrogen atom emit or absorb a photon of energy? What would be the energy of the photon? To what region of the electromagnetic spectrum does this energy correspond?
8. What quantum number defines each of the following?
    1. the overall shape of an orbital
    2. the orientation of an electron with respect to a magnetic field
    3. the orientation of an orbital in space
    4. the average energy and distance of an electron from the nucleus
9. In an attempt to explain the properties of the elements, Niels Bohr initially proposed electronic structures for several elements with orbits holding a certain number of electrons, some of which are in the following table:

Element	Number of Electrons	Electrons in orbits with n =			
		4	3	2	1
H	1				1
He	2				2
Ne	10			8	2
Ar	18		8	8	2
Li	3			1	2
Na	11		1	8	2
K	19	1	8	8	2
Be	4			2	2

    1. Draw the electron configuration of each atom based only on the information given in the table. What are the differences between Bohr's initially proposed structures and those accepted today?
    2. Using Bohr's model, what are the implications for the reactivity of each element?
    3. Give the actual electron configuration of each element in the table.
10. What happens to the energy of a given orbital as the nuclear charge Z of a species increases? In a multielectron atom and for a given nuclear charge, the Z_{eff} experienced by an electron depends on its value of l. Why?

11. The electron density of a particular atom is divided into two general regions. Name these two regions and describe what each represents.
12. As the principal quantum number increases, the energy difference between successive energy levels decreases. Why? What would happen to the electron configurations of the transition metals if this decrease did not occur?
13. Describe the relationship between electron shielding and Z_{eff} on the outermost electrons of an atom. Predict how chemical reactivity is affected by a decreased effective nuclear charge.
14. If a given atom or ion has a single electron in each of the following subshells, which electron is easier to remove?
    1. 2*s*, 3*s*
    2. 3*p*, 4*d*
    3. 2*p*, 1*s*
    4. 3*d*, 4*s*

Numerical Problems

1. How many subshells are possible for $n = 3$? What are they?
2. How many subshells are possible for $n = 5$? What are they?
3. What value of l corresponds to a *d* subshell? How many orbitals are in this subshell?
4. What value of l corresponds to an *f* subshell? How many orbitals are in this subshell?
5. State the number of orbitals and electrons that can occupy each subshell.
    1. 2*s*
    2. 3*p*
    3. 4*d*
    4. 6*f*
6. State the number of orbitals and electrons that can occupy each subshell.
    1. 1*s*
    2. 4*p*
    3. 5*d*
    4. 4*f*
7. How many orbitals and subshells are found within the principal shell $n = 6$? How do these orbital energies compare with those for $n = 4$?
8. How many nodes would you expect a 4*p* orbital to have? A 5*s* orbital?
9. A *p* orbital is found to have one node in addition to the nodal plane that bisects the lobes. What would you predict to be the value of *n*? If an *s* orbital has two nodes, what is the value of *n*?

Answers

1. Three subshells, with $l = 0$ (*s*), $l = 1$ (*p*), and $l = 2$ (*d*).
2.
3. A *d* subshell has $l = 2$ and contains 5 orbitals.
4.
5.
    1. 2 electrons; 1 orbital
    2. 6 electrons; 3 orbitals
    3. 10 electrons; 5 orbitals
    4. 14 electrons; 7 orbitals

6.
7. A principal shell with $n = 6$ contains six subshells, with $l = 0$, 1, 2, 3, 4, and 5, respectively. These subshells contain 1, 3, 5, 7, 9, and 11 orbitals, respectively, for a total of 36 orbitals. The energies of the orbitals with $n = 6$ are higher than those of the corresponding orbitals with the same value of l for $n = 4$.
8.
9.

Contributors

- Anonymous

Modified by Joshua Halpern, Scott Sinex and Scott Johnson

Imaginary Number Video from IceDave33 on YouTube

Wave Phase Video from Khan Academy

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Chapter 2.3: Building Up The Periodic Table

Learning Objective

- To write the electron configuration of any element and relate its electron configuration to its position in the periodic table.

Now you can use the information you learned in Section 2.2 to determine the electronic structure of every element in the periodic table. The process of describing each atom's electronic structure consists, essentially, of beginning with hydrogen and adding one proton and one electron at a time to create the next heavier element in the table.All stable nuclei other than hydrogen also contain one or more neutrons. Because neutrons have no electrical charge, however, they can be ignored in the following discussion. Before demonstrating how to do this, however, we must introduce the concept of electron spin and the Pauli principle.

Electron Spin: The Fourth Quantum Number

When scientists analyzed the emission and absorption spectra of the elements more closely, they saw that for elements having more than one electron, nearly all the lines in the spectra were actually *pairs* of very closely spaced lines. Because each line represents an energy level available to electrons in the atom, there are twice as many energy levels available as would be predicted solely based on the quantum numbers n, l, and m_l. Scientists also discovered that applying a magnetic field caused the lines in the pairs to split farther apart. In 1925, two graduate students in physics in the Netherlands, George Uhlenbeck (1900–1988) and Samuel Goudsmit (1902–1978), proposed that the splittings were caused by an electron spinning about its axis, much as Earth spins about its axis. When an electrically charged object spins, it produces a magnetic moment parallel to the axis of rotation, making it behave like a magnet.

We know that the electron cannot be viewed solely as a particle spinning, due to its wavelike properties. Worse, electrons are very weird things, no one for example, has ever been able to measure the radius of an electron, on the atomic scale it behaves as a point. On smaller scales there have been a lot of ideas but no agreement or proof. What is spinning, or how it is spins, or i it is spinning at all is a subject of speculation. The behavior of a quantum particle such as the electron cannot be visualized using concepts from our common experience. What is indisputable that electrons do have a magnetic moment which interacts with magnetic fields.This magnetic moment is called electron spinThe magnetic moment that results when an electron spins. Electrons have two possible orientations (spin up and spin down), which are described by a fourth quantum number (m_s)..

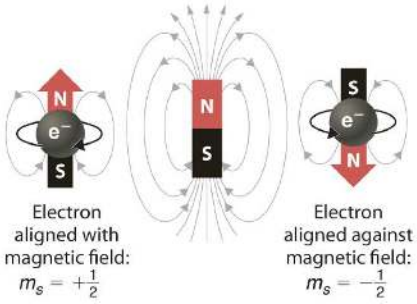


Figure 2.3.1 Electron Spin*In a magnetic field, an electron has two possible orientations with different energies, one with spin up, aligned with the magnetic field, and one with spin down, aligned against it. All other orientations are forbidden.*

In an external magnetic field, the electron has two possible orientations (Figure 2.3.1). These are described by a fourth quantum number (m_s), which for any electron can have only two possible values, designated +½ (up) and −½ (down) to indicate that the two orientations are opposites; the subscript s is for spin. An electron behaves like a magnet that has one of two possible orientations, aligned either with the magnetic field or against it.

The Pauli Principle

The implications of electron spin for chemistry were recognized almost immediately by an Austrian physicist,Wolfgang Pauli (1900–1958; Nobel Prize in Physics, 1945), who determined that each orbital can contain no more than two electrons. He developed the Pauli exclusion principleA principle stating that no two electrons in an atom can have the same value of all four quantum numbers.: *No two electrons in an atom can have the same values of all four quantum numbers (n, l, m_l, m_s).*

By giving the values of n, l, and m_l, we also specify a particular orbital (e.g., 1*s* with $n = 1$, $l = 0$, $m_l = 0$). Because m_s has only two possible values (+½ or −½), two electrons, *and only two electrons*, can occupy any given orbital, one with spin up and one with spin down. With this information, we can proceed to construct the entire periodic table, which, as you learned in Chapter 1 , was originally based on the physical and chemical properties of the known elements.

Example 2.3.1

List all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for electrons in a 2*p* orbital and predict the maximum number of electrons the 2*p* subshell can accommodate.

Given: orbital

Asked for: allowed quantum numbers and maximum number of electrons in orbital

Strategy:

A List the quantum numbers (n, l, m_l) that correspond to an $n = 2p$ orbital. List all allowed combinations of (n, l, m_l).

B Build on these combinations to list all the allowed combinations of (n, l, m_l, m_s).

C Add together the number of combinations to predict the maximum number of electrons the 2*p* subshell can accommodate.

Solution:

A For a 2*p* orbital, we know that $n = 2$, $l = n − 1 = 1$, and $m_l = −l$, $(−l + 1)$,…, $(l − 1)$, l. There are only three possible combinations of (n, l, m_l): (2, 1, 1), (2, 1, 0), and (2, 1, −1).

B Because m_s is independent of the other quantum numbers and can have values of only +½ and −½, there are six possible combinations of (n, l, m_l, m_s): (2, 1, 1, +½), (2, 1, 1, −½), (2, 1, 0, +½), (2, 1, 0, −½), (2, 1, −1, +½), and (2, 1, −1, −½).

C Hence the 2*p* subshell, which consists of three 2*p* orbitals ($2p_x$, $2p_y$, and $2p_z$), can contain a total of six electrons, two in each orbital.

Exercise

List all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for a 6*s* orbital, and predict the total number of electrons it can contain.

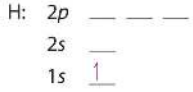
Answer: (6, 0, 0, +½), (6, 0, 0, −½); two electrons

Electron Configurations of the Elements

The electron configurationThe arrangement of an element's electrons in its atomic orbitals. of an element is the arrangement of its electrons in its atomic orbitals. By knowing the electron configuration of an element, we can predict and explain a great deal of its chemistry.

The Aufbau Principle

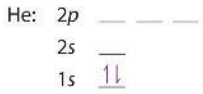
We construct the periodic table by following the aufbau principleThe process used to build up the periodic table by adding protons one by one to the nucleus and adding the corresponding electrons to the lowest-energy orbital available without violating the Pauli exclusion principle. (from German, meaning "building up"). First we determine the number of electrons in the atom; then we add electrons one at a time to the lowest-energy orbital available *without violating the Pauli principle*. We use the orbital energy diagram of Figure 2.2.10 , recognizing that each orbital can hold two electrons, one with spin up ↑, corresponding to $m_s = +½$, which is arbitrarily written first, and one with spin down ↓, corresponding to $m_s = −½$. A filled orbital is indicated by ↑↓, in which the electron spins are said to be *paired*. Here is a schematic orbital diagram for a hydrogen atom in its ground state:



From the orbital diagram, we can write the electron configuration in an abbreviated form in which the occupied orbitals are identified by their principal quantum number n and their value of l (*s*, *p*, *d*, or *f*), with the number of electrons in the subshell

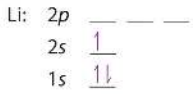
indicated by a superscript. For hydrogen, therefore, the single electron is placed in the 1*s* orbital, which is the orbital lowest in energy (Figure 2.2.10), and the electron configuration is written as $1s^1$ and read as “one-s-one.”

A neutral helium atom, with an atomic number of 2 ($Z = 2$), has two electrons. We place one electron in the orbital that is lowest in energy, the 1*s* orbital. From the Pauli exclusion principle, we know that an orbital can contain two electrons with opposite spin, so we place the second electron in the same orbital as the first but pointing down, so that the electrons are paired. The orbital diagram for the helium atom is therefore



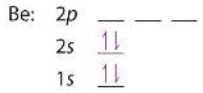
written as $1s^2$, where the superscript 2 implies the pairing of spins. Otherwise, our configuration would violate the Pauli principle. Remember that because the helium nucleus has a positive charge of +2, the 1s level of helium lies considerably below the 1s level of hydrogen, although for the purposes of building up the periodic table we do not take that into consideration. The orbital diagrams are energy ordered, the levels are in the proper energy order from bottom (most bound) to least, but the energies are not scaled.

The next element is lithium, with $Z = 3$ and three electrons in the neutral atom. We know that the 1*s* orbital can hold two of the electrons with their spins paired. Figure 2.2.10 tells us that the next lowest energy orbital is 2*s*, so the orbital diagram for lithium is

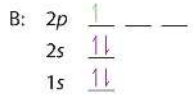


This electron configuration is written as $1s^22s^1$.

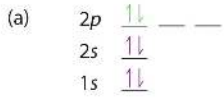
The next element is beryllium, with $Z = 4$ and four electrons. We fill both the 1*s* and 2*s* orbitals to achieve a $1s^22s^2$ electron configuration:

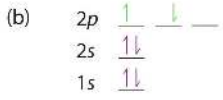


When we reach boron, with $Z = 5$ and five electrons, we must place the fifth electron in one of the 2*p* orbitals. Remember that the actual energy difference between the *2s* and *2p* levels is much smaller than that between the *1s* and *2s* levels. Because all three *2p* orbitals are degenerate, it doesn’t matter which one we select. The electron configuration of boron is $1s^22s^22p^1$:



At carbon, with $Z = 6$ and six electrons, we are faced with a choice. Should the sixth electron be placed in the same 2*p* orbital that already has an electron, or should it go in one of the empty 2*p* orbitals? If it goes in an empty 2*p* orbital, will the sixth electron have its spin aligned with or be opposite to the spin of the fifth? In short, which of the following three orbital diagrams is correct for carbon, remembering that the 2*p* orbitals are degenerate?





(c) 2p ↑ ↑ _ _
2s ↑↓
1s ↑↓

Because of electron-electron repulsions, it is more favorable energetically for an electron to be in an unoccupied orbital than in one that is already occupied; hence we can eliminate choice a. Similarly, experiments have shown that choice b is slightly higher in energy (less stable) than choice c because electrons in degenerate orbitals prefer to line up with their spins parallel; thus, we can eliminate choice b. Choice c illustrates Hund's ruleA rule stating that the lowest-energy electron configuration for an atom is the one that has the maximum number of electrons with parallel spins in degenerate orbitals. (named after the German physicist Friedrich H. Hund, 1896–1997), which today says that the lowest-energy electron configuration for an atom is the one that has the maximum number of electrons with parallel spins in degenerate orbitals. By Hund's rule, the electron configuration of carbon, which is $1s^2 2s^2 2p^2$, is understood to correspond to the orbital diagram shown in c. Experimentally, it is found that the ground state of a neutral carbon atom does indeed contain two unpaired electrons.

When we get to nitrogen ($Z = 7$, with seven electrons), Hund's rule tells us that the lowest-energy arrangement is

N: 2p ↑ ↑ ↑
2s ↑↓
1s ↑↓

with three unpaired electrons. The electron configuration of nitrogen is thus $1s^2 2s^2 2p^3$.

At oxygen, with $Z = 8$ and eight electrons, we have no choice. One electron must be paired with another in one of the 2*p* orbitals, which gives us two unpaired electrons and a $1s^2 2s^2 2p^4$ electron configuration. Because all the 2*p* orbitals are degenerate, it doesn't matter which one has the pair of electrons.

O: 2p ↑↓ ↑ ↑
2s ↑↓
1s ↑↓

Similarly, fluorine has the electron configuration $1s^2 2s^2 2p^5$:

F: 2p ↑↓ ↑↓ ↑
2s ↑↓
1s ↑↓

When we reach neon, with $Z = 10$, we have filled the 2*p* subshell, giving a $1s^2 2s^2 2p^6$ electron configuration:

Ne: 2p ↑↓ ↑↓ ↑↓
2s ↑↓
1s ↑↓

Notice that for neon, as for helium, all the orbitals through the 2*p* level are completely filled. This fact is very important in dictating both the chemical reactivity and the bonding of helium and neon, as you will see.

Valence Electrons

As we continue through the periodic table in this way, writing the electron configurations of larger and larger atoms, it becomes tedious to keep copying the configurations of the filled inner subshells. In practice, chemists simplify the notation by using a bracketed noble gas symbol to represent the configuration of the noble gas from the preceding row because all the orbitals in a noble gas are filled. For example, [Ne] represents the $1s^2 2s^2 2p^6$ electron configuration of neon ($Z = 10$), so the electron configuration of sodium, with $Z = 11$, which is $1s^2 2s^2 2p^6 3s^1$, is written as $[Ne]3s^1$:

Neon	Z = 10	$1s^2 2s^2 2p^6$
Sodium	Z = 11	$1s^2 2s^2 2p^6 \mathbf{3}s^1 = [Ne]\mathbf{3}s^1$

Because electrons in filled inner orbitals are closer to the nucleus and more tightly bound to it, they are rarely involved in chemical reactions. This means that the chemistry of an atom depends mostly on the electrons in its outermost shell, which are called the

valence electronsElectrons in the outermost shell of an atom.. The simplified notation allows us to see the valence-electron configuration more easily. Using this notation to compare the electron configurations of sodium and lithium, we have:

Sodium	$1s^2 2s^2 2p^6 3s^1 = [Ne]3s^1$
Lithium	$1s^2 2s^1 = [He]2s^1$

It is readily apparent that both sodium and lithium have one *s* electron in their valence shell. We would therefore predict that sodium and lithium have very similar chemistry, which is indeed the case.

As we continue to build the eight elements of period 3, the 3*s* and 3*p* orbitals are filled, one electron at a time. This row concludes with the noble gas argon, which has the electron configuration $[Ne]3s^2 3p^6$, corresponding to a filled valence shell.

Example 2.3.2

Draw an orbital diagram and use it to derive the electron configuration of phosphorus, $Z = 15$. What is its valence electron configuration?

Given: atomic number

Asked for: orbital diagram and valence electron configuration for phosphorus

Strategy:

A Locate the nearest noble gas preceding phosphorus in the periodic table. Then subtract its number of electrons from those in phosphorus to obtain the number of valence electrons in phosphorus.

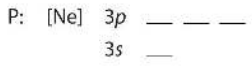
B Referring to Figure 2.2.10 , draw an orbital diagram to represent those valence orbitals. Following Hund's rule, place the valence electrons in the available orbitals, beginning with the orbital that is lowest in energy. Write the electron configuration from your orbital diagram.

C Ignore the inner orbitals (those that correspond to the electron configuration of the nearest noble gas) and write the valence electron configuration for phosphorus.

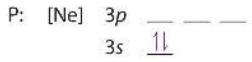
Solution:

A Because phosphorus is in the third row of the periodic table, we know that it has a [Ne] closed shell with 10 electrons. We begin by subtracting 10 electrons from the 15 in phosphorus.

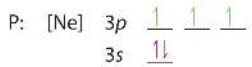
B The additional five electrons are placed in the next available orbitals, which Figure 2.2.10 tells us are the 3*s* and 3*p* orbitals:



Because the 3*s* orbital is lower in energy than the 3*p* orbitals, we fill it first:



Hund's rule tells us that the remaining three electrons will occupy the degenerate 3*p* orbitals separately but with their spins aligned:



The electron configuration is $[Ne]3s^2 3p^3$.

C We obtain the valence electron configuration by ignoring the inner orbitals, which for phosphorus means that we ignore the [Ne] closed shell. This gives a valence-electron configuration of $3s^2 3p^3$.

Exercise

Draw an orbital diagram and use it to derive the electron configuration of chlorine, $Z = 17$. What is its valence electron configuration?

Answer: [Ne]$3s^2 3p^5$; $3s^2 3p^5$

The general order in which orbitals are filled is depicted in Figure 2.3.2 . Subshells corresponding to each value of *n* are written from left to right on successive horizontal lines, where each row represents a row in the periodic table. The order in which the orbitals are filled is indicated by the diagonal lines running from the upper right to the lower left. Accordingly, the 4*s* orbital is filled prior to the 3*d* orbital because of shielding and penetration effects. Consequently, the electron configuration of potassium, which begins the fourth period, is [Ar]$4s^1$, and the configuration of calcium is [Ar]$4s^2$. Five 3*d* orbitals are filled by the next 10 elements, the transition metals, followed by three 4*p* orbitals. Notice that the last member of this row is the noble gas krypton (Z = 36), [Ar]$4s^2 3d^{10} 4p^6$ = [Kr], which has filled 4*s*, 3*d*, and 4*p* orbitals. The fifth row of the periodic table is essentially the same as the fourth, except that the 5*s*, 4*d*, and 5*p* orbitals are filled sequentially.

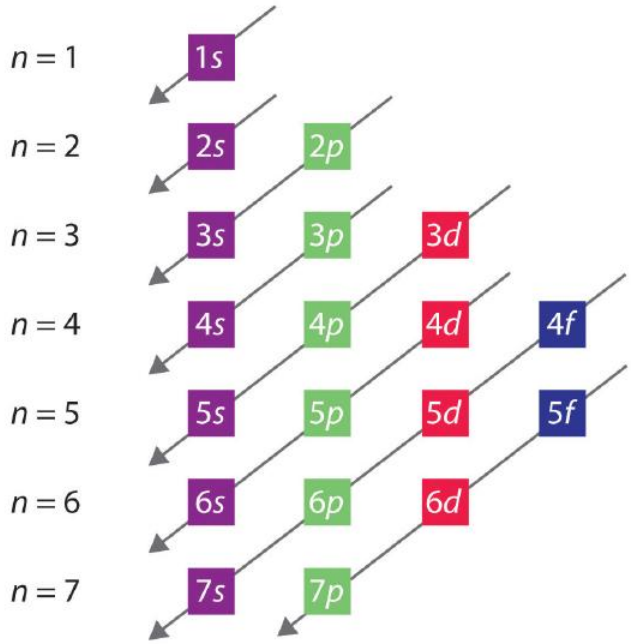


Figure 2.3.2 Predicting the Order in Which Orbitals Are Filled in Multielectron Atoms *If you write the subshells for each value of the principal quantum number on successive lines, the observed order in which they are filled is indicated by a series of diagonal lines running from the upper right to the lower left.*

The sixth row of the periodic table will be different from the preceding two because the 4*f* orbitals, which can hold 14 electrons, are filled between the 6*s* and the 5*d* orbitals. The elements that contain 4*f* orbitals in their valence shell are the lanthanides. When the 6*p* orbitals are finally filled, we have reached the next (and last known) noble gas, radon (Z = 86), [Xe]$6s^2 4f^{14} 5d^{10} 6p^6$ = [Rn]. In the last row, the 5*f* orbitals are filled between the 7*s* and the 6*d* orbitals, which gives the 14 actinide elements. Because the large number of protons makes their nuclei unstable, all the actinides are radioactive.

Example 2.3.3

Write the electron configuration of mercury (Z = 80), showing all the inner orbitals.

Given: atomic number

Asked for: complete electron configuration

Strategy:

Using the orbital diagram in Figure 2.3.2 and the periodic table as a guide, fill the orbitals until all 80 electrons have been placed.

Solution:

By placing the electrons in orbitals following the order shown in Figure 2.3.2 and using the periodic table as a guide, we obtain

$1s^2$	row 1	2 electrons
$2s^2 2p^6$	row 2	8 electrons
$3s^2 3p^6$	row 3	8 electrons
$4s^2 3d^{10} 4p^6$	row 4	18 electrons
$5s^2 4d^{10} 5p^6$	row 5	18 electrons
	row 1–5	54 electrons

After filling the first five rows, we still have 80 − 54 = 26 more electrons to accommodate. According to Figure 2.3.3 , we need to fill the 6*s* (2 electrons), 4*f* (14 electrons), and 5*d* (10 electrons) orbitals. The result is mercury's electron configuration:

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10}$ = Hg = [Xe]$6s^2 4f^{14} 5d^{10}$

with a filled 5*d* subshell, a $6s^2 4f^{14} 5d^{10}$ valence shell configuration, and a total of 80 electrons. (You should always check to be sure that the total number of electrons equals the atomic number.)

Exercise

Although element 114 is not stable enough to occur in nature, two isotopes of element 114 were created for the first time in a nuclear reactor in 1999 by a team of Russian and American scientists. Write the complete electron configuration for element 114.

Answer: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{14} 6d^{10} 7p^2$

The electron configurations of the elements are presented in Figure 2.3.5 , which lists the orbitals in the order in which they are filled. In several cases, the ground state electron configurations are different from those predicted by Figure 2.3.2 . Some of these anomalies occur as the 3*d* orbitals are filled. For example, the observed ground state electron configuration of chromium is [Ar]$4s^1 3d^5$ rather than the predicted [Ar]$4s^2 3d^4$. Similarly, the observed electron configuration of copper is [Ar]$4s^1 3d^{10}$ instead of [Ar]$s^2 3d^9$. The actual electron configuration may be rationalized in terms of an added stability associated with a half-filled (ns^1, np^3, nd^5, nf^7) or filled (ns^2, np^6, nd^{10}, nf^{14}) subshell. Given the small differences between higher energy levels, this added stability is enough to shift an electron from one orbital to another. In heavier elements, other more complex effects can also be important, leading to some of the additional anomalies indicated in Figure 2.3.5 For example, cerium has an electron configuration of [Xe]$6s^2 4f^1 5d^1$, which is impossible to rationalize in simple terms. In most cases, however, these apparent anomalies do not have important chemical consequences.

Note the Pattern

Additional stability is associated with half-filled or filled subshells.

Blocks in the Periodic Table

The electron configurations of the elements explain the otherwise peculiar shape of the periodic table. Although the table was originally organized on the basis of physical and chemical similarities between the elements within groups, these similarities are ultimately attributable to orbital energy levels and the Pauli principle, which cause the individual subshells to be filled in a particular order. As a result, the periodic table can be divided into "blocks" corresponding to the type of subshell that is being filled, as illustrated in Figure 2.3.3 . For example, the two columns on the left, known as the *s* blockThe elements in the left two columns of the periodic table in which the *ns* orbital is being filled., consist of elements in which the *ns* orbitals are being filled. The six columns on the right, elements in which the *np* orbitals are being filled, constitute the *p* blockThe elements in the six columns on the right of the periodic table in which the *np* orbitals are being filled.. In between are the 10 columns of the *d* blockThe elements in the periodic table in which the $(n-1)d$ orbitals are being filled., elements in which the $(n-1)d$ orbitals are filled. At the bottom lie the 14 columns of the *f* blockThe elements in the periodic table in which the $(n-2)f$ orbitals are being filled., elements in which the $(n-2)f$ orbitals are filled. Because two electrons can be accommodated per orbital, the number of columns in each block is the same as the maximum electron capacity of the subshell: 2 for *ns*, 6 for *np*, 10 for $(n-1)d$, and 14 for $(n-2)f$. Within each column,

each element has the same valence electron configuration—for example, ns^1 (group 1) or ns^2np^1 (group 13). As you will see, this is reflected in important similarities in the chemical reactivity and the bonding for the elements in each column.

Note the Pattern

Because each orbital can have a maximum of 2 electrons, there are 2 columns in the *s* block, 6 columns in the *p* block, 10 columns in the *d* block, and 14 columns in the *f* block.

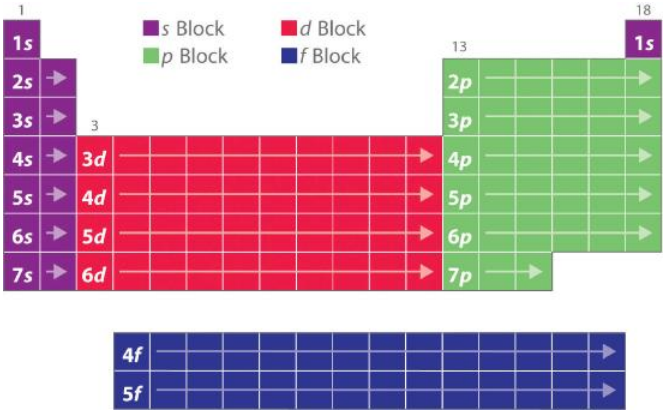


Figure 2.3.3 The Periodic Table, Showing How the Elements Are Grouped According to the Kind of Subshell (*s*, *p*, *d*, *f*) Being Filled with Electrons in the Valence Shell of Each Element

The electron configurations of the elements are in Figure 2.3.5 .

There is an alternate form, which integrates the f orbitals into the main table

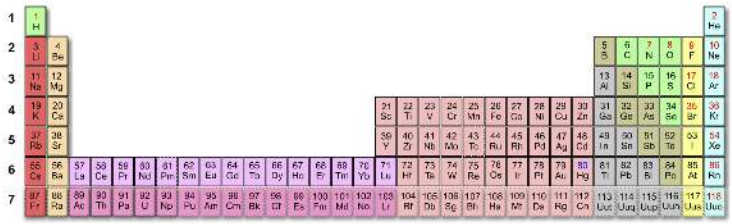


Figure 2.3.4 An Alternate Form of the Periodic Table *This wide form of the periodic table shows how the 4f/5f orbitals fit between the 6s/7s and 5d/6d orbitals*

Hydrogen and helium are placed somewhat arbitrarily. Although hydrogen is not an alkali metal, its $1s^1$ electron configuration suggests a similarity to lithium ([He]$2s^1$) and the other elements in the first column. Although helium, with a filled *ns* subshell, should be similar chemically to other elements with an ns^2 electron configuration, the closed principal shell dominates its chemistry making it unreactive like the other noble gases, justifying its placement above neon on the right. In Chapter 3, we will examine how electron configurations affect the properties and reactivity of the elements.

Atomic number	Symbol	Electron configuration	Atomic number	Symbol	Electron configuration	Atomic number	Symbol	Electron configuration
1	H	$1s^1$	37	Rb	$[Kr]5s^1$	73	Ta	$[Xe]6s^24f^{14}5d^3$
2	He	$1s^2$	38	Sr	$[Kr]5s^2$	74	W	$[Xe]6s^24f^{14}5d^4$
3	Li	$[He]2s^1$	39	Y	$[Kr]5s^24d^1$	75	Re	$[Xe]6s^24f^{14}5d^5$
4	Be	$[He]2s^2$	40	Zr	$[Kr]5s^24d^2$	76	Os	$[Xe]6s^24f^{14}5d^6$
5	B	$[He]2s^22p^1$	41	Nb	$[Kr]5s^14d^4$	77	Ir	$[Xe]6s^24f^{14}5d^7$
6	C	$[He]2s^22p^2$	42	Mo	$[Kr]5s^14d^5$	78	Pt	$[Xe]6s^14f^{14}5d^9$
7	N	$[He]2s^22p^3$	43	Tc	$[Kr]5s^24d^5$	79	Au	$[Xe]6s^14f^{14}5d^{10}$
8	O	$[He]2s^22p^4$	44	Ru	$[Kr]5s^14d^7$	80	Hg	$[Xe]6s^24f^{14}5d^{10}$
9	F	$[He]2s^22p^5$	45	Rh	$[Kr]5s^14d^8$	81	Tl	$[Xe]6s^24f^{14}5d^{10}6p^1$
10	Ne	$[He]2s^22p^6$	46	Pd	$[Kr]4d^{10}$	82	Pb	$[Xe]6s^24f^{14}5d^{10}6p^2$
11	Na	$[Ne]3s^1$	47	Ag	$[Kr]5s^14d^{10}$	83	Bi	$[Xe]6s^24f^{14}5d^{10}6p^3$
12	Mg	$[Ne]3s^2$	48	Cd	$[Kr]5s^24d^{10}$	84	Po	$[Xe]6s^24f^{14}5d^{10}6p^4$
13	Al	$[Ne]3s^23p^1$	49	In	$[Kr]5s^14d^{10}5p^1$	85	At	$[Xe]6s^24f^{14}5d^{10}6p^5$
14	Si	$[Ne]3s^23p^2$	50	Sn	$[Kr]5s^14d^{10}5p^2$	86	Rn	$[Xe]6s^24f^{14}5d^{10}6p^6$
15	P	$[Ne]3s^23p^3$	51	Sb	$[Kr]5s^14d^{10}5p^3$	87	Fr	$[Rn]7s^1$
16	S	$[Ne]3s^23p^4$	52	Te	$[Kr]5s^14d^{10}5p^4$	88	Ra	$[Rn]7s^2$
17	Cl	$[Ne]3s^23p^5$	53	I	$[Kr]5s^14d^{10}5p^5$	89	Ac	$[Rn]7s^26d^1$
18	Ar	$[Ne]3s^23p^6$	54	Xe	$[Kr]5s^14d^{10}5p^6$	90	Th	$[Rn]7s^26d^2$
19	K	$[Ar]4s^1$	55	Cs	$[Xe]6s^1$	91	Pa	$[Rn]7s^25f^26d^1$
20	Ca	$[Ar]4s^2$	56	Ba	$[Xe]6s^2$	92	U	$[Rn]7s^25f^36d^1$
21	Sc	$[Ar]4s^23d^1$	57	La	$[Xe]6s^25d^1$	93	Np	$[Rn]7s^25f^46d^1$
22	Ti	$[Ar]4s^23d^2$	58	Ce	$[Xe]6s^24f^15d^1$	94	Pu	$[Rn]7s^25f^6$
23	V	$[Ar]4s^23d^3$	59	Pr	$[Xe]6s^24f^3$	95	Am	$[Rn]7s^25f^7$
24	Cr	$[Ar]4s^13d^5$	60	Nd	$[Xe]6s^24f^4$	96	Cm	$[Rn]7s^25f^76d^1$
25	Mn	$[Ar]4s^23d^5$	61	Pm	$[Xe]6s^24f^5$	97	Bk	$[Rn]7s^25f^9$
26	Fe	$[Ar]4s^23d^6$	62	Sm	$[Xe]6s^24f^6$	98	Cf	$[Rn]7s^25f^{10}$
27	Co	$[Ar]4s^23d^7$	63	Eu	$[Xe]6s^24f^7$	99	Es	$[Rn]7s^25f^{11}$
28	Ni	$[Ar]4s^23d^8$	64	Gd	$[Xe]6s^24f^75d^1$	100	Fm	$[Rn]7s^25f^{12}$
29	Cu	$[Ar]4s^13d^{10}$	65	Tb	$[Xe]6s^24f^9$	101	Md	$[Rn]7s^25f^{13}$
30	Zn	$[Ar]4s^23d^{10}$	66	Dy	$[Xe]6s^24f^{10}$	102	No	$[Rn]7s^25f^{14}$
31	Ga	$[Ar]4s^23d^{10}4p^1$	67	Ho	$[Xe]6s^24f^{11}$	103	Lr	$[Rn]7s^25f^{14}6d^1$
32	Ge	$[Ar]4s^23d^{10}4p^2$	68	Er	$[Xe]6s^24f^{12}$	104	Rf	$[Rn]7s^25f^{14}6d^2$
33	As	$[Ar]4s^23d^{10}4p^3$	69	Tm	$[Xe]6s^24f^{13}$	105	Db	$[Rn]7s^25f^{14}6d^3$
34	Se	$[Ar]4s^23d^{10}4p^4$	70	Yb	$[Xe]6s^24f^{14}$	106	Sg	$[Rn]7s^25f^{14}6d^4$
35	Br	$[Ar]4s^23d^{10}4p^5$	71	Lu	$[Xe]6s^24f^{14}5d^1$	107	Bh	$[Rn]7s^25f^{14}6d^5$
36	Kr	$[Ar]4s^23d^{10}4p^6$	72	Hf	$[Xe]6s^24f^{14}5d^2$	108	Hs	$[Rn]7s^25f^{14}6d^6$
						109	Mt	$[Rn]7s^25f^{14}6d^7$
						110	Ds	$[Rn]7s^15f^{14}6d^9$
						111	Rg	$[Rn]7s^15f^{14}6d^{10}$

Figure 2.3.5 Electron Configurations of the Elements

The electron configurations of elements indicated in red are exceptions due to the added stability associated with half-filled and filled subshells. The electron configurations of the elements indicated in blue are also anomalous, but the reasons for the observed configurations are more complex. For elements after No, the electron configurations are tentative.

Example 2.3.4

Use the periodic table to predict the valence electron configuration of all the elements of group 2 (beryllium, magnesium, calcium, strontium, barium, and radium).

Given: series of elements

Asked for: valence electron configurations

Strategy:

A Identify the block in the periodic table to which the group 2 elements belong. Locate the nearest noble gas preceding each element and identify the principal quantum number of the valence shell of each element.

B Write the valence electron configuration of each element by first indicating the filled inner shells using the symbol for the nearest preceding noble gas and then listing the principal quantum number of its valence shell, its valence orbitals, and the number of

valence electrons in each orbital as superscripts.

Solution:

A The group 2 elements are in the *s* block of the periodic table, and as group 2 elements, they all have two valence electrons. Beginning with beryllium, we see that its nearest preceding noble gas is helium and that the principal quantum number of its valence shell is $n = 2$.

B Thus beryllium has an [He]s^2 electron configuration. The next element down, magnesium, is expected to have exactly the same arrangement of electrons in the $n = 3$ principal shell: [Ne]s^2. By extrapolation, we expect all the group 2 elements to have an ns^2 electron configuration.

Exercise

Use the periodic table to predict the characteristic valence electron configuration of the halogens in group 17.

Answer: All have an ns^2np^5 electron configuration, one electron short of a noble gas electron configuration. (Note that the heavier halogens also have filled $(n - 1)d^{10}$ subshells, as well as an $(n - 2)f^{14}$ subshell for Rn; these do not, however, affect their chemistry in any significant way.

Summary

In addition to the three quantum numbers (n, l, m_l) dictated by quantum mechanics, a fourth quantum number is required to explain certain properties of atoms. This is the **electron spin** quantum number (m_s), which can have values of +½ or −½ for any electron, corresponding to the two possible orientations of an electron in a magnetic field. The concept of electron spin has important consequences for chemistry because the **Pauli exclusion principle** implies that no orbital can contain more than two electrons (with opposite spin). Based on the Pauli principle and a knowledge of orbital energies obtained using hydrogen-like orbitals, it is possible to construct the periodic table by filling up the available orbitals beginning with the lowest-energy orbitals (the **aufbau principle**), which gives rise to a particular arrangement of electrons for each element (its **electron configuration**). **Hund's rule** says that the lowest-energy arrangement of electrons is the one that places them in degenerate orbitals with their spins parallel. For chemical purposes, the most important electrons are those in the outermost principal shell, the **valence electrons**. The arrangement of atoms in the periodic table results in blocks corresponding to filling of the *ns*, *np*, *nd*, and *nf* orbitals to produce the distinctive chemical properties of the elements in the *s* **block**, *p* **block**, *d* **block**, and *f* **block**, respectively.

Key Takeaway

- The arrangement of atoms in the periodic table arises from the lowest energy arrangement of electrons in the valence shell.

Conceptual Problems

1. A set of four quantum numbers specifies each wave function. What information is given by each quantum number? What does the specified wave function describe?
2. List two pieces of evidence to support the statement that electrons have a spin.
3. The periodic table is divided into blocks. Identify each block and explain the principle behind the divisions. Which quantum number distinguishes the horizontal rows?
4. Identify the element with each ground state electron configuration.
    1. [He]$2s^2 2p^3$
    2. [Ar]$4s^2 3d^1$
    3. [Kr]$5s^2 4d^{10} 5p^3$
    4. [Xe]$6s^2 4f^6$
5. Identify the element with each ground state electron configuration.
    1. [He]$2s^2 2p^1$
    2. [Ar]$4s^2 3d^8$
    3. [Kr]$5s^2 4d^{10} 5p^4$
    4. [Xe]$6s^2$

6. Propose an explanation as to why the noble gases are inert.

Numerical Problems

1. How many magnetic quantum numbers are possible for a 4*p* subshell? A 3*d* subshell? How many orbitals are in these subshells?
2. How many magnetic quantum numbers are possible for a 6*s* subshell? A 4*f* subshell? How many orbitals does each subshell contain?
3. If $l = 2$ and $m_l = 2$, give all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for electrons in the corresponding 3*d* subshell.
4. Give all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for electrons in a 4*d* subshell. How many electrons can the 4*d* orbital accommodate? How would this differ from a situation in which there were only three quantum numbers (n, l, m)?
5. Given the following sets of quantum numbers (n, l, m_l, m_s), identify each principal shell and subshell.
    1. 1, 0, 0, ½
    2. 2, 1, 0, ½
    3. 3, 2, 0, ½
    4. 4, 3, 3, ½
6. Is each set of quantum numbers allowed? Explain your answers.
    1. $n = 2$; $l = 1$; $m_l = 2$; $m_s = +½$
    2. $n = 3$, $l = 0$; $m_l = −1$; $m_s = −½$
    3. $n = 2$; $l = 2$; $m_l = 1$; $m_s = +½$
    4. $n = 3$; $l = 2$; $m_l = 2$; $m_s = +½$
7. List the set of quantum numbers for each electron in the valence shell of each element.
    1. beryllium
    2. xenon
    3. lithium
    4. fluorine
8. List the set of quantum numbers for each electron in the valence shell of each element.
    1. carbon
    2. magnesium
    3. bromine
    4. sulfur
9. Sketch the shape of the periodic table if there were three possible values of m_s for each electron (+½, −½, and 0); assume that the Pauli principle is still valid.
10. Predict the shape of the periodic table if eight electrons could occupy the *p* subshell.
11. If the electron could only have spin +½, what would the periodic table look like?
12. If three electrons could occupy each *s* orbital, what would be the electron configuration of each species?
    1. sodium
    2. titanium
    3. fluorine
    4. calcium
13. If Hund's rule were not followed and maximum pairing occurred, how many unpaired electrons would each species have? How do these numbers compare with the number found using Hund's rule?
    1. phosphorus

2. iodine
3. manganese

14. Write the electron configuration for each element in the ground state.

    1. aluminum
    2. calcium
    3. sulfur
    4. tin
    5. nickel
    6. tungsten
    7. neodymium
    8. americium

15. Write the electron configuration for each element in the ground state.

    1. boron
    2. rubidium
    3. bromine
    4. germanium
    5. vanadium
    6. palladium
    7. bismuth
    8. europium

16. Give the complete electron configuration for each element.

    1. magnesium
    2. potassium
    3. titanium
    4. selenium
    5. iodine
    6. uranium
    7. germanium

17. Give the complete electron configuration for each element.

    1. tin
    2. copper
    3. fluorine
    4. hydrogen
    5. thorium
    6. yttrium
    7. bismuth

18. Write the valence electron configuration for each element:

    1. samarium
    2. praseodymium
    3. boron
    4. cobalt

19. Using the Pauli exclusion principle and Hund’s rule, draw valence orbital diagrams for each element.

    1. barium
    2. neodymium
    3. iodine

20. Using the Pauli exclusion principle and Hund's rule, draw valence orbital diagrams for each element.
    1. chlorine
    2. silicon
    3. scandium
21. How many unpaired electrons does each species contain?
    1. lead
    2. cesium
    3. copper
    4. silicon
    5. selenium
22. How many unpaired electrons does each species contain?
    1. helium
    2. oxygen
    3. bismuth
    4. silver
    5. boron
23. For each element, give the complete electron configuration, draw the valence electron configuration, and give the number of unpaired electrons present.
    1. lithium
    2. magnesium
    3. silicon
    4. cesium
    5. lead
24. Use an orbital diagram to illustrate the aufbau principle, the Pauli exclusion principle, and Hund's rule for each element.
    1. carbon
    2. sulfur

Answers

1. For a 4*p* subshell, $n = 4$ and $l = 1$. The allowed values of the magnetic quantum number, *ml*, are therefore +1, 0, −1, corresponding to three 4*p* orbitals. For a 3*d* subshell, $n = 3$ and $l = 2$. The allowed values of the magnetic quantum number, *ml*, are therefore +2, +1, 0, −1, −2, corresponding to five 3*d* orbitals.
2.
3. $n = 3$, $l = 2$, $ml = 2$, $m_s = 1/2$; $n = 3$, $l = 2$, $m_l = 2$, $m_s = -1/2$
4.
5.
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Contributors

- Anonymous

Modified by Joshua Halpern, Scott Sinex and Scott Johnson

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Chapter 2.4: Electronic Structure of the Transition Metals

Learning Objective

- To write the electron configuration of the transition metals and understand the basis for the exceptions to the normal order of filling.

Now you can use the information you learned in Section 2.3 to determine the electronic structure of every element in the periodic table. The process of describing each atom's electronic structure consists, essentially, of beginning with hydrogen and adding one proton and one electron at a time to create the next heavier element in the table. Well almost, but the exceptions are instructional.

Adding a proton and an electron to form the next atom results in small changes in the energy levels relative to each other but the order remains the same, at least until we get to the *d* levels, where in some atoms the relative energies of the *ns* and the *(n-1)d* orbitals shifts. In the fourth period, this happens for Cr and Cu, which, instead of having two electrons in the *4s* orbital have only one. The first three elements in the d block of the fourth period sequentially have one more d electron than the last. In agreement with Hund's rules each of these is added to a different d orbital with parallel spins.

For Cr, something different happens, of the six electrons, five are found in the *4d* level and only one in the *4s*. Electron repulsion and favoring parallel spins moves the *3d* level below the *4s* when there are 6 electrons. The normal pattern resumes with Mn (manganese).

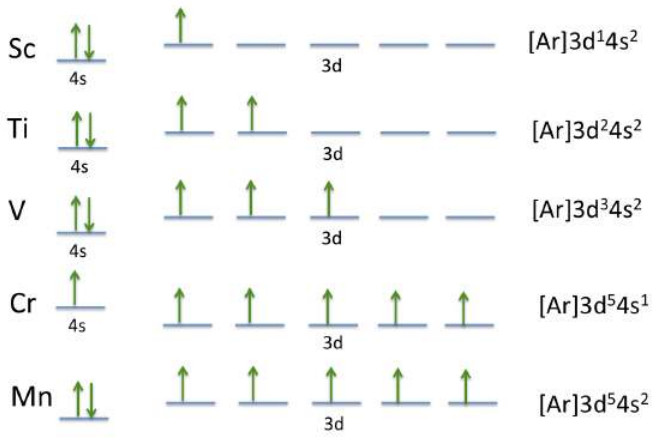


Figure 2.4.1 The electronic configurations of the first five fourth period transition metals *Notice how the relative positions of the 4s and 3d orbitals move relative to each other as more electrons are added.*

If we continue on to Zn, the "exception" repeats itself with Cu, where there are now 10 electrons in the *3d* level and only one in the *4s*.

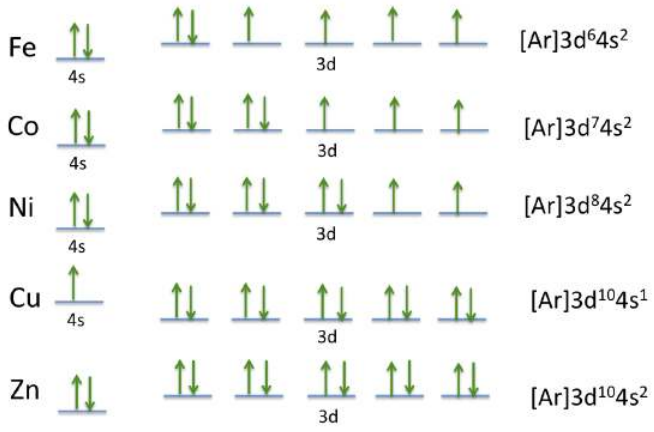


Figure 2.4.2 The electronic configurations of the last five fourth period transition metals

We can look at the electron configurations of the rest of the *d* block elements.

21 Sc $[Ar]3d^1 4s^2$	22 Ti $[Ar]3d^2 4s^2$	23 V $[Ar]3d^3 4s^2$	24 Cr $[Ar]\ 3d^5 4s^1$	25 Mn $[Ar]3d^5 4s^2$	26 Fe $[Ar]3d^6 4s^2$	27 Co $[Ar]3d^7 4s^2$	28 Ni $[Ar]3d^8 4s^2$	29 Cu $[Ar]3d^{10} 4s^1$	30 Zn $[Ar]3d^{10} 4s^2$
39 Y $[Kr]4d^1 5s^2$	40 Zr $[Kr]4d^2 5s^2$	41 Nb $[Kr]4d^3 5s^2$	42 Mo $[Kr]4d^5 5s^1$	43 Tc $[Kr]4d^5 5s^2$	44 Ru $[Kr]4d^7 5s^1$	45 Rh $[Kr]4d^8 5s^1$	46 Pd $[Kr]4d^{10}$	47 Ag $[Kr]4d^{10} 5s^1$	48 Cd $[Kr]4d^{10} 5s^2$
57 La $[Xe]6s^2 5d^1$	72 Hf $[Xe]5d^2 6s^2$	73 Ta $[Xe]5d^3 6s^2$	74 W $[Xe]5d^6 6s^2$	75 Re $[Xe]5d^6 6s^2$	76 Os $[Xe]5d^6 6s^2$	77 Ir $[Xe]5d^7 6s^2$	78 Pt $[Xe]5d^9 6s^1$	79 Au $[Xe]5d^{10} 6s^1$	80 Hg $[Xe]5d^{10} 6s^2$

Figure 2.4.3 The electronic configurations of the transition metals. Only the ns and (n-1)d electrons have been shown to save space. The 14 electrons in the atoms from Hf to Hg have not been written in. *The electron configuration of Mo (molybdenum) is similar to that of Cr, and both are shown in green. Those metals shown in blue, with the exception of Pd, paladium, have only one ns electron. Pd has none. Cu, Ag, Au and Pd have ten electrons in the (n-1)d orbitals. These metals are all very soft, fairly unreactive, rare, and with the exception of Cu used in jewelry.*

The transition metals, as a general rule, have similar properties. The reason for this is that the extent of the orbitals from the nucleus depends on the principal quantum numbers. Thus, the orbitals of the *ns* electrons extend further out than those of the *(n-1) d* electrons in the same periods, and therefore are more available for bonding and reactions. As other atoms and molecules approach the metal atoms, the *ns* electrons are the ones that are first affected.

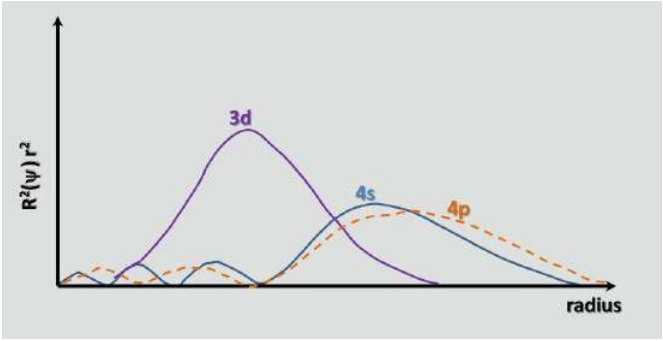


Figure 2.4.4 The Probability Density of the 4s, 4p and 3d Electrons as a Function of Radial Distance from the Nucleus *The ns orbitals of the transition metals extend further from the nucleus than those of the (n-1)d orbitals, making them more available*

for bonding and reactions. This is illustrated here for the fourth period. Similarly the f orbitals of the rare earths and the lanthanides are packed in closer to the nucleus than those of the s and p orbitals in the same periods.

Contributors

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Chapter 2.5: Atomic Spectra and Models of the Atom

Learning Objective

- To know the relationship between atomic spectra and the electronic structure of atoms.

The photoelectric effect provided indisputable evidence for the existence of the photon and thus the particle-like behavior of electromagnetic radiation. The concept of the photon, however, emerged from experimentation with *thermal radiation*, electromagnetic radiation emitted as the result of a source's temperature, which produces a continuous spectrum of energies. More direct evidence was needed to verify the quantized nature of electromagnetic radiation. In this section, we describe how experimentation with visible light provided this evidence.

Line Spectra

Although objects at high temperature emit a continuous spectrum of electromagnetic radiation , a different kind of spectrum is observed when pure samples of individual elements are heated. For example, when a high-voltage electrical discharge is passed through a sample of hydrogen gas at low pressure, the resulting individual isolated hydrogen atoms caused by the dissociation of H_2 emit a red light. Unlike blackbody radiation, the color of the light emitted by the hydrogen atoms does not depend greatly on the temperature of the gas in the tube. When the emitted light is passed through a prism, only a few narrow lines, called a line spectrum. A spectrum in which light of only a certain wavelength is emitted or absorbed, rather than a continuous range of wavelengths., are seen (Figure 2.5.1), rather than a continuous range of colors. The light emitted by hydrogen atoms is red because, of its four characteristic lines, the most intense line in its spectrum is in the red portion of the visible spectrum, at 656 nm. With sodium, however, we observe a yellow color because the most intense lines in its spectrum are in the yellow portion of the spectrum, at about 589 nm.

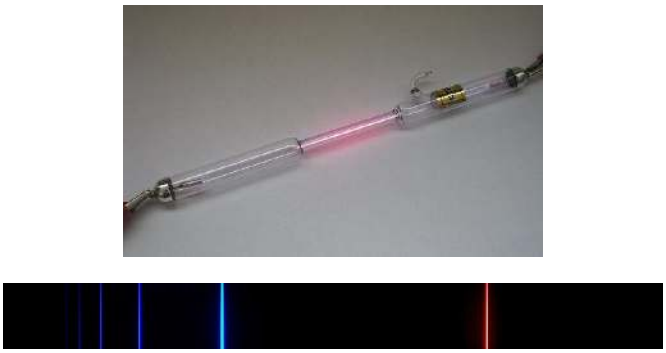


Figure 2.5.1 The Emission of Light by Hydrogen Atoms *(a) A sample of excited hydrogen atoms emits a characteristic red light. (b) When the light emitted by a sample of excited hydrogen atoms is split into its component wavelengths by a prism, four characteristic violet, blue, green, and red emission lines can be observed, the most intense of which is at 656 nm.*

Such *emission spectra* were observed for many other elements in the late 19th century, which presented a major challenge because classical physics was unable to explain them. Part of the explanation is provided by Planck: the observation of only a few values of λ (or ν) in the line spectrum meant that only a few values of *E* were possible. Thus *the energy levels of a hydrogen atom had to be quantized*; in other words, only states that had certain values of energy were possible, or *allowed*. If a hydrogen atom could have *any* value of energy, then a continuous spectrum would have been observed, similar to blackbody radiation.

In 1885, a Swiss mathematics teacher, Johann Balmer (1825–1898), showed that the frequencies of the lines observed in the visible region of the spectrum of hydrogen fit a simple equation that can be expressed as follows:

$$\nu = constant \left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

where n = 3, 4, 5, 6. As a result, these lines are known as the *Balmer series*. The Swedish physicist Johannes Rydberg (1854–1919) subsequently restated and expanded Balmer's result in the *Rydberg equation*:

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

where n_1 and n_2 are positive integers, $n_2 > n_1$, and $\mathfrak{R}$ the *Rydberg constant*, has a value of $1.09737 \times 10^7\ m^{-1}$.

Johann Balmer (1825–1898)

A mathematics teacher at a secondary school for girls in Switzerland, Balmer was 60 years old when he wrote the paper on the spectral lines of hydrogen that made him famous. He published only one other paper on the topic, which appeared when he was 72 years old.

Like Balmer's equation, Rydberg's simple equation described the wavelengths of the visible lines in the emission spectrum of hydrogen (with $n_1 = 2$, $n_2 = 3, 4, 5,\ldots$). More important, Rydberg's equation also described the wavelengths of other series of lines that would be observed in the emission spectrum of hydrogen: one in the ultraviolet ($n_1 = 1$, $n_2 = 2, 3, 4,\ldots$) and one in the infrared ($n_1 = 3$, $n_2 = 4, 5, 6$). Unfortunately, scientists had not yet developed any theoretical justification for an equation of this form.

Videos

- Demonstration of the Balmer series spectrum - Mike Jones
- Bohr's Model Problems - Chemistry Solution
- Bohr Model of H - Jchorton

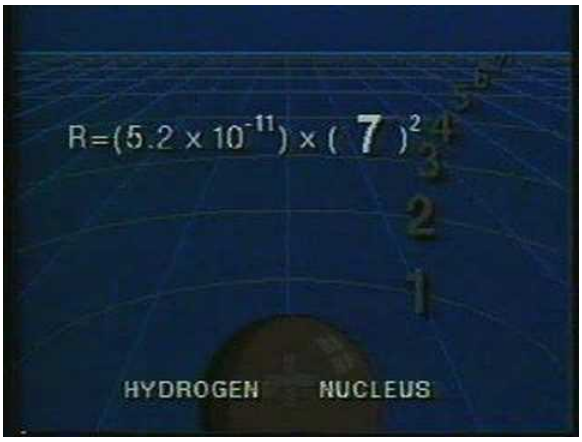
Examples

- Quantum Chemistry - Ohio State
- Bohr Atom Energy Levels and Bohr Atom Energy Change - About Education
- Bohr Model Quiz - Thurston High School

The Bohr Model

In 1913, a Danish physicist, Niels Bohr (1885–1962; Nobel Prize in Physics, 1922), proposed a theoretical model for the hydrogen atom that explained its emission spectrum. Bohr's model required an assumption: *The electron moves around the nucleus in circular orbits that can have only certain allowed radii.* Bohr developed his model in Rutherford's lab where the nuclear model of the atom had been discovered not long previously. Although we now know that the assumption of circular orbits was incorrect, Bohr's insight was to propose that *the electron could occupy only certain regions of space*.





Niels Bohr (1885–1962)

During the Nazi occupation of Denmark in World War II, Bohr escaped to the United States, where he became associated with the Atomic Energy Project. In his final years, he devoted himself to the peaceful application of atomic physics and to resolving political problems arising from the development of atomic weapons.

Using classical physics, Bohr showed that the energy of an electron in a particular orbit is given by

$$E_n = \frac{-\mathfrak{R}hc}{n^2} \tag{2.5.3}$$

where $\mathfrak{R}$ is the Rydberg constant, h is Planck's constant, c is the speed of light, and n is a positive integer corresponding to the number assigned to the orbit, with $n = 1$ corresponding to the orbit closest to the nucleus. In this model $n = \infty$ corresponds to the level where the energy holding the electron and the nucleus together is zero. In that level, the electron is unbound from the nucleus and the atom has been separated into a negatively charged (the electron) and a positively charged (the nucleus) ion. In this state the radius of the orbit is also infinite. The atom has been ionized.

As n decreases, the energy holding the electron and the nucleus together becomes increasingly negative, the radius of the orbit shrinks and more energy is needed to ionize the atom. The orbit with $n = 1$ is the lowest lying and most tightly bound. The negative sign in Equation 2.5.3 indicates that the electron-nucleus pair is more tightly bound when they are near each other than when they are far apart. Because a hydrogen atom with its one electron in this orbit has the lowest possible energy, this is the ground state. The most stable arrangement of electrons for an element or a compound., the most stable arrangement for a hydrogen atom. As n increases, the radius of the orbit increases; the electron is farther from the proton, which results in a less stable arrangement with higher potential energy. A hydrogen atom with an electron in an orbit with $n > 1$ is therefore in an excited state. Any arrangement of electrons that is higher in energy than the ground state.: its energy is higher than the energy of the ground state. When an atom in an excited state undergoes a transition to the ground state in a process called *decay*, it loses energy by emitting a photon whose energy corresponds to the difference in energy between the two states (Figure 2.5.3).

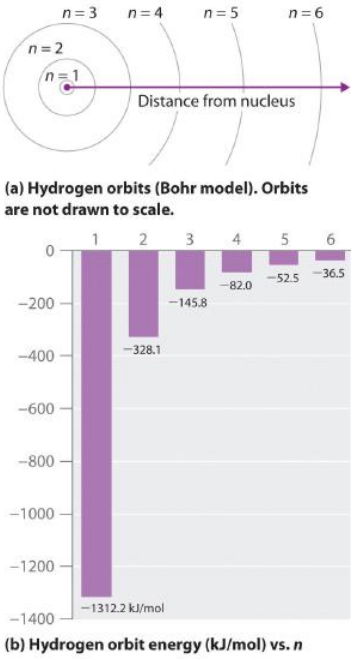


Figure 2.5.2 The Bohr Model of the Hydrogen Atom *(a) The distance of the orbit from the nucleus increases with increasing n. (b) The energy of the orbit becomes increasingly less negative with increasing n.*

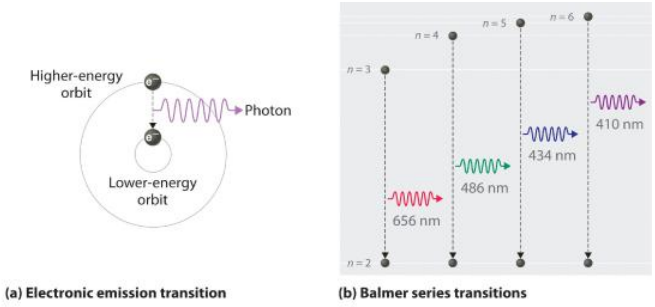


Figure 2.5.3 The Emission of Light by a Hydrogen Atom in an Excited State *(a) Light is emitted when the electron undergoes a transition from an orbit with a higher value of n (at a higher energy) to an orbit with a lower value of n (at lower energy). (b) The Balmer series of emission lines is due to transitions from orbits with n ≥ 3 to the orbit with n = 2. The differences in energy between these levels corresponds to light in the visible portion of the electromagnetic spectrum.*

So the difference in energy (ΔE) between any two orbits or energy levels is given by $\boldsymbol{\Delta E = E_{n_1} - E_{n_2}}$ where n_1 is the final orbit and n_2 the initial orbit. Substituting from Bohr's equation (Equation 2.5.3) for each energy value gives

$$\Delta E = E_{final} - E_{initial} = -\frac{\Re hc}{n_2^2} - \left(\frac{\Re hc}{n_1^2}\right) = -\Re hc\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{2.5.4}$$

If $n_2 > n_1$, the transition is from a higher energy state (larger-radius orbit) to a lower energy state (smaller-radius orbit), as shown by the dashed arrow in part (a) in Figure 2.5.3 . Substituting hc/λ for ΔE gives

\(\Delta E = \dfrac{hc}{\lambda }=-\Re hc\left (\dfrac{1}{n_{2}^{2}} - \dfrac{1}{n_{1}^{2}}\right) \tag{2.5.5} \)

Canceling *hc* on both sides gives

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

Except for the negative sign, this is the same equation that Rydberg obtained experimentally. The negative sign in Equation 2.5.5 and Equation 2.5.6 indicates that energy is released as the electron moves from orbit n_2 to orbit n_1 because orbit n_2 is at a higher

energy than orbit n_1. Bohr calculated the value of <math xml:id="av_1.0-ch02_m019" display="inline"><semantics><mi>ℜ</mi></semantics></math> from fundamental constants such as the charge and mass of the electron and Planck's constate and obtained a value of $1.0974 \times 10^7\ m^{-1}$, the same number Rydberg had obtained by analyzing the emission spectra.

We can now understand the physical basis for the Balmer series of lines in the emission spectrum of hydrogen (Figure 2.5.1). As shown in Figure 2.5.4, the lines in this series correspond to transitions from higher-energy orbits ($n > 2$) to the *second* orbit ($n = 2$). Thus the hydrogen atoms in the sample have absorbed energy from the electrical discharge and decayed from a higher-energy excited state ($n > 2$) to a lower-energy state ($n = 2$) by emitting a photon of electromagnetic radiation whose energy corresponds exactly to the *difference* in energy between the two states (Figure 2.5.4). The $n = 3$ to $n = 2$ transition gives rise to the line at 656 nm (red), the $n = 4$ to $n = 2$ transition to the line at 486 nm (green), the $n = 5$ to $n = 2$ transition to the line at 434 nm (blue), and the $n = 6$ to $n = 2$ transition to the line at 410 nm (violet). Because a sample of hydrogen contains a large number of atoms, the intensity of the various lines in a line spectrum depends on the number of atoms in each excited state. At the temperature in the gas discharge tube, more atoms are in the $n = 3$ than the $n \geq 4$ levels. Consequently, the $n = 3$ to $n = 2$ transition is the most intense line, producing the characteristic red color of a hydrogen discharge (part (a) in Figure 2.5.1). Other families of lines are produced by transitions from excited states with $n > 1$ to the orbit with $n = 1$ or to orbits with $n \geq 3$. These transitions are shown schematically in Figure 2.5.4

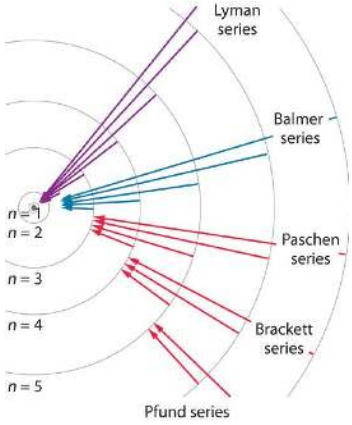


Figure 2.5.4 Electron Transitions Responsible for the Various Series of Lines Observed in the Emission Spectrum of Hydrogen *The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit (n = 1); these transitions release a great deal of energy, corresponding to radiation in the ultraviolet portion of the electromagnetic spectrum. The Paschen, Brackett, and Pfund series of lines are due to transitions from higher-energy orbits to orbits with n = 3, 4, and 5, respectively; these transitions release substantially less energy, corresponding to infrared radiation. (Orbits are not drawn to scale.)*

In contemporary applications, electron transitions are used in timekeeping that needs to be exact. Telecommunications systems, such as cell phones, depend on timing signals that are accurate to within a millionth of a second per day, as are the devices that control the US power grid. Global positioning system (GPS) signals must be accurate to within a billionth of a second per day, which is equivalent to gaining or losing no more than one second in 1,400,000 years. Quantifying time requires finding an event with an interval that repeats on a regular basis. To achieve the accuracy required for modern purposes, physicists have turned to the atom. The current standard used to calibrate clocks is the cesium atom. Supercooled cesium atoms are placed in a vacuum chamber and bombarded with microwaves whose frequencies are carefully controlled. When the frequency is exactly right, the atoms absorb enough energy to undergo an electronic transition to a higher-energy state. Decay to a lower-energy state emits radiation. The microwave frequency is continually adjusted, serving as the clock's pendulum. In 1967, the second was defined as the duration of 9,192,631,770 oscillations of the resonant frequency of a cesium atom, called the *cesium clock*. Research is currently under way to develop the next generation of atomic clocks that promise to be even more accurate. Such devices would allow scientists to monitor vanishingly faint electromagnetic signals produced by nerve pathways in the brain and geologists to measure variations in gravitational fields, which cause fluctuations in time, that would aid in the discovery of oil or minerals.

Example 2.5.1

The so-called Lyman series of lines in the emission spectrum of hydrogen corresponds to transitions from various excited states to the n = 1 orbit. Calculate the wavelength of the lowest-energy line in the Lyman series to three significant figures. In what region of the electromagnetic spectrum does it occur?

Given: lowest-energy orbit in the Lyman series

Asked for: wavelength of the lowest-energy Lyman line and corresponding region of the spectrum

Strategy:

A Substitute the appropriate values into Equation 2.5.2 (the Rydberg equation) and solve for λ.

B Use Figure 2.5.1 to locate the region of the electromagnetic spectrum corresponding to the calculated wavelength.

Solution:

We can use the Rydberg equation to calculate the wavelength:

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

A For the Lyman series, n_1 = 1. The lowest-energy line is due to a transition from the n = 2 to n = 1 orbit because they are the closest in energy.

$$\frac{1}{\lambda} = -\Re\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) = 1.097 \times m^{-1}\left(\frac{1}{1} - \frac{1}{4}\right) = 8.228 \times 10^6\ m^{-1}$$

It turns out that spectroscopists (the people who study spectroscopy) use cm^{-1} rather than m^{-1} as a common unit. Wavelength is inversely proportional to energy but frequency is directly proportional as shown by Planck's formula, E=hν. Spectroscopists often talk about energy and frequency as equivalent. The cm^{-1} unit is particularly convenient. The infrared range is roughy 200 - 5,000 cm^{-1}, the visible from 11,000 to 25.000 cm^{-1} and the UV between 25,000 and 100,000 cm^{-1}. The units of cm^{-1} are called wavenumbers, although people often verbalize it as inverse centimeters. We can convert the answer in part A to cm^{-1}.

$$\varpi = \tfrac{1}{\lambda} = 8.228 \times 10^6\ \cancel{m^{-1}}\left(\tfrac{m}{100\ cm}\right) = 82,280\ cm^{-1}$$

and

$\lambda = 1.215 \times 10^{-7}$ m = 122 nm

This emission line is called Lyman alpha. It is the strongest atomic emission line from the sun and drives the chemistry of the upper atmosphere of all the planets producing ions by stripping electrons from atoms and molecules. It is completely absorbed by oxygen in the upper stratosphere, dissociating O_2 molecules to O atoms which react with other O_2 molecules to form stratospheric ozone

B This wavelength is in the ultraviolet region of the spectrum.

Exercise

The Pfund series of lines in the emission spectrum of hydrogen corresponds to transitions from higher excited states to the n = 5 orbit. Calculate the wavelength of the *second* line in the Pfund series to three significant figures. In which region of the spectrum does it lie?

Answer: 4.65×10^3 nm; infrared

Bohr's model of the hydrogen atom gave an exact explanation for its observed emission spectrum. The following are his key contributions to our understanding of atomic structure:

- Electrons can occupy only certain regions of space, called *orbits*.
- Orbits closer to the nucleus are lower in energy.
- Electrons can move from one orbit to another by absorbing or emitting energy, giving rise to characteristic spectra.

Unfortunately, Bohr could not explain *why* the electron should be restricted to particular orbits. Also, despite a great deal of tinkering, such as assuming that orbits could be ellipses rather than circles, his model could not quantitatively explain the emission spectra of any element other than hydrogen (Figure 2.5.5). In fact, Bohr's model worked only for species that contained just one

electron: H, He^{+}, Li^{2+}, and so forth. Scientists needed a fundamental change in their way of thinking about the electronic structure of atoms to advance beyond the Bohr model.

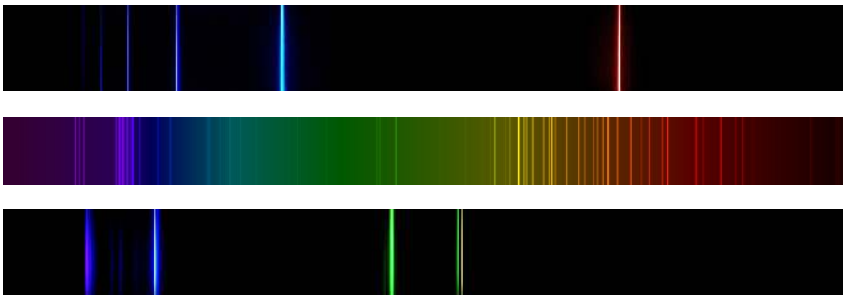


Figure 2.5.5 The Emission Spectra of Elements Compared with Hydrogen *These images show (a) hydrogen gas, which is atomized to hydrogen atoms in the discharge tube; (b) neon; and (c) mercury. The strongest lines in the hydrogen spectrum are in the far UV Lyman series starting at 124 nm and below. The strongest lines in the mercury spectrum are at 181 and 254 nm, also in the UV. These are not shown.*

Thus far we have explicitly considered only the emission of light by atoms in excited states, which produces an emission spectrumA spectrum produced by the emission of light by atoms in excited states.. The converse, absorption of light by ground-state atoms to produce an excited state, can also occur, producing an absorption spectrumA spectrum produced by the absorption of light by ground-state atoms.. Because each element has characteristic emission and absorption spectra, scientists can use such spectra to analyze the composition of matter

Note the Pattern

When an atom emits light, it decays to a lower energy state; when an atom absorbs light, it is excited to a higher energy state.

Applications of Emission and Absorption Spectra

If white light is passed through a sample of hydrogen, hydrogen atoms absorb energy as an electron is excited to higher energy levels (orbits with $n \geq 2$). If the light that emerges is passed through a prism, it forms a continuous spectrum with *black* lines (corresponding to no light passing through the sample) at 656, 468, 434, and 410 nm. These wavelengths correspond to the $n = 2$ to $n = 3$, $n = 2$ to $n = 4$, $n = 2$ to $n = 5$, and $n = 2$ to $n = 6$ transitions. Any given element therefore has both a characteristic emission spectrum and a characteristic absorption spectrum, which are essentially complementary images.

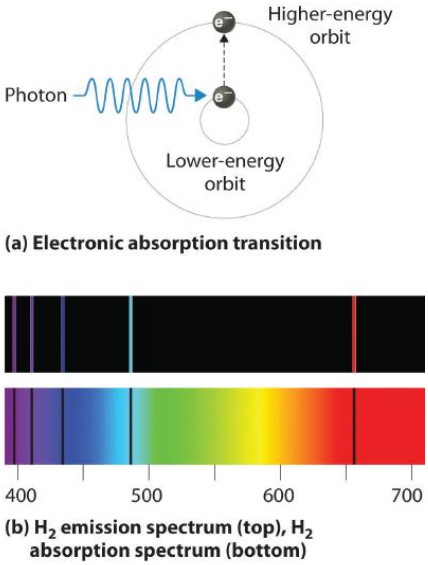


Figure 2.5.6 Absorption and Emission Spectra ***Absorption of light by a hydrogen atom.*** *(a) When a hydrogen atom absorbs a photon of light, an electron is excited to an orbit that has a higher energy and larger value of n. (b) Images of the emission and*

absorption spectra of hydrogen are shown here.

Emission and absorption spectra form the basis of *spectroscopy*, which uses spectra to provide information about the structure and the composition of a substance or an object. In particular, astronomers use emission and absorption spectra to determine the composition of stars and interstellar matter. As an example, consider the spectrum of sunlight shown in Figure 2.3.7 Because the sun is very hot, the light it emits is in the form of a continuous emission spectrum. Superimposed on it, however, is a series of dark lines due primarily to the absorption of specific frequencies of light by cooler atoms in the outer atmosphere of the sun. By comparing these lines with the spectra of elements measured on Earth, we now know that the sun contains large amounts of hydrogen, iron, and carbon, along with smaller amounts of other elements. During the solar eclipse of 1868, the French astronomer Pierre Janssen (1824–1907) observed a set of lines that did not match those of any known element. He suggested that they were due to the presence of a new element, which he named *helium*, from the Greek *helios*, meaning "sun." Helium was finally discovered in uranium ores on Earth in 1895. Alpha particles are helium nuclei. Alpha particles emitted by the radioactive uranium, pick up electrons from the rocks to form helium atoms.

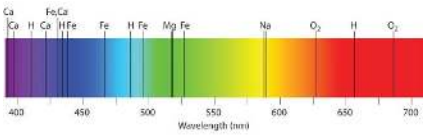


Figure 2.5.7 The Visible Spectrum of Sunlight *The characteristic dark lines are mostly due to the absorption of light by elements that are present in the cooler outer part of the sun's atmosphere; specific elements are indicated by the labels. The lines at 628 and 687 nm, however, are due to the absorption of light by oxygen molecules in Earth's atmosphere.*

The familiar red color of "neon" signs used in advertising is due to the emission spectrum of neon shown in part (b) in Figure 2.3.5 . Similarly, the blue and yellow colors of certain street lights are caused, respectively, by mercury and sodium discharges. In all these cases, an electrical discharge excites neutral atoms to a higher energy state, and light is emitted when the atoms decay to the ground state. In the case of mercury, most of the emission lines are below 450 nm, which produces a blue light (part (c) in Figure 2.3.5). In the case of sodium, the most intense emission lines are at 589 nm, which produces an intense yellow light.

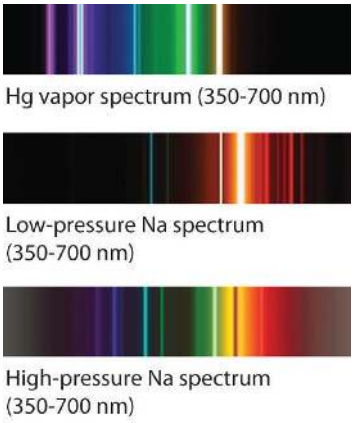


Figure 2.5.8 The emission spectra of sodium and mercury *Many street lights use bulbs that contain sodium or mercury vapor. Due to the very different emission spectra of these elements, they emit light of different colors. The lines in the sodium lamp are broadened by collisions. The dark line in the center of the high pressure sodium lamp where the low pressure lamp is strongest is cause by absorption of light in the cooler outer part of the lamp.*

The Chemistry of Fireworks



Figure 2.5.9 The Chemistry of Fireworks *(a) In the "multibreak" shell used for fireworks, the chambers contain mixtures of fuels and oxidizers plus compounds for special effects ("stars") connected by time-delay fuses so that the chambers explode in stages. (b) The finale of a fireworks display usually consists of many shells fired simultaneously to give a dazzling multicolor display. The labels indicate the substances that are responsible for the colors of some of the fireworks shown.*

The colors of fireworks are also due to atomic emission spectra. As shown in part (a) in Figure 2.5.9 , a typical shell used in a fireworks display contains gunpowder to propel the shell into the air and a fuse to initiate a variety of reactions that produce heat and small explosions. Thermal energy excites the atoms to higher energy states; as they decay to lower energy states, the atoms emit light that gives the familiar colors. When oxidant/reductant mixtures listed in Table 2.5.1 are ignited, a flash of white or yellow light is produced along with a loud bang. Achieving the colors shown in part (b) in Figure 2.5.9 requires adding a small amount of a substance that has an emission spectrum in the desired portion of the visible spectrum. For example, sodium is used for yellow because of its 589 nm emission lines. The intense yellow color of sodium would mask most other colors, so potassium and ammonium salts, rather than sodium salts, are usually used as oxidants to produce other colors, which explains the preponderance of such salts in Table 2.5.1. Strontium salts, which are also used in highway flares, emit red light, whereas barium gives a green color. Blue is one of the most difficult colors to achieve. Copper(II) salts emit a pale blue light, but copper is dangerous to use because it forms highly unstable explosive compounds with anions such as chlorate. As you might guess, preparing fireworks with the desired properties is a complex, challenging, and potentially hazardous process. If you have the time here is a NOVA program about how fireworks are made





Oh heck, take a look:)

Table 2.5.1 Common Chemicals Used in the Manufacture of Fireworks*

Oxidizers	Fuels (reductants)	Special effects
ammonium perchlorate	aluminum	*blue flame*: copper carbonate, copper sulfate, or copper oxide
barium chlorate	antimony sulfide	*red flame*: strontium nitrate or strontium carbonate
barium nitrate	charcoal	*white flame*: magnesium or aluminum
potassium chlorate	magnesium	*yellow flame*: sodium oxalate or cryolite (Na_3AlF_6)
potassium nitrate	sulfur	*green flame*: barium nitrate or barium chlorate
potassium perchlorate	titanium	*white smoke*: potassium nitrate plus sulfur
strontium nitrate		*colored smoke*: potassium chlorate and sulfur, plus organic dye
		whistling noise: potassium benzoate or sodium salicylate
		white sparks: aluminum, magnesium, or titanium
		gold sparks: iron fillings or charcoal

*Almost any combination of an oxidizer and a fuel may be used along with the compounds needed to produce a desired special effect.

Lasers

Most light emitted by atoms is *polychromatic*—containing more than one wavelength. In contrast, *lasers* (from *l*ight *a*mplification by *s*timulated *e*mission of *r*adiation) emit *monochromatic* light—a single wavelength only. Lasers have many applications in fiber-optic telecommunications, the reading and recording of compact discs (CDs) and digital video discs (DVDs), metal cutting, semiconductor fabrication, supermarket checkout scanners and laser pointers. Laser beams are generated by the same general phenomenon that gives rise to emission spectra, with one difference: only a single excited state is produced, which in principle results in only a single frequency of emitted light. In practice, however, inexpensive commercial lasers actually emit light with a very narrow range of wavelengths. The ones used in commercial products today are usually inexpensive red semiconductor diode lasers.

When used in a DVD player or a CD player, light emitted by a semiconductor diode laser passes through a transparent layer of plastic on the CD and is reflected by an underlying aluminum layer, which contains pits or flat regions that were created when the CD was recorded. Differences in the intensities of the transmitted and reflected light are detected by light-sensitive equipment that converts these differences into binary code, a series of 1s and 0s, which is translated electronically into recognizable sounds and images.

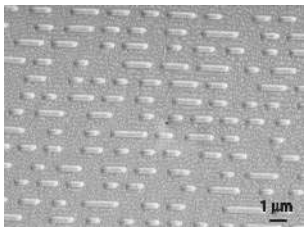


Figure 2.5.10 How a CD player uses a laser to read a CD *Inside a CD is a flat, light-reflecting layer called "land." On the land are many "pits" recorded in a spiral-shaped track. (From the laser's point of view, pits are actually the "bumps" shown here because the master disc with pits is duplicated negatively, turning the pits into bumps.) The pits spread (scatter) the reflected light. The amount of light reflected directly into the detactor by pits is low compared with that reflected by land.*

The operation of a ruby laser, the first type of laser to be demonstrated, is shown schematically in Figure 2.5.11 Ruby is an impure form of aluminum oxide (Al_2O_3) in which Cr^{3+} replaces some of the Al^{3+} ions. It also, of course, is a gem when it occurs naturally. The ruby grown for laser rods is defect free. The red color of the gem is caused by the absorption of light in the blue region of the visible spectrum by Cr^{3+} ions, which leaves only the longer wavelengths to be reflected back to the eye. One end of a ruby bar is coated with a fully reflecting mirror, and the mirror on the other end is only partially reflecting. When flashes of white light from a flash lamp excite the Cr^{3+} ions, they initially decay to a relatively long-lived excited state and can subsequently decay to the ground state by emitting a photon of red light. Some of these photons are reflected back and forth by the mirrored surfaces. As shown in part (b) in Figure 2.3.11 , each time a photon interacts with an excited Cr^{3+} ion, it can stimulate that ion to emit another photon that has the same wavelength and is synchronized (*in phase*) with the first wave. This process produces a *cascade* of photons traveling back and forth, until the intense beam emerges through the partially reflecting mirror. Ruby is only one substance that is used to produce a laser; the choice of material determines the wavelength of light emitted, from infrared to ultraviolet, and the light output can be either continuous or pulsed.

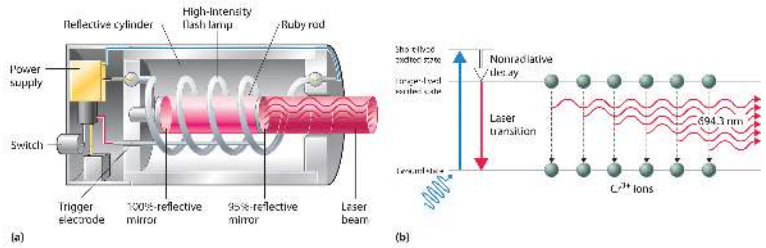


Figure 2.5.11 A Ruby Laser *(a) This cutaway view of a ruby laser shows the ruby rod, the flash lamp used to excite the Cr^{3+} ions in the ruby, and the totally and partially reflective mirrors. (b) This schematic drawing illustrates how light from the flash lamp excites the Cr^{3+} ions to a short-lived excited state, which is followed by decay to a longer-lived excited state that is responsible for the stimulated in-phase emission of light by the laser.*

Key Equation

Rydberg equation

Equation 2.3.1: $\frac{1}{\lambda} = \mathfrak{R}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

Summary

Atoms of individual elements emit light at only specific wavelengths, producing a **line spectrum** rather than the continuous spectrum of all wavelengths produced by a hot object. Niels Bohr explained the line spectrum of the hydrogen atom by assuming that the electron moved in circular orbits and that orbits with only certain radii were allowed. Lines in the spectrum were due to transitions in which an electron moved from a higher-energy orbit with a larger radius to a lower-energy orbit with smaller radius. The orbit closest to the nucleus represented the **ground state** of the atom and was most stable; orbits farther away were higher-energy **excited states**. Transitions from an excited state to a lower-energy state resulted in the emission of light with only a limited number of wavelengths. Bohr's model could not, however, explain the spectra of atoms heavier than hydrogen.

Most light is polychromatic and contains light of many wavelengths. Light that has only a single wavelength is monochromatic and is produced by devices called lasers, which use transitions between two atomic energy levels to produce light in a very narrow range of wavelengths. Atoms can also absorb light of certain energies, resulting in a transition from the ground state or a lower-energy excited state to a higher-energy excited state. This produces an **absorption spectrum**, which has dark lines in the same position as the bright lines in the **emission spectrum** of an element.

Key Takeaway

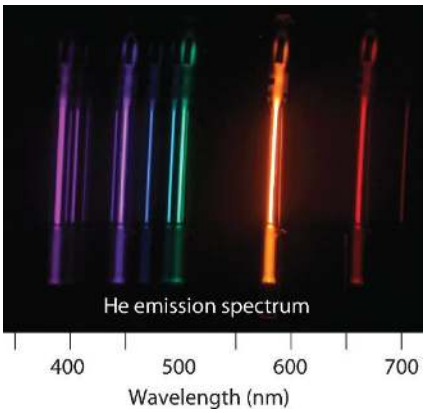
- There is an intimate connection between the atomic structure of an atom and its spectral characteristics.

Conceptual Problems

1. Is the spectrum of the light emitted by isolated atoms of an element discrete or continuous? How do these spectra differ from those obtained by heating a bulk sample of a solid element? Explain your answers.
2. Explain why each element has a characteristic emission and absorption spectra. If spectral emissions had been found to be continuous rather than discrete, what would have been the implications for Bohr's model of the atom?
3. Explain the differences between a ground state and an excited state. Describe what happens in the spectrum of a species when an electron moves from a ground state to an excited state. What happens in the spectrum when the electron falls from an excited state to a ground state?
4. What phenomenon causes a neon sign to have a characteristic color? If the emission spectrum of an element is constant, why do some neon signs have more than one color?
5. How is light from a laser different from the light emitted by a light source such as a light bulb? Describe how a laser produces light.

Numerical Problems

1. Using a Bohr model and the transition from $n = 2$ to $n = 3$ in an atom with a single electron, describe the mathematical relationship between an emission spectrum and an absorption spectrum. What is the energy of this transition? What does the sign of the energy value represent in this case? What range of light is associated with this transition?
2. If a hydrogen atom is excited from an $n = 1$ state to an $n = 3$ state, how much energy does this correspond to? Is this an absorption or an emission? What is the wavelength of the photon involved in this process? To what region of the electromagnetic spectrum does this correspond?
3. The hydrogen atom emits a photon with a 486 nm wavelength, corresponding to an electron decaying from the $n = 4$ level to which level? What is the color of the emission?
4. An electron in a hydrogen atom can decay from the $n = 3$ level to $n = 2$ level. What is the color of the emitted light? What is the energy of this transition?
5. Calculate the wavelength and energy of the photon that gives rise to the third line in order of increasing energy in the Lyman series in the emission spectrum of hydrogen. In what region of the spectrum does this wavelength occur? Describe qualitatively what the absorption spectrum looks like.
6. The wavelength of one of the lines in the Lyman series of hydrogen is 121 nm. In what region of the spectrum does this occur? To which electronic transition does this correspond?
7. The emission spectrum of helium is shown. Estimate what change in energy (ΔE) gives rise to each line?



8. Removing an electron from solid potassium requires 222 kJ/mol. Would you expect to observe a photoelectric effect for potassium using a photon of blue light (λ = 485 nm)? What is the longest wavelength of energy capable of ejecting an electron from potassium? What is the corresponding color of light of this wavelength?
9. The binding energy of an electron is the energy needed to remove an electron from its lowest energy state. According to Bohr's postulates, calculate the binding energy of an electron in a hydrogen atom. There are 6.02 x 10^{23} atoms in 1g of hydrogen atoms What wavelength in nanometers is required to remove such an electron from one hydrogen atom?
10. As a radio astronomer, you have observed spectral lines for hydrogen corresponding to a state with n = 320, and you would like to produce these lines in the laboratory. Is this feasible? Why or why not?

Answers

1. 656 nm; red light
2.
3. n = 2, blue-green light
4.
5. 97.2 nm, 2.04 × 10^{-18} J/photon, ultraviolet light, absorption spectrum is a single dark line at a wavelength of 97.2 nm
6.
7. Violet: 390 nm, 307 kJ/mol photons; Blue-purple: 440 nm, 272 kJ/mol photons; Blue-green: 500 nm, 239 kJ/mol photons; Orange: 580 nm, 206 kJ/mol photons; Red: 650 nm, 184 kJ/mol photons
8.
9. 1313 kJ/mol, λ ≤ 91.1 nm
10.

Contributors

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Chapter 2.6: End of Chapter Material

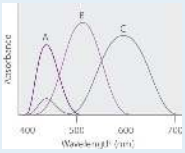
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APPLICATION PROBLEMS

1. The lamps in street lights use emission of light from excited states of atoms to produce a characteristic glow. Light is generated by electron bombardment of a metal vapor. Of calcium and strontium, which metal vapor would you use to produce yellow light? Which metal would you use to produce red light? Calculate the energy associated with each transition and propose an explanation for the colors of the emitted light.
2. Lasers have useful medical applications because their light is directional (permitting tight focus of the laser beam for precise cutting), monochromatic, and intense. Carbon dioxide lasers, emitting at a wavelength of 1.06×10^4 nm, are typically used in surgery.
   a. What are the frequency and energy (in kilojoules per mole) of a photon from a carbon dioxide laser?
   b. Why is monochromatic light desirable in a surgical procedure?
   c. Biological tissue consists primarily of water, which absorbs electromagnetic radiation in the infrared region of the spectrum. Suggest a plausible reason for using carbon dioxide lasers in surgery.
3. An excimer (meaning “excited dimer”) laser emits light in the ultraviolet region of the spectrum. An example of such a laser is krypton fluoride (KrF), which emits light at a wavelength of 248 nm. What is the energy in joules of a mole of photons emitted from this laser? How much more energetic is a single photon of this wavelength than a photon from a carbon dioxide laser used in surgery (10,600 nm)?
4. The magnitude of the energy gap between an excited state and a ground state determines the color of visible light that is absorbed. The observed color of an object is not the color of the light it absorbs but rather the complement of that color. The accompanying rosette, first developed by Isaac Newton, shows the colors increasing in energy from red to violet. Any two colors that are opposite each other are said to be *complementary* (e.g., red and green are complementary).



   a. Given the absorption spectra and following table, what are the colors of the objects that produce spectra A, B, and C?



Wavelength (nm)	Color of Light
390–453	violet
453–492	blue
492–577	green
577–597	yellow
597–622	orange
622–780	red

b. The decomposition of a pigment depends on many factors, but the rate of decomposition often depends on the energy of the radiation absorbed by the pigment. Which of these compounds—A, B, or C—will likely fade fastest?

c. A painter has a sample of yellow paint. What would you expect the absorption spectrum of the paint to look like? What would the absorption spectrum look like if the paint had been contaminated with traces of a violet pigment?

5. Photodegradation of atmospheric ozone occurs via the reaction $O_3 + h\nu \rightarrow O_2 + O$; the maximum absorption occurs at approximately 255 nm. In what region of the electromagnetic spectrum does this occur? Based on this information, what would be the effect of depleting the ozone layer of Earth's atmosphere?
6. A microscope's resolution (its ability to distinguish between two points separated by a given distance) depends on the wavelength of light used to illuminate an object. The resolution R is given by the equation $R = \lambda/2N$, where N is a constant related to the aperture. If a microscope has an aperture constant of 0.25, what is the smallest distance between two objects that can be resolved using the following light sources?
   a. red light (E = 171 kJ/mol)
   b. ultraviolet light ($E = 1.20 \times 10^3$ kJ/mol)
   c. x-rays ($E = 1.20 \times 10^5$ kJ/mol)
7. Silver bromide is the photosensitive material in 35 mm photographic film. When monochromatic light falls on film, the photons are recorded if they contain sufficient energy to react with silver bromide in the film. Given that the minimum energy needed to do this is approximately 57.9 kJ/mol, explain why red light is used to light a darkroom. What happens when the door to the darkroom is opened, allowing yellow light to enter?
8. A lighting system has recently been developed that uses a quartz bulb the size of a golf ball filled with an inert gas and a small amount of sulfur. When irradiated by microwaves, the bulb puts out as much light as hundreds of high-intensity mercury vapor lamps. Because 1000 kJ/mol is needed to ionize sulfur, can this process occur simply by irradiating sulfur atoms with microwaves? Explain your answer.
9. The following table lists the ionization energies of some common atmospheric species:

Species	Ionization Energy (kJ/mol)
NO	897
CO_2	1330
O_2	1170

   a. Can radiant energy corresponding to the lowest energy line in the Lyman series be used to ionize these molecules?
   b. According to the table, can radiation of this energy be transmitted through an oxygen atmosphere?
10. An artist used a pigment that has a significant absorption peak at 450 nm, with a trace absorption at 530 nm. Based on the color chart and table in Problem 6, what was the color of the paint? Draw the absorption pattern. What would the absorption spectrum have looked like if the artist had wanted green? Using absorption spectra, explain why an equal combination of red and yellow paints produces orange.
11. You live in a universe where an electron has four different spins (m_S = +½, +¼, −½, −¼) and the periodic table has only 36 elements. Which elements would be noble gases? What would the periodic table look like? (Assume that the Pauli exclusion principle is still valid.)
12. If you were living on a planet where there were three quantum numbers (n, l, m) instead of four, what would be the allowed combinations for an electron in a 3p orbital? How many electrons would this orbital contain assuming the Pauli exclusion principle were still in effect? How does this compare with the actual number of allowed combinations found on Earth?
13. X-rays are frequently used to project images of the human body. Recently, however, a superior technique called magnetic resonance imaging (MRI) has been developed that uses *proton* spin to image tissues in spectacular detail. In MRI, spinning hydrogen nuclei in an organic material are irradiated with photons that contain enough energy to flip the protons to the opposite orientation. If 33.121 kJ/mol of energy is needed to flip a proton, what is the resonance frequency required to produce an MRI spectrum? Suggest why this frequency of electromagnetic radiation would be preferred over x-rays.
14. Vanadium has been found to be a key component in a biological catalyst that reduces nitrogen to ammonia. What is the valence electron configuration of vanadium? What are the quantum numbers for each valence electron? How many unpaired

electrons does vanadium have?

15. Tellurium, a metal used in semiconductor devices, is also used as a coloring agent in porcelains and enamels. Illustrate the aufbau principle, the Pauli exclusion principle, and Hund's rule using tellurium metal.
16. A new element is believed to have been discovered by a team of Russian and American scientists, although its existence is yet to be independently confirmed. Six atoms of element 117, temporarily named ununseptium, were created by smashing together isotopes of calcium with the element berkelium. Give the following:
    a. the complete electron configuration of this element
    b. the valence electron configuration
    c. the number of unpaired electrons in the valence shell

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CHAPTER OVERVIEW

Chapter 3: The Periodic Table

The modern periodic table emphasizes the electronic structure of atoms. The original periodic table emphasized the reactivity of the elements. In this chapter we will learn about the connection between the two, how the electronic structure is related to the macroscopic properties of the elements.

Chapter 3.1: Sizes of Atoms and Ions

Chapter 3.2: Energetics of Ion Formation

Chapter 3.3: The Chemical Families

Chapter 3.4: The History of the Periodic Table

Chapter 3.5: End of Chapter Material

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Chapter 3.1: Sizes of Atoms and Ions

Learning Objectives

- To understand periodic trends in atomic radii.
- To predict relative ionic sizes within an isoelectronic series.

Although some people fall into the trap of visualizing atoms and ions as small, hard spheres similar to miniature table-tennis balls or marbles, the quantum mechanical model tells us that their shapes and boundaries are much less definite than those images suggest. As a result, atoms and ions cannot be said to have exact sizes. In this section, we discuss how atomic and ion "sizes" are defined and obtained.

Atomic Radii

Recall from Chapter 2 " that the probability of finding an electron in the various available orbitals falls off slowly as the distance from the nucleus increases. This point is illustrated in Figure 3.1.1 which shows a plot of total electron density for all occupied orbitals for three noble gases as a function of their distance from the nucleus. Electron density diminishes gradually with increasing distance, which makes it impossible to draw a sharp line marking the boundary of an atom.

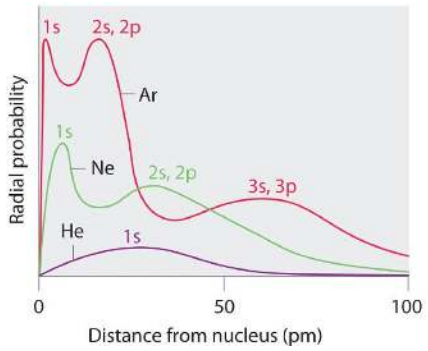


Figure 3.1.1 Plots of Radial Probability as a Function of Distance from the Nucleus for He, Ne, and Ar *In He, the 1s electrons have a maximum radial probability at ≈30 pm from the nucleus. In Ne, the 1s electrons have a maximum at ≈8 pm, and the 2s and 2p electrons combine to form another maximum at ≈35 pm (the n = 2 shell). In Ar, the 1s electrons have a maximum at ≈2 pm, the 2s and 2p electrons combine to form a maximum at ≈18 pm, and the 3s and 3p electrons combine to form a maximum at ≈70 pm.*

Figure 3.1.1 also shows that there are distinct peaks in the total electron density at particular distances and that these peaks occur at different distances from the nucleus for each element. Each peak in a given plot corresponds to the electron density in a given principal shell. Because helium has only one filled shell (n = 1), it shows only a single peak. In contrast, neon, with filled n = 1 and 2 principal shells, has two peaks. Argon, with filled n = 1, 2, and 3 principal shells, has three peaks. The peak for the filled n = 1 shell occurs at successively shorter distances for neon (Z = 10) and argon (Z = 18) because, with a greater number of protons, their nuclei are more positively charged than that of helium. Because the $1s^2$ shell is closest to the nucleus, its electrons are very poorly shielded by electrons in filled shells with larger values of n. Consequently, the two electrons in the n = 1 shell experience nearly the full nuclear charge, resulting in a strong electrostatic interaction between the electrons and the nucleus. It is important to point out that we measure the energy of the electron relative to the energy the electron would have if it were an infinite distance from the nucleus. This means that when we say the energy decreases, or is lower we mean that the electron is held more tightly to the nucleus. The energy of the n = 1 shell decreases tremendously (the filled 1s orbital becomes more stable) as the nuclear charge increases. For similar reasons, the filled n = 2 shell in argon is located closer to the nucleus and has a lower energy relative to the separated electron and nucleus than the n = 2 shell in neon.

Figure 3.1.1 illustrates the difficulty of measuring the dimensions of an individual atom. Because distances between the nuclei in pairs of covalently bonded atoms can be measured quite precisely, however, chemists use these distances as a basis for describing the approximate sizes of atoms. For example, the internuclear distance in the diatomic Cl_2 molecule is known to be 198 pm. We assign half of this distance to each chlorine atom, giving chlorine a covalent atomic radius (r_{cov})Half the distance between the

nuclei of two like atoms joined by a covalent bond in the same molecule. of 99 pm or 0.99 Å (part (a) in Figure 3.1.2).Atomic radii are often measured in angstroms (Å), a non-SI unit: 1 Å = 1×10^{-10} m = 100 pm.

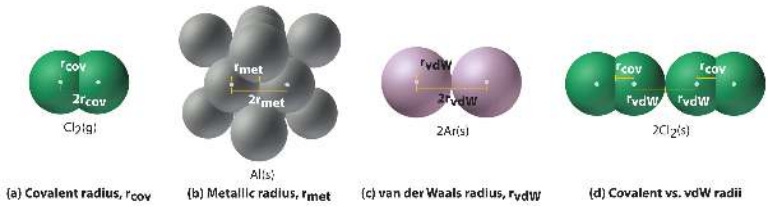


Figure 3.1.2 Definitions of the Atomic Radius*(a) The covalent atomic radius, r_{cov}, is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, such as Cl_2. (b) The metallic atomic radius, r_{met}, is half the distance between the nuclei of two adjacent atoms in a pure solid metal, such as aluminum. (c) The van der Waals atomic radius, r_{vdW}, is half the distance between the nuclei of two like atoms, such as argon, that are closely packed but not bonded. (d) This is a depiction of covalent versus van der Waals radii of chlorine. The covalent radius of Cl_2 is the distance between the two chlorine atoms in a single molecule of Cl_2. The van der Waals radius is the distance between chlorine nuclei in two different but touching Cl_2 molecules. Which do you think is larger? Why?*

In a similar approach, we can use the lengths of carbon–carbon single bonds in organic compounds, which are remarkably uniform at 154 pm, to assign a value of 77 pm as the covalent atomic radius for carbon. If these values do indeed reflect the actual sizes of the atoms, then we should be able to predict the lengths of covalent bonds formed between different elements by adding them. For example, we would predict a carbon–chlorine distance of 77 pm + 99 pm = 176 pm for a C–Cl bond, which is very close to the average value observed in many organochlorine compounds. A similar approach for measuring the size of ions is discussed later in this section.

Covalent atomic radii can be determined for most of the nonmetals, but how do chemists obtain atomic radii for elements that do not form covalent bonds? For these elements, a variety of other methods have been developed. With a metal, for example, the metallic atomic radius(r_{met})Half the distance between the nuclei of two adjacent metal atoms. is defined as half the distance between the nuclei of two adjacent metal atoms (part (b) in Figure 3.1.2). For elements such as the noble gases, most of which form no stable compounds, we can use what is called the van der Waals atomic radius(r_{vdW})Half the internuclear distance between two nonbonded atoms in the solid., which is half the internuclear distance between two nonbonded atoms in the solid (part (c) in Figure 3.1.2). This is somewhat difficult for helium which does not form a solid at any temperature. An atom such as chlorine has both a covalent radius (the distance between the two atoms in a Cl_2 molecule) and a van der Waals radius (the distance between two Cl atoms in different molecules in, for example, Cl_2(s) at low temperatures). These radii are generally not the same (part (d) in Figure 3.1.2).

Periodic Trends in Atomic Radii

Because it is impossible to measure the sizes of both metallic and nonmetallic elements using any one method, chemists have developed a self-consistent way of calculating atomic radii using the quantum mechanical functions described in Chapter 2 . Although the radii values obtained by such calculations are not identical to any of the experimentally measured sets of values, they do provide a way to compare the intrinsic sizes of all the elements and clearly show that atomic size varies in a periodic fashion (Figure 3.1.3). In the periodic table, atomic radii decrease from left to right across a row and increase from top to bottom down a column. Because of these two trends, the largest atoms are found in the lower left corner of the periodic table, and the smallest are found in the upper right corner (Figure 3.1.4).

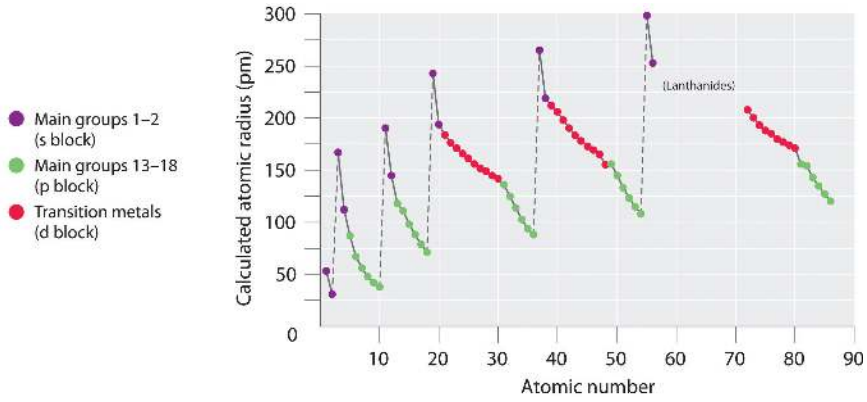


Figure 3.1.3 A Plot of Periodic Variation of Atomic Radius with Atomic Number for the First Six Rows of the Periodic Table*There is a similarity to the plot of atomic volume versus atomic number (* Figure 3.1..4 *)—a variation of Meyer's early plot.*

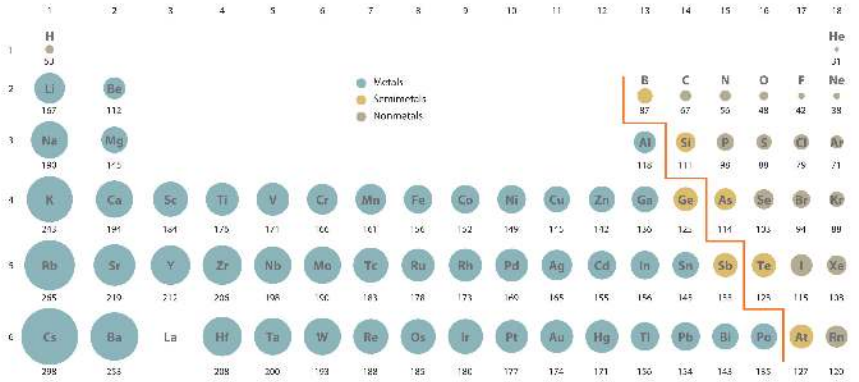


Figure 3.1.4 Calculated Atomic Radii (in Picometers) of the *s*-, *p*-, and *d*-Block Elements *The sizes of the circles illustrate the relative sizes of the atoms. The calculated values are based on quantum mechanical wave functions.*

Source: http://www.webelements.com. Web Elements is an excellent on line source for looking up atomic properties. Visit the site.

Note the Pattern

Atomic radii decrease from left to right across a row and increase from top to bottom down a column.

Trends in atomic size result from differences in the **effective nuclear charges (Z_{eff})** experienced by electrons in the outermost orbitals of the elements. As we described in Chapter 2, for all elements except H, the effective nuclear charge is always *less* than the actual nuclear charge because of shielding effects. The greater the effective nuclear charge, the more strongly the outermost electrons are attracted to the nucleus and the smaller the atomic radius.

The atoms in the second row of the periodic table (Li through Ne) illustrate the effect of electron shielding. (For more information on electron shielding, see Chapter 2 Section 2.2, and Figure 2.2.10 .) All have a filled $1s^2$ inner shell, but as we go from left to right across the row, the nuclear charge increases from +3 to +10. Although electrons are being added to the 2*s* and 2*p* orbitals, *electrons in the same principal shell are not very effective at shielding one another from the nuclear charge*. Thus the single 2*s* electron in lithium experiences an effective nuclear charge of approximately +1 because the electrons in the filled $1s^2$ shell effectively neutralize two of the three positive charges in the nucleus. (More detailed calculations give a value of Z_{eff} = +1.26 for Li.) In contrast, the two 2*s* electrons in beryllium do not shield each other very well, although the filled $1s^2$ shell effectively neutralizes two of the four positive charges in the nucleus. This means that the effective nuclear charge experienced by the 2*s* electrons in beryllium is between +1 and +2 (the calculated value is +1.66). Consequently, beryllium is significantly smaller than lithium. Similarly, as we proceed across the row, the increasing nuclear charge is not effectively neutralized by the electrons being added to the 2*s* and 2*p* orbitals. The result is a steady increase in the effective nuclear charge and a steady decrease in atomic size.

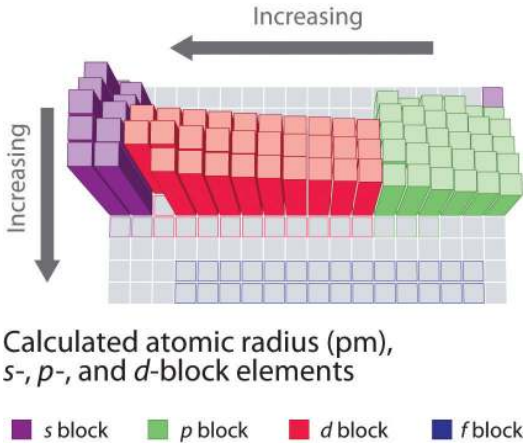


Figure 3.1.5 The Atomic Radius of the Elements*The atomic radius of the elements increases as we go from right to left across a period and as we go down the periods in a group.*

The increase in atomic size going down a column is also due to electron shielding, but the situation is more complex because the principal quantum number *n* is not constant. As we saw in Chapter 2 the size of the orbitals increases as *n* increases, *provided the nuclear charge remains the same*. In group 1, for example, the size of the atoms increases substantially going down the column. It may at first seem reasonable to attribute this effect to the successive addition of electrons to *ns* orbitals with increasing values of *n*. However, it is important to remember that the radius of an orbital depends dramatically on the nuclear charge. As we go down the column of the group 1 elements, the principal quantum number *n* increases from 2 to 6, but the nuclear charge increases from +3 to +55!

As a consequence the radii of the **lower electron orbitals** in Cesium are much smaller than those in lithium and the electrons in those orbitals experience a much larger force of attraction to the nucleus. That force depends on the effective nuclear charge experienced by the the inner electrons. If the outermost electrons in cesium experienced the full nuclear charge of +55, a cesium atom would be very small indeed. In fact, the effective nuclear charge felt by the outermost electrons in cesium is much less than expected (6 rather than 55). This means that cesium, with a $6s^1$ valence electron configuration, is much larger than lithium, with a $2s^1$ valence electron configuration. The effective nuclear charge changes relatively little for electrons in the outermost, or valence shell, from lithium to cesium because *electrons in filled inner shells are highly effective at shielding electrons in outer shells from the nuclear charge*. Even though cesium has a nuclear charge of +55, it has 54 electrons in its filled $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$ shells, abbreviated as $[Xe]5s^2 4d^{10} 5p^6$, which effectively neutralize most of the 55 positive charges in the nucleus. The same dynamic is responsible for the steady increase in size observed as we go down the other columns of the periodic table. Irregularities can usually be explained by variations in effective nuclear charge.

Note the Pattern

Electrons in the same principal shell are not very effective at shielding one another from the nuclear charge, whereas electrons in filled inner shells are highly effective at shielding electrons in outer shells from the nuclear charge.

Example 3.1.1

On the basis of their positions in the periodic table, arrange these elements in order of increasing atomic radius: aluminum, carbon, and silicon.

Given: three elements

Asked for: arrange in order of increasing atomic radius

Strategy:

A Identify the location of the elements in the periodic table. Determine the relative sizes of elements located in the same column from their principal quantum number *n*. Then determine the order of elements in the same row from their effective nuclear charges. If the elements are not in the same column or row, use pairwise comparisons.

B List the elements in order of increasing atomic radius.

Solution:

A These elements are not all in the same column or row, so we must use pairwise comparisons. Carbon and silicon are both in group 14 with carbon lying above, so carbon is smaller than silicon (C < Si). Aluminum and silicon are both in the third row with aluminum lying to the left, so silicon is smaller than aluminum (Si < Al) because its effective nuclear charge is greater. **B** Combining the two inequalities gives the overall order: C < Si < Al.

Exercise

On the basis of their positions in the periodic table, arrange these elements in order of increasing size: oxygen, phosphorus, potassium, and sulfur.

Answer: O < S < P < K

Ionic Radii and Isoelectronic Series

An ion is formed when either one or more electrons are removed from a neutral atom (cations) to form a positive ion or when additional electrons attach themselves to neutral atoms (anions) to form a negative one. The designations cation or anion come from the early experiments with electricity which found that positively charged particles were attracted to the negative pole of a battery, the cathode, while negatively charged ones were attracted to the positive pole, the anode.

Ionic compounds consist of regular repeating arrays of alternating positively charged cations and negatively charges anions. Although it is not possible to measure an ionic radius directly for the same reason it is not possible to directly measure an atom's radius, it *is* possible to measure the distance between the nuclei of a cation and an adjacent anion in an ionic compound to determine the ionic radiusThe radius of a cation or anion. of one or both. As illustrated in Figure 3.1.6 , the internuclear distance corresponds to the *sum* of the radii of the cation and anion. A variety of methods have been developed to divide the experimentally measured distance proportionally between the smaller cation and larger anion. These methods produce sets of ionic radii that are internally consistent from one ionic compound to another, although each method gives slightly different values. For example, the radius of the Na^+ ion is essentially the same in NaCl and Na_2S, as long as the same method is used to measure it. Thus despite minor differences due to methodology, certain trends can be observed.

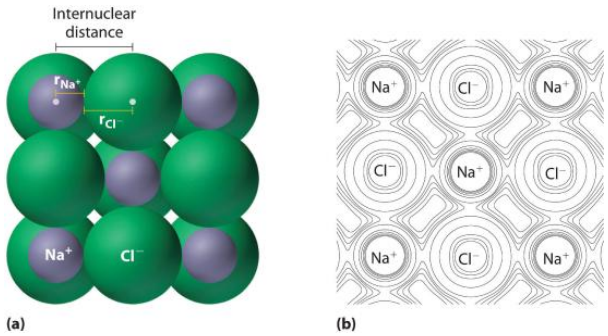


Figure 3.1.6 Definition of Ionic Radius *(a) The internuclear distance is apportioned between adjacent cations (positively charged ions) and anions (negatively charged ions) in the ionic structure, as shown here for Na^+ and Cl^- in sodium chloride. (b) This depiction of electron density contours for a single plane of atoms in the NaCl structure shows how the lines connect points of equal electron density. Note the relative sizes of the electron density contour lines around Cl^- and Na^+.*

A comparison of ionic radii with atomic radii (Figure 3.1.7 *cation, having lost an electron, is always smaller than its parent neutral atom, and an anion, having gained an electron, is always larger than the parent neutral atom*. When one or more electrons is removed from a neutral atom, two things happen: (1) repulsions between electrons in the same principal shell decrease because fewer electrons are present, and (2) the effective nuclear charge felt by the remaining electrons increases because there are fewer electrons to shield one another from the nucleus. Consequently, the size of the region of space occupied by electrons decreases (compare Li at 167 pm with Li^+ at 76 pm). If different numbers of electrons can be removed to produce ions with different charges, the ion with the greatest positive charge is the smallest (compare Fe^{2+} at 78 pm with Fe^{3+} at 64.5 pm). Conversely, adding one or more electrons to a neutral atom causes electron–electron repulsions to increase and the effective nuclear charge to decrease, so the size of the probability region increases (compare F at 42 pm with F^- at 133 pm).

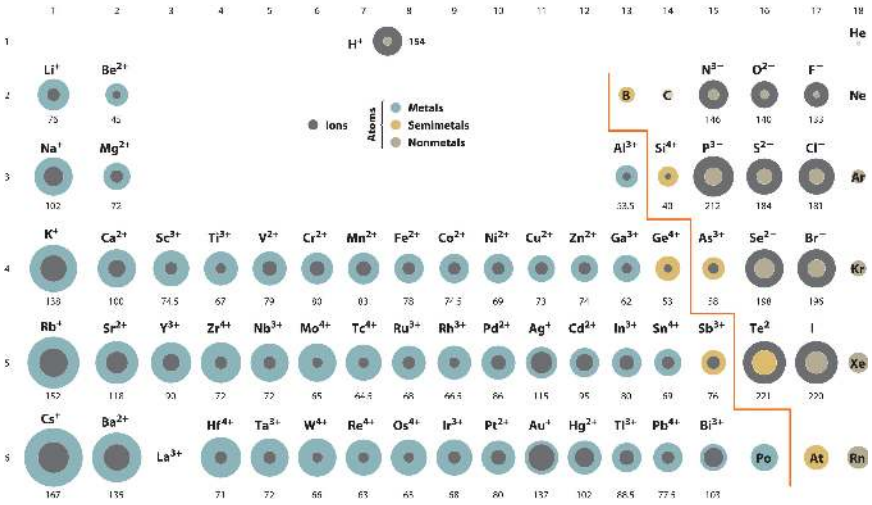


Figure 3.1.7 Ionic Radii (in Picometers) of the Most Common Ionic States of the *s*-, *p*-, and *d*-Block Elements *Gray circles indicate the sizes of the ions shown; colored circles indicate the sizes of the neutral atoms, previously shown in Figure 3.1.4*

Source: Ionic radius data from R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," Acta Crystallographica 32, no. 5 (1976): 751–767.

Note the Pattern

Cations are always smaller than the neutral atom, and anions are always larger.

Because most elements form either a cation or an anion but not both, there are few opportunities to compare the sizes of a cation and an anion derived from the same neutral atom. A few compounds of sodium, however, contain the Na^- ion, allowing comparison of its size with that of the far more familiar Na^+ ion, which is found in *many* compounds. The radius of sodium in each of its three known oxidation states is given in Table 3.1.1. All three species have a nuclear charge of +11, but they contain 10 (Na^+), 11 (Na^0), and 12 (Na^-) electrons. The Na^+ ion is significantly smaller than the neutral Na atom because the $3s^1$ electron has been removed to give a closed shell with $n = 2$. The Na^- ion is larger than the parent Na atom because the additional electron produces a $3s^2$ valence electron configuration, while the nuclear charge remains the same.

Table 3.1.1 Experimentally Measured Values for the Radius of Sodium in Its Three Known Oxidation States

	Na^+	Na^0	Na^-
Electron Configuration	$1s^22s^22p^6$	$1s^22s^22p^63s^1$	$1s^22s^22p^63s^2$
Radius (pm)	102	154*	202†
*The metallic radius measured for Na(s).			
†Source: M. J. Wagner and J. L. Dye, "Alkalides, Electrides, and Expanded Metals," *Annual Review of Materials Science* 23 (1993): 225–253.			

Ionic radii follow the same vertical trend as atomic radii; that is, for ions with the same charge, the ionic radius increases going down a column. The reason is the same as for atomic radii: shielding by filled inner shells produces little change in the effective nuclear charge felt by the outermost electrons. Again, principal shells with larger values of *n* lie at successively greater distances from the nucleus.

Because elements in different columns tend to form ions with different charges, it is not possible to compare ions of the same charge across a row of the periodic table. Instead, elements that are next to each other tend to form ions with the same number of electrons but with different overall charges because of their different atomic numbers. Such a set of species is known as an isoelectronic seriesA group of ions or atoms and ions that have the same number of electrons and thus the same ground-state

electron configuration.. For example, the isoelectronic series of species with the neon closed-shell configuration ($1s^2 2s^2 2p^6$) is shown in Table 3.1.2.

The sizes of the ions in this series decrease smoothly from N^{3-} to Al^{3+}. All six of the ions contain 10 electrons in the 1*s*, 2*s*, and 2*p* orbitals, but the nuclear charge varies from +7 (N) to +13 (Al). As the positive charge of the nucleus increases while the number of electrons remains the same, there is a greater electrostatic attraction between the electrons and the nucleus, which causes a decrease in radius. Consequently, the ion with the greatest nuclear charge (Al^{3+}) is the smallest, and the ion with the smallest nuclear charge (N^{3-}) is the largest. One member of this isoelectronic series is not listed in Table 7.3: the neon atom. Because neon forms no covalent or ionic compounds, its radius is difficult to measure.

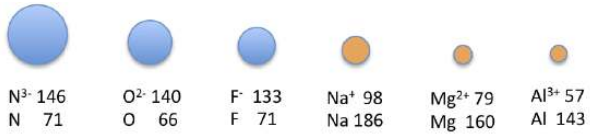


Table 3.1.2 Radius of Ions with the Neon Closed-Shell Electron Configuration

Ion	Radius (pm)	Atomic Number
N^{3-}	146	7
O^{2-}	140	8
F^-	133	9
Na^+	102	11
Mg^{2+}	72	12
Al^{3+}	53.5	13

Source: R. D. Shannon, “Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides,” *Acta Crystallographica* 32, no. 5 (1976): 751–767.

Example 3.1.2

Based on their positions in the periodic table, arrange these ions in order of increasing radius: Cl^-, K^+, S^{2-}, and Se^{2-}.

Given: four ions

Asked for: order by increasing radius

Strategy:

A Determine which ions form an isoelectronic series. Of those ions, predict their relative sizes based on their nuclear charges. For ions that do not form an isoelectronic series, locate their positions in the periodic table.

B Determine the relative sizes of the ions based on their principal quantum numbers *n* and their locations within a row.

Solution:

A We see that S and Cl are at the right of the third row, while K and Se are at the far left and right ends of the fourth row, respectively. K^+, Cl^-, and S^{2-} form an isoelectronic series with the [Ar] closed-shell electron configuration; that is, all three ions contain 18 electrons but have different nuclear charges. Because K^+ has the greatest nuclear charge ($Z = 19$), its radius is smallest, and S^{2-} with $Z = 16$ has the largest radius. Because selenium is directly below sulfur, we expect the Se^{2-} ion to be even larger than S^{2-}. **B** The order must therefore be $K^+ < Cl^- < S^{2-} < Se^{2-}$.

Exercise

Based on their positions in the periodic table, arrange these ions in order of increasing size: Br^-, Ca^{2+}, Rb^+, and Sr^{2+}.

Answer: $Ca^{2+} < Sr^{2+} < Rb^+ < Br^-$

Summary

A variety of methods have been established to measure the size of a single atom or ion. The **covalent atomic radius (r_{cov})** is half the internuclear distance in a molecule with two identical atoms bonded to each other, whereas the **metallic atomic radius (r_{met})** is defined as half the distance between the nuclei of two adjacent atoms in a metallic element. The **van der Waals radius (r_{vdW})** of an element is half the internuclear distance between two nonbonded atoms in a solid. Atomic radii decrease from left to right across a row because of the increase in effective nuclear charge due to poor electron screening by other electrons in the same principal shell. Moreover, atomic radii increase from top to bottom down a column because the effective nuclear charge remains relatively constant as the principal quantum number increases. The **ionic radii** of cations and anions are always smaller or larger, respectively, than the parent atom due to changes in electron–electron repulsions, and the trends in ionic radius parallel those in atomic size. A comparison of the dimensions of atoms or ions that have the same number of electrons but different nuclear charges, called an **isoelectronic series**, shows a clear correlation between increasing nuclear charge and decreasing size.

Key Takeaway

- Ionic radii share the same vertical trend as atomic radii, but the horizontal trends differ due to differences in ionic charges.

Conceptual Problems

1. The electrons of the 1*s* shell have a stronger electrostatic attraction to the nucleus than electrons in the 2*s* shell. Give two reasons for this.
2. Predict whether Na or Cl has the more stable $1s^2$ shell and explain your rationale.
3. Arrange K, F, Ba, Pb, B, and I in order of decreasing atomic radius.
4. Arrange Ag, Pt, Mg, C, Cu, and Si in order of increasing atomic radius.
5. Using the periodic table, arrange Li, Ga, Ba, Cl, and Ni in order of increasing atomic radius.
6. Element M is a metal that forms compounds of the type MX_2, MX_3, and MX_4, where X is a halogen. What is the expected trend in the ionic radius of M in these compounds? Arrange these compounds in order of decreasing ionic radius of M.
7. The atomic radii of Na and Cl are 190 and 79 pm, respectively, but the distance between sodium and chlorine in NaCl is 282 pm. Explain this discrepancy.
8. Are shielding effects on the atomic radius more pronounced across a row or down a group? Why?
9. What two factors influence the size of an ion relative to the size of its parent atom? Would you expect the ionic radius of S^{2-} to be the same in both MgS and Na_2S? Why or why not?
10. Arrange Br^-, Al^{3+}, Sr^{2+}, F^-, O^{2-}, and I^- in order of increasing ionic radius.
11. Arrange P^{3-}, N^{3-}, Cl^-, In^{3+}, and S^{2-} in order of decreasing ionic radius.
12. How is an isoelectronic series different from a series of ions with the same charge? Do the cations in magnesium, strontium, and potassium sulfate form an isoelectronic series? Why or why not?
13. What isoelectronic series arises from fluorine, nitrogen, magnesium, and carbon? Arrange the ions in this series by
    1. increasing nuclear charge.
    2. increasing size.
14. What would be the charge and electron configuration of an ion formed from calcium that is isoelectronic with
    1. a chloride ion?
    2. Ar^+?

Answers

1. The 1*s* shell is closer to the nucleus and therefore experiences a greater electrostatic attraction. In addition, the electrons in the 2*s* subshell are shielded by the filled $1s^2$ shell, which further decreases the electrostatic attraction to the nucleus.
2.

3. Ba > K > Pb > I > B > F
4.
5.
6.
7. The sum of the calculated atomic radii of sodium and chlorine *atoms* is 253 pm. The sodium cation is significantly smaller than a neutral sodium atom (102 versus 154 pm), due to the loss of the single electron in the 3*s* orbital. Conversely, the chloride ion is much larger than a neutral chlorine atom (181 versus 99 pm), because the added electron results in greatly increased electron–electron repulsions within the filled $n = 3$ principal shell. Thus, transferring an electron from sodium to chlorine decreases the radius of sodium by about 50%, but causes the radius of chlorine to almost double. The net effect is that the distance between a sodium ion and a chloride ion in NaCl is *greater* than the sum of the atomic radii of the neutral atoms.
8.
9.
10.
11.
12.
13.
14.

Numerical Problems

1. Plot the ionic charge versus ionic radius using the following data for Mo: Mo^{3+}, 69 pm; Mo^{4+}, 65 pm; and Mo^{5+}, 61 pm. Then use this plot to predict the ionic radius of Mo^{6+}. Is the observed trend consistent with the general trends discussed in the chapter? Why or why not?
2. Internuclear distances for selected ionic compounds are given in the following table.
    1. If the ionic radius of Li^+ is 76 pm, what is the ionic radius of each of the anions?

	LiF	LiCl	LiBr	LiI
Distance (pm)	209	257	272	296

    2. What is the ionic radius of Na^+?

	NaF	NaCl	NaBr	NaI
Distance (pm)	235	282	298	322

3. Arrange the gaseous species Mg^{2+}, P^{3-}, Br^-, S^{2-}, F^-, and N^{3-} in order of increasing radius and justify your decisions.

Contributors

- Anonymous

Modified by Joshua Halpern, Scott Sinex and Scott Johnson

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Chapter 3.2: Energetics of Ion Formation

Learning Objectives

- To correlate ionization energies, electron affinities, and electronegativities with the chemistry of the elements.

We have seen that when elements react, they often gain or lose enough electrons to achieve the valence electron configuration of the nearest noble gas. In this section, we develop a more quantitative approach to predicting such reactions by examining periodic trends in the energy changes that accompany ion formation.

Ionization Energies

Because atoms do not spontaneously lose electrons, energy is required to remove an electron from an atom to form a cation. Chemists define the ionization energy (I) (The minimum amount of energy needed to remove an electron from the gaseous atom in its ground state: $E_{(g)} + I \rightarrow E^{+} + e^{-}$) of an element as the amount of energy needed to remove an electron from the gaseous atom E in its ground state. I is therefore the energy required for the reaction

$$E\,(g) + I \rightarrow E\,(g)^{+} + e^{-} \quad energy\ required = I$$

because an input of energy is required, the ionization energy is always positive ($I > 0$) for the reaction as written in Equation 3.2.1. Larger values of I mean that the electron is more tightly bound to the atom and harder to remove. Typical units for ionization energies are kilojoules/mole (kJ/mol) or electron volts (eV):

$$1 \text{ eV/atom} = 96.49 \text{ kJ/mol}$$

An electron volt is the appropriate unit to describe the energy needed to remove an electron from one atom. kJ/mole is the energy needed to ionize a mole of atoms.

If an atom possesses more than one electron, the amount of energy needed to remove successive electrons increases steadily. We can define a first ionization energy (I_1), a second ionization energy (I_2), and in general an nth ionization energy (I_n) according to the following reactions:

- $I_1 = First\ Ionization\ energy \quad E\,(g) + I_1 \rightarrow E\,(g)^{+} + e^{-}$
- $I_2 = Second\ Ionization\ energy \quad E\,(g)^{+} + I_2 \rightarrow E\,(g)^{2+} + e^{-}$
- $I_n = nth\ Ionization\ energy \quad E\,(g)^{(n-1)+} + I_n \rightarrow E\,(g)^{n+} + e^{-}$

Values for the ionization energies of Li and Be listed in Table 3.2.1 " show that successive ionization energies for an element increase steadily; that is, it takes more energy to remove the second electron from an atom than the first, and so forth. There are two reasons for this trend:

1. First, the second electron is being removed from a positively charged species rather than a neutral one, so in accordance with Coulomb's law, more energy is required.
2. Second, removing the first electron reduces the repulsive forces among the remaining electrons, so the attraction of the remaining electrons to the nucleus is stronger.

Note the Pattern

Successive ionization energies for an element increase steadily.

Table 3.2.1 Ionization Energies (in kJ/mol) for Removing Successive Electrons from Li and Be

Reaction	I	Reaction	I
$\underset{1s^22s^1}{Li\,(g)} \rightarrow \underset{1s^2}{Li^+} + e^-$	I_1 = 520.2	$\underset{1s^22s^2}{Be\,(g)} \rightarrow \underset{1s^22s^1}{Be^+} + e^-$	I_1 = 899.5
$\underset{1s^1}{Li^{2+}\,(g)} \rightarrow \underset{1s^0}{Li^{3+}} + e^-$	I_2 = 7298.2	$\underset{1s^22s^1}{Be^+\,(g)} \rightarrow \underset{1s^2}{Be^{2+}} + e^-$	I_2 = 1757.1
$\underset{1s^1}{Li^{2+}\,(g)} \rightarrow \underset{1s^0}{Li^{3+}} + e^-$	I_3 = 11,815.0	$\underset{1s^2}{Be^{2+}\,(g)} \rightarrow \underset{1s^1}{Be^{3+}} + e^-$	I_3 = 14,848.8
		$\underset{1s^1}{Be^{3+}\,(g)} \rightarrow \underset{1s^0}{Be^{4+}} + e^-$	I_4 = 21,006.6

Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

The most important consequence of the values listed in Table 3.2.1 is that the chemistry of Li is dominated by the Li^+ ion, while the chemistry of Be is dominated by the +2 oxidation state. The energy required to remove the *second* electron from Li

$$Li^+_{(g)} \rightarrow Li^{2+}_{(g)} + e^- \tag{Chapter 3.2.1}$$

is more than 10 times greater than the energy needed to remove the first electron. Similarly, the energy required to remove the *third* electron from Be

$$Be^{2+}_{(g)} \rightarrow Be^{3+}_{(g)} + e^- \tag{Chapter 3.2.2}$$

is about 15 times greater than the energy needed to remove the first electron and around 8 times greater than the energy required to remove the second electron. Both Li^+ and Be^{2+} have $1s^2$ closed-shell configurations, and much more energy is required to remove an electron from the $1s^2$ core than from the 2*s* valence orbital of the same element. The chemical consequences are enormous: lithium (and all the alkali metals) forms compounds with the 1+ ion but not the 2+ or 3+ ions. Similarly, beryllium (and all the alkaline earth metals) forms compounds with the 2+ ion but not the 3+ or 4+ ions. *The energy required to remove electrons from a filled core is prohibitively large and simply cannot be achieved in normal chemical reactions.*

Note the Pattern

The energy required to remove electrons from a filled core is prohibitively large under normal reaction conditions.

Ionization Energies of *s*- and *p*-Block Elements

Ionization energies of the elements in the third row of the periodic table exhibit the same pattern as those of Li and Be (Table 3.2.2): successive ionization energies increase steadily as electrons are removed from the valence orbitals (3*s* or 3*p*, in this case), followed by an especially large increase in ionization energy when electrons are removed from filled core levels as indicated by the bold diagonal line in Table 3.2.2 . Thus in the third row of the periodic table, the largest increase in ionization energy corresponds to removing the fourth electron from Al, the fifth electron from Si, and so forth—that is, removing an electron from an ion that has the valence electron configuration of the preceding noble gas. **This pattern explains why the chemistry of the elements normally involves only valence electrons. Too much energy is required to either remove or share the inner electrons.**

Table 3.2.2 Successive Ionization Energies (in kJ/mol) for the Elements in the Third Row of the Periodic Table

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495.8	**4562.4***	—	—	—	—	—
Mg	737.7	1450.7	**7732.7**	—	—	—	—
Al	577.5	1816.7	2744.8	**11,577.5**	—	—	—
Si	786.5	1577.1	3231.6	4355.5	**16,090.6**	—	—
P	1011.8	1907.5	2914.1	4963.6	6274.0	**21,267.4**	—
S	999.6	2251.8	3357	4556.2	7004.3	8495.8	**27,107.4**
Cl	1251.2	2297.7	3822	5158.6	6540	9362	11,018.2
Ar	1520.6	2665.9	3931	5771	7238	8781.0	11,995.3
*Inner-shell electron							

Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

Example 3.2.1

From their locations in the periodic table, predict which of these elements has the highest fourth ionization energy: B, C, or N.

Given: three elements

Asked for: element with highest fourth ionization energy

Strategy:

A List the electron configuration of each element.

B Determine whether electrons are being removed from a filled or partially filled valence shell. Predict which element has the highest fourth ionization energy, recognizing that the highest energy corresponds to the removal of electrons from a filled electron core.

Solution:

A These elements all lie in the second row of the periodic table and have the following electron configurations:

$$\text{B: [He]}2s^2 2p^1 \quad \text{C: [He]}2s^2 2p^2 \quad \text{N: [He]}2s^2 2p^3$$

B The fourth ionization energy of an element (I_4) is defined as the energy required to remove the fourth electron:

$$E^{3+}(g) \rightarrow E^{4+}(g) + e^-$$

Because carbon and nitrogen have four and five valence electrons, respectively, their fourth ionization energies correspond to removing an electron from a partially filled valence shell. The fourth ionization energy for boron, however, corresponds to removing an electron from the filled $1s^2$ subshell. This should require much more energy. The actual values are as follows: B, 25,026 kJ/mol; C, 6223 kJ/mol; and N, 7475 kJ/mol.

Exercise

From their locations in the periodic table, predict which of these elements has the lowest second ionization energy: Sr, Rb, or Ar.

Answer: Sr

The first column of data in Table 3.2.2 shows that first ionization energies tend to increase across the third row of the periodic table. This is because the valence electrons do not screen each other very well, allowing the effective nuclear charge to increase steadily across the row. The valence electrons are therefore attracted more strongly to the nucleus, so atomic sizes decrease and ionization energies increase. These effects represent two sides of the same coin: stronger electrostatic interactions between the electrons and the nucleus further increase the energy required to remove the electrons.

However, the first ionization energy decreases at Al ([Ne]$3s^2 3p^1$) and at S ([Ne]$3s^2 3p^4$). The electrons in aluminum's filled $3s^2$ subshell are better at screening the $3p^1$ electron than they are at screening each other from the nuclear charge, so the *s* electrons penetrate closer to the nucleus than the *p* electron does. The decrease at S occurs because the two electrons in the same *p* orbital repel each other. This makes the S atom slightly less stable than would otherwise be expected, as is true of all the group 16 elements.

The first ionization energies of the elements in the first six rows of the periodic table are plotted in Figure 3.2.1 . They are presented numerically and graphically in Figure 3.2.2 . These figures illustrate three important trends:

1. The changes seen in the second (Li to Ne), fourth (K to Kr), fifth (Rb to Xe), and sixth (Cs to Rn) rows of the *s* and *p* blocks follow a pattern similar to the pattern described for the third row of the periodic table. The transition metals are included in the fourth, fifth, and sixth rows, however, and the lanthanides are included in the sixth row. The first ionization energies of the transition metals are somewhat similar to one another, as are those of the lanthanides. Ionization energies increase from left to right across each row, with discrepancies occurring at ns^2np^1 (group 13), ns^2np^4 (group 16), and $ns^2(n-1)d^{10}$ (group 12) electron configurations.
2. First ionization energies generally decrease down a column. Although the principal quantum number *n* increases down a column, filled inner shells are effective at screening the valence electrons, so there is a relatively small increase in the effective nuclear charge. Consequently, the atoms become larger as they acquire electrons. Valence electrons that are farther from the nucleus are less tightly bound, making them easier to remove, which causes ionization energies to decrease. *A larger radius corresponds to a lower ionization energy*.
3. Because of the first two trends, the elements that form positive ions most easily (have the lowest ionization energies) lie in the lower left corner of the periodic table, whereas those that are hardest to ionize lie in the upper right corner of the periodic table. Consequently, ionization energies generally increase diagonally from lower left (Cs) to upper right (He).

Note the Pattern

Generally, I_1 increases diagonally from the lower left of the periodic table to the upper right.

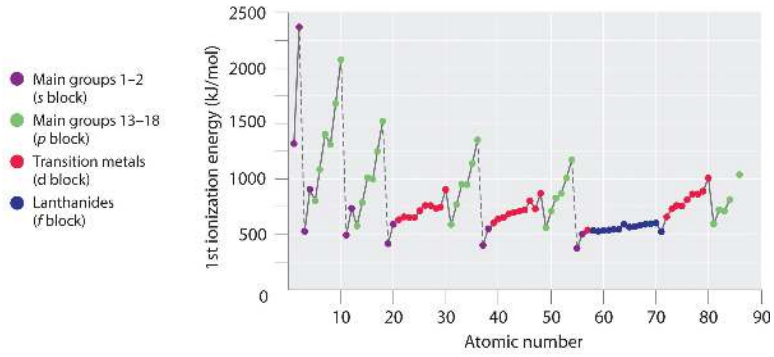


Figure 3.2.1 A Plot of Periodic Variation of First Ionization Energy with Atomic Number for the First Six Rows of the Periodic Table *There is a decrease in ionization energy within a group (most easily seen here for groups 1 and 18).* Can you explain the breaks in Figure 3.10 based on what you know about atomic structure and filled and half filled orbitals? Note the break after two electrons fill the *ns* orbitals and three the *np* orbitals. What does this say about ionizing half filled shells.

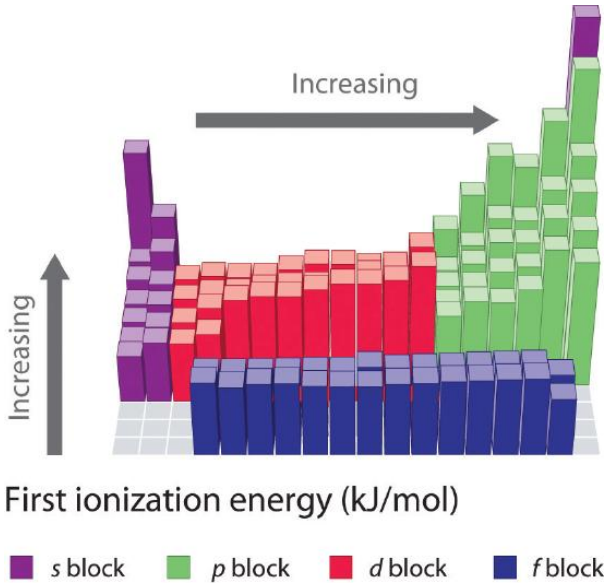


Figure 3.2.2 A Bar Chart of the Periodic Variation of First Ionization Energy with Atomic Number for the First Six Rows of the Periodic Table

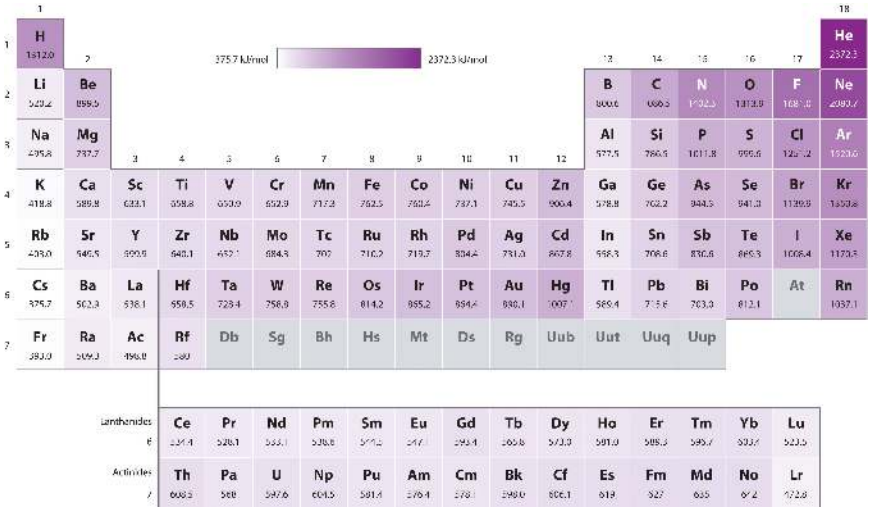


Figure 3.2.3 First Ionization Energies of the *s*-, *p*-, *d*-, and *f*-Block Elements *The darkness of the shading inside the cells of the table indicates the relative magnitudes of the ionization energies. Elements in gray have undetermined first ionization energies. Source: Data from CRC Handbook of Chemistry and Physics (2004). The CRC Handbook is a basic reference for Chemistry, Physics and Engineering. Every science and engineering major should own a copy. There are special student editions.*

Gallium (Ga), which is the first element following the first row of transition metals, has the electron configuration: [Ar]$4s^2 3d^{10} 4p^1$. Its first ionization energy is significantly lower than that of the immediately preceding element, zinc, because the filled $3d^{10}$ subshell of gallium lies inside the 4*p* subshell, screening the single 4*p* electron from the nucleus. Experiments have revealed something of even greater interest: the second and third electrons that are removed when gallium is ionized come from the $4s^2$ orbital, *not* the $3d^{10}$ subshell. The chemistry of gallium is dominated by the resulting Ga^{3+} ion, with its [Ar]$3d^{10}$ electron configuration. This and similar electron configurations are particularly stable and are often encountered in the heavier *p*-block elements. They are sometimes referred to as pseudo noble gas configurations The $(n\text{-}1)d^{10}$and similar electron configurations that are particularly stable and are often encountered in the heavier *p*-block elements.. In fact, for elements that exhibit these configurations, *no chemical compounds are known in which electrons are removed from the* $(n - 1)d^{10}$ *filled subshell*.

Ionization Energies of Transition Metals and Lanthanides

As we noted, the first ionization energies of the transition metals and the lanthanides change very little across each row. Differences in their second and third ionization energies are also rather small, in sharp contrast to the pattern seen with the *s*- and *p*-block elements. The reason for these similarities is that the transition metals and the lanthanides form cations by losing the *ns* electrons before the $(n - 1)d$ or $(n - 2)f$ electrons, respectively. This means that transition metal cations have $(n - 1)d^n$ valence electron configurations, and lanthanide cations have $(n - 2)f^n$ valence electron configurations. Because the $(n - 1)d$ and $(n - 2)f$ shells are closer to the nucleus than the *ns* shell, the $(n - 1)d$ and $(n - 2)f$ electrons screen the *ns* electrons quite effectively, reducing the effective nuclear charge felt by the *ns* electrons. As *Z* increases, the increasing positive charge is largely canceled by the electrons added to the $(n - 1)d$ or $(n - 2)f$ orbitals.

That the *ns* electrons are removed before the $(n - 1)d$ or $(n - 2)f$ electrons may surprise you because the orbitals were filled in the reverse order. (For more information on shell filling order, see Section 2.3 .) In fact, the *ns*, the $(n - 1)d$, and the $(n - 2)f$ orbitals are so close to one another in energy, and interpenetrate one another so extensively, that very small changes in the effective nuclear charge can change the order of their energy levels. As the *d* orbitals are filled, the effective nuclear charge causes the 3*d* orbitals to be slightly lower in energy than the 4*s* orbitals. The $[Ar]3d^2$ electron configuration of Ti^{2+} tells us that the 4*s* electrons of titanium are lost before the 3*d* electrons; this is confirmed by experiment. A similar pattern is seen with the lanthanides, producing cations with an $(n - 2)f^n$ valence electron configuration.

Because their first, second, and third ionization energies change so little across a row, these elements have important *horizontal* similarities in chemical properties in addition to the expected vertical similarities. For example, all the first-row transition metals except scandium form stable compounds as M^{2+} ions, whereas the lanthanides primarily form compounds in which they exist as M^{3+} ions.

Example 3.2.2

Use their locations in the periodic table to predict which element has the lowest first ionization energy: Ca, K, Mg, Na, Rb, or Sr.

Given: six elements

Asked for: element with lowest first ionization energy

Strategy:

Locate the elements in the periodic table. Based on trends in ionization energies across a row and down a column, identify the element with the lowest first ionization energy.

Solution:

These six elements form a rectangle in the two far-left columns of the periodic table. Because we know that ionization energies increase from left to right in a row and from bottom to top of a column, we can predict that the element at the bottom left of the rectangle will have the lowest first ionization energy: Rb.

Exercise

Use their locations in the periodic table to predict which element has the highest first ionization energy: As, Bi, Ge, Pb, Sb, or Sn.

Answer: As

Electron Affinities

The electron affinity (*EA*)The energy change that occurs when an electron is added to a gaseous atom: $E_{(g)} + e^- \rightarrow E^-_{(g)}$ of an element E is defined as the energy change that occurs when an electron is added to a gaseous atom:

$$E\,(g) + e^- \rightarrow E\,(g)^- \quad energy\ change = Ea$$

Unlike ionization energies, which are always positive for a neutral atom because energy is required to remove an electron, electron affinities can be negative (energy is released when an electron is added), positive (energy must be added to the system to produce an anion), or zero (the process is energetically neutral). This sign convention is consistent with our discussion of energy changes later in the course, where a negative value corresponded to the energy change for an exothermic process, which is one in which heat is released. Such a process represents a **loss** of energy from the chemicals in a reaction.

Chlorine has the most negative electron affinity of any element, which means that more energy is released when an electron is added to a gaseous chlorine atom than to an atom of any other element:

$$Cl\,(g) + e^- \rightarrow Cl\,(g)^- \quad Ea = -348.6\ kJ/mol$$

In contrast, beryllium does not form a stable anion, so its effective electron affinity is

$$Be\,(g) + e^- \rightarrow Be\,(g)^- \quad Ea \geq 0\ kJ/mol$$

Nitrogen is unique in that it has an electron affinity of approximately zero. Adding an electron neither releases nor requires a significant amount of energy. We might remember that nitrogen has a half filled p orbital which adds to its stability:

$$N\,(g) + e^- \rightarrow N\,(g)^- \quad Ea \approx\ kJ/mol$$

Electron affinities for the first six rows of the periodic table are plotted in Figure 3.2.4 and presented numerically and graphically in Figure 3.2.6 . Both figures show that the halogens, with their ns^2np^5 valence electron configuration, have the most negative electron affinities. In general, electron affinities become more negative as we go across a row of the periodic table. This pattern corresponds to the increased effective nuclear charge felt by the valence electrons across a row, which leads to increased electrostatic attraction between the added electron and the nucleus (a more negative electron affinity). The trend, however, is not as uniform as the one observed for ionization energies. Some of the alkaline earths (group 2), the elements of group 12, and all the noble gases (group 18) have effective electron affinities that are greater than or equal to zero, while the electron affinities for the elements of group 15 are usually less negative than those for the group 14 elements. These exceptions can be explained by the groups' electron configurations. Both the alkaline earth metals and the noble gases have valence electron shells with filled subshells (ns^2 and ns^2np^6, respectively). In each case, the added electron must enter a higher-energy orbital, requiring an input of energy. All the group 15 elements have an ns^2np^3 valence electron configuration, in which each of the three *p* orbitals has a single electron, in accordance with Hund's rule; hence the added electron must enter an already occupied *p* orbital. The resulting electron–electron repulsions destabilize the anion, causing the electron affinities of these elements to be less negative than we would otherwise expect. In the case of nitrogen, the 2*p* orbital is quite small, and the electron–electron repulsions are so strong that nitrogen has approximately zero affinity for an extra electron. In the heavier elements, however, the effect is relatively small because they have larger valence *p* orbitals.

Note the Pattern

Generally, electron affinities become more negative across a row of the periodic table.

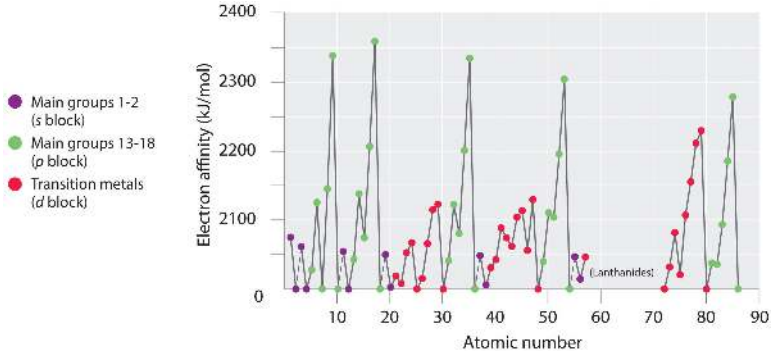


Figure 3.2.4 A Plot of Periodic Variation of Electron Affinity with Atomic Number for the First Six Rows of the Periodic Table*Can you explain the breaks in Figure 3.2.4 based on what you know about atomic structure and filled and half filled orbitals? This is more difficult than the equivalent for ionization energy.*

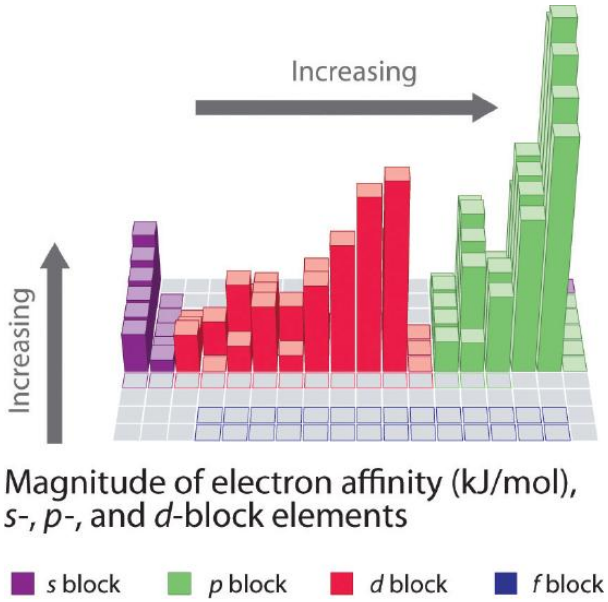


Figure 3.2.5 Bar Chart of the Periodic Variation of Electron Affinity with Atomic Number for the First Six Rows of the Periodic Table

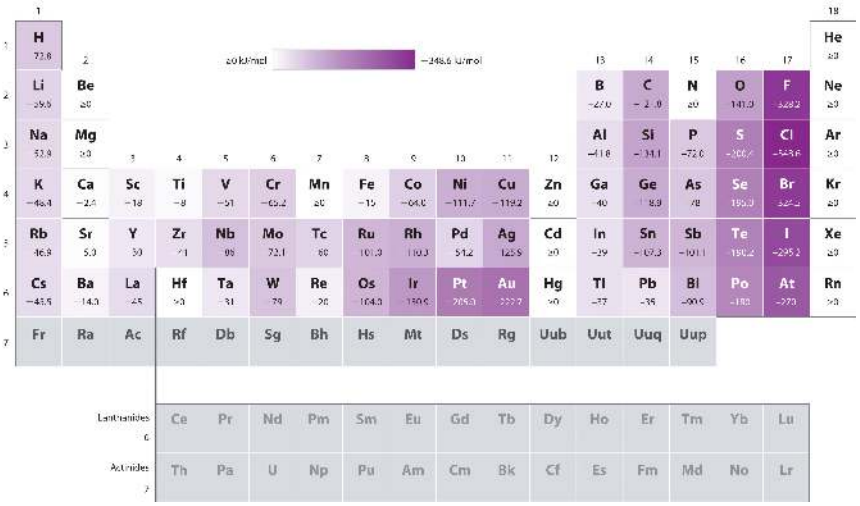


Figure 3.2.6 Electron Affinities (in kJ/mol) of the *s*-, *p*-, and *d*-Block Elements *There are many more exceptions to the trends across rows and down columns than with first ionization energies. Elements that do not form stable ions, such as the noble gases, are assigned an effective electron affinity that is greater than or equal to zero. Elements for which no data are available are shown in gray. Source: Data from Journal of Physical and Chemical Reference Data 28, no. 6 (1999).*

In general, electron affinities of the main-group elements become less negative as we proceed down a column. This is because as n increases, the extra electrons enter orbitals that are increasingly far from the nucleus. Atoms with the largest radii, which have the lowest ionization energies (affinity for their own valence electrons), also have the lowest affinity for an added electron. There are, however, two major exceptions to this trend:

1. The electron affinities of elements B through F in the second row of the periodic table are *less* negative than those of the elements immediately below them in the third row. Apparently, the increased electron–electron repulsions experienced by electrons confined to the relatively small 2*p* orbitals overcome the increased electron–nucleus attraction at short nuclear distances. Fluorine, therefore, has a lower affinity for an added electron than does chlorine. Consequently, the elements of the *third* row (n = 3) have the most negative electron affinities. Farther down a column, the attraction for an added electron decreases because the electron is entering an orbital more distant from the nucleus. Electron–electron repulsions also decrease

because the valence electrons occupy a greater volume of space. These effects tend to cancel one another, so the changes in electron affinity within a family are much smaller than the changes in ionization energy.

2. The electron affinities of the alkaline earth metals become more negative from Be to Ba. As you learned in Chapter 2, the energy separation between the filled ns^2 and the empty np subshells decreases with increasing n, so that formation of an anion from the heavier elements becomes energetically more favorable.

Note the Pattern

In general, electron affinities become more negative across a row and less negative down a column.

The equations for second and higher electron affinities are analogous to those for second and higher ionization energies:

$$E(g) + e^- \rightarrow E(g)^- \quad energy\ change\ = Ea_1$$

$$E(g)^- + e^- \rightarrow E(g)^{2-} \quad energy\ change\ = Ea_2$$

As we have seen, the first electron affinity can be greater than or equal to zero or negative, depending on the electron configuration of the atom. In contrast, the second electron affinity is *always* positive because the increased electron–electron repulsions in a dianion are far greater than the attraction of the nucleus for the extra electrons. For example, the first electron affinity of oxygen is −141 kJ/mol, but the second electron affinity is +744 kJ/mol:

$$O(g) + e^- \rightarrow O(g)^- \quad Ea = -141\ kJ/mol$$

$$O(g)^- + e^- \rightarrow O(g)^{2-} \quad Ea_2 = +744\ kJ/mol$$

Thus the formation of a gaseous oxide (O^{2-}) ion is energetically quite unfavorable:

$$O(g) + 2e^- \rightarrow O(g)^{2-} \quad Ea_1 + Ea_2 = +603\ kJ/mol$$

Similarly, the formation of all common dianions (such as S^{2-}) or trianions (such as P^{3-}) is energetically unfavorable in the gas phase.

Note the Pattern

While first electron affinities can be negative, positive, or zero, second electron affinities are always positive.

If energy is required to form both positively charged ions and monatomic polyanions, why do ionic compounds such as MgO, Na_2S, and Na_3P form at all? The key factor in the formation of stable ionic compounds is the favorable electrostatic interactions between the cations and the anions *in the crystalline salt*. We will describe the energetics of ionic compounds in more detail in Chapter 4 "Chemical Bonding".

Example 3.2.3

Based on their positions in the periodic table, which of Sb, Se, or Te would you predict to have the most negative electron affinity?

Given: three elements

Asked for: element with most negative electron affinity

Strategy:

A Locate the elements in the periodic table. Use the trends in electron affinities going down a column for elements in the same group. Similarly, use the trends in electron affinities from left to right for elements in the same row.

B Place the elements in order, listing the element with the most negative electron affinity first.

Solution:

A We know that electron affinities become less negative going down a column (except for the anomalously low electron affinities of the elements of the second row), so we can predict that the electron affinity of Se is more negative than that of Te. We also know that electron affinities become more negative from left to right across a row, and that the group 15 elements tend to have values that are less negative than expected. Because Sb is located to the left of Te and belongs to group 15, we predict that the electron affinity of Te is more negative than that of Sb. The overall order is Se < Te < Sb, so Se has the most negative electron affinity among the three elements.

Exercise

Based on their positions in the periodic table, which of Rb, Sr, or Xe would you predict to most likely form a gaseous anion?

Answer: Rb

Electronegativity

The elements with the highest ionization energies are generally those with the most negative electron affinities, which are located toward the upper right corner of the periodic table (compare Figure 3.2.1). Conversely, the elements with the lowest ionization energies are generally those with the least negative electron affinities and are located in the lower left corner of the periodic table.

Because the tendency of an element to gain or lose electrons is so important in determining its chemistry, various methods have been developed to quantitatively describe this tendency. The most important method uses a measurement called electronegativityThe relative ability of an atom to attract electrons to itself in a chemical compound. (represented by the Greek letter *chi*, χ, pronounced “ky” as in “sky”), defined as the *relative* ability of an atom to attract electrons to itself *in a chemical compound*. Elements with high electronegativities tend to acquire electrons in chemical reactions and are found in the upper right corner of the periodic table. Elements with low electronegativities tend to lose electrons in chemical reactions and are found in the lower left corner of the periodic table.

Unlike ionization energy or electron affinity, the electronegativity of an atom is not a simple, fixed property that can be directly measured in a single experiment. In fact, an atom’s electronegativity should depend to some extent on its chemical environment because the properties of an atom are influenced by its neighbors in a chemical compound. Nevertheless, when different methods for measuring the electronegativity of an atom are compared, they all tend to assign similar relative values to a given element. For example, all scales predict that fluorine has the highest electronegativity and cesium the lowest of the stable elements, which suggests that all the methods are measuring the same fundamental property.

The Pauling Electronegativity Scale

The original electronegativity scale, developed in the 1930s by Linus Pauling (1901– 1994) was based on measurements of the strengths of covalent bonds between different elements. Pauling arbitrarily set the electronegativity of fluorine at 4.0 (although today it has been refined to 3.98), thereby creating a scale in which all elements have values between 0 and 4.0.

Periodic variations in Pauling’s electronegativity values are illustrated in Figure 3.2.7 and Figure 3.2.9 . If we ignore the inert gases and elements for which no stable isotopes are known, we see that fluorine (χ = 3.98) is the most electronegative element and cesium is the least electronegative nonradioactive element (χ = 0.79). Because electronegativities generally increase diagonally from the lower left to the upper right of the periodic table, elements lying on diagonal lines running from upper left to lower right tend to have comparable values (e.g., O and Cl and N, S, and Br).

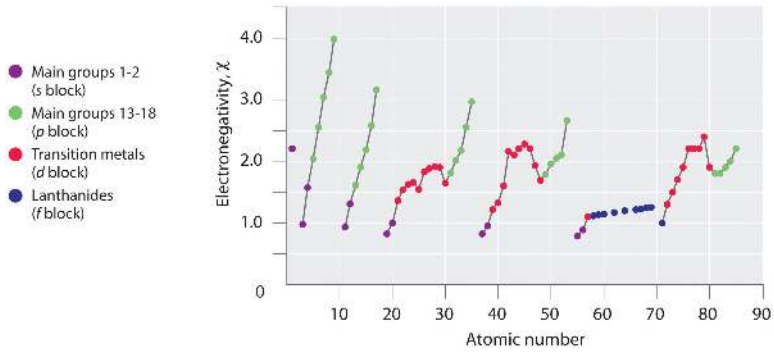


Figure 3.2.7 A Plot of Periodic Variation of Electronegativity with Atomic Number for the First Six Rows of the Periodic Table

Can you explain the breaks in Figure 3.2.7 based on what you know about atomic structure and filled and half filled d orbitals? Note how the electronegativity dependence on atomic number is smoother than the ionization and electron affinity.

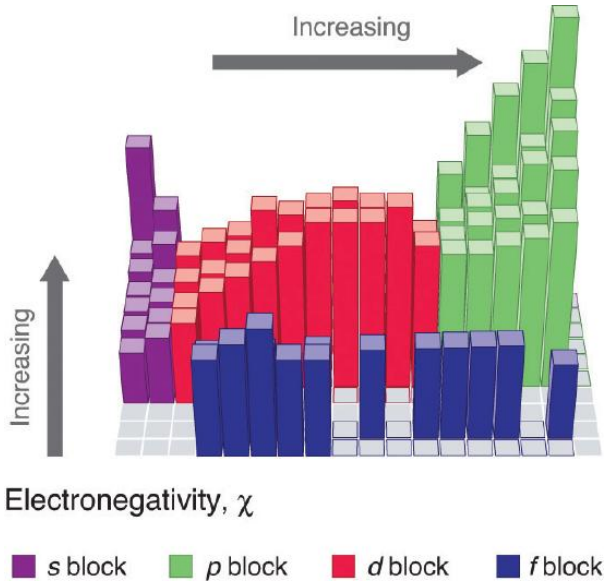


Figure 3.2.8 A Bar Graph of Electronegativity for Atoms in the First Six Rows of the Periodic Table

Linus Pauling (1901–1994)

Pauling won two Nobel Prizes, one for chemistry in 1954 and one for peace in 1962. When he was nine, Pauling's father died, and his mother tried to convince him to quit school to support the family. He did not quit school but was denied a high school degree because of his refusal to take a civics class.

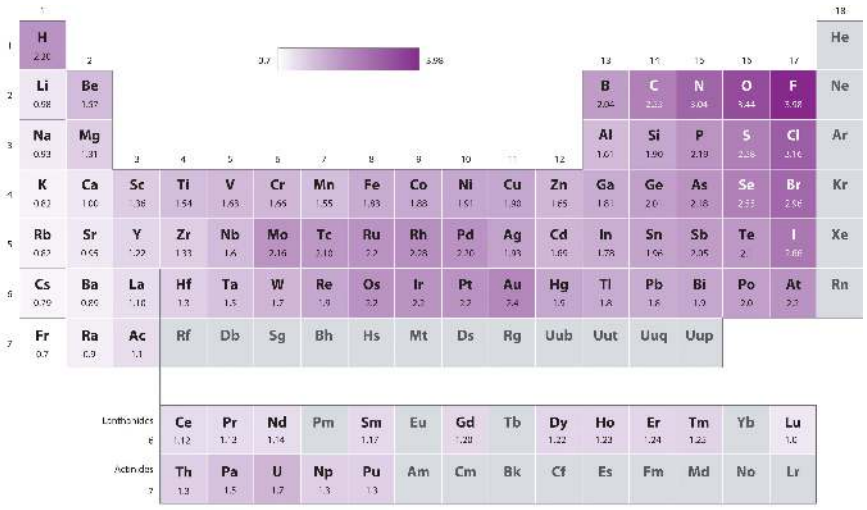


Figure 3.2.9 Pauling Electronegativity Values of the *s*-, *p*-, *d*-, and *f*-Block Elements*Values for most of the actinides are approximate. Elements for which no data are available are shown in gray. Source: Data from L. Pauling, The Nature of the Chemical Bond, 3rd ed. (1960).*

Pauling's method is limited by the fact that many elements do not form stable covalent compounds with other elements; hence their electronegativities cannot be measured by his method. Other definitions have since been developed that address this problem.

The Mulliken Definition

An alternative method for measuring electronegativity was developed by Robert Mulliken (1896–1986; Nobel Prize in Chemistry 1966). Mulliken noticed that elements with large first ionization energies tend to have very negative electron affinities and gain electrons in chemical reactions. Conversely, elements with small first ionization energies tend to have slightly negative (or even positive) electron affinities and lose electrons in chemical reactions. Mulliken recognized that an atom's tendency to gain or lose electrons could therefore be described quantitatively by the average of the values of its first ionization energy and the absolute

value of its electron affinity. Using our definition of electron affinity, we can write Mulliken's original expression for electronegativity as follows:Mulliken's definition used the magnitude of the ionization energy and the electron affinity. By definition, the magnitude of a quantity is a positive number. Our definition of electron affinity produces negative values for the electron affinity for most elements, so vertical lines indicating absolute value are needed in Equation 3.2.13 to make sure that we are adding two positive numbers in the numerator.

$$x = \frac{I+|EA|}{2}$$

Bearing in mind that the magnitude of ionization energies are generally large compared to the those of electron affinities, elements with a large first ionization energy and a very negative electron affinity have a large positive value in the numerator of Equation 3.2.13 so their electronegativity is high. Elements with a small first ionization energy and a small electron affinity have a small positive value for the numerator in Equation 3.2.13, so they have a low electronegativity.Inserting the appropriate data for ionization energy and electron affinity into Equation 3.2.13 gives a Mulliken electronegativity value for fluorine of 1004.6 kJ/mol. To compare Mulliken's electronegativity values with those obtained by Pauling, Mulliken's values are divided by 252.4 kJ/mol, which gives Pauling's value (3.98).

As noted previously, all electronegativity scales give essentially the same results for one element relative to another. Even though the Mulliken scale is based on the properties of individual *atoms* and the Pauling scale is based on the properties of atoms in *molecules*, they both apparently measure the same basic property of an element. In the following discussion, we will focus on the relationship between electronegativity and the tendency of *atoms* to form positive or negative ions. We will therefore be implicitly using the Mulliken definition of electronegativity. Because of the parallels between the Mulliken and Pauling definitions, however, the conclusions are likely to apply to atoms in molecules as well.

Electronegativity Differences between Metals and Nonmetals

An element's electronegativity provides us with a single value that we can use to characterize the chemistry of an element. Elements with a high electronegativity ($\chi \geq 2.2$ in Figure 3.2.9) have very negative electron affinities and large ionization potentials, so they are generally nonmetals and electrical insulators that tend to gain electrons in chemical reactions (i.e., they are *oxidants*). In contrast, elements with a low electronegativity ($\chi \leq 1.8$) have electron affinities that have either positive or small negative values and small ionization potentials, so they are generally metals and good electrical conductors that tend to lose their valence electrons in chemical reactions (i.e., they are *reductants*). In between the metals and nonmetals, along the diagonal line running from B to At is a group of elements with intermediate electronegativities ($\chi \sim 2.0$). These are the **semimetals**, elements that have some of the chemical properties of both nonmetals and metals. The distinction between metals and nonmetals is one of the most fundamental we can make in categorizing the elements and predicting their chemical behavior. Figure 3.2.10 shows the strong correlation between electronegativity values, metallic versus nonmetallic character, and location in the periodic table.

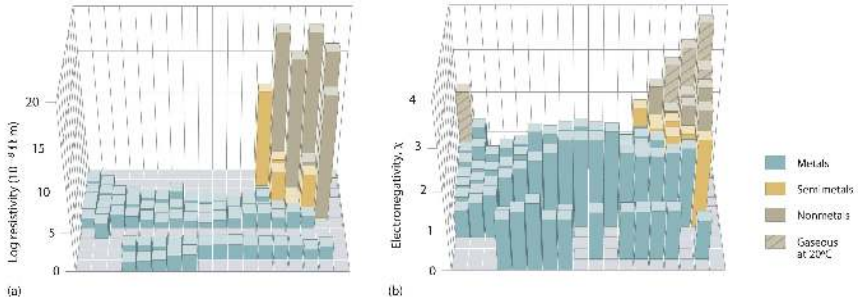


Figure 3.2.10 Three-Dimensional Plots Demonstrating the Relationship between Electronegativity and the Metallic/Nonmetallic Character of the Elements *(a) A plot of electrical resistivity (measured resistivity to electron flow) at or near room temperature shows that substances with high resistivity (little to no measured electron flow) are electrical insulators, whereas substances with low resistivity (high measured electron flow) are metals. (b) A plot of Pauling electronegativities for a like set of elements shows that high electronegativity values (≥ about 2.2) correlate with high electrical resistivities (insulators). Low electronegativity values (≤ about 2.2) correlate with low resistivities (metals). Because electrical resistivity is typically measured only for solids and liquids, the gaseous elements do not appear in part (a).*

Example 3.2.4

On the basis of their positions in the periodic table, arrange Cl, Se, Si, and Sr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a semimetal.

Given: four elements

Asked for: order by increasing electronegativity and classification

Strategy:

A Locate the elements in the periodic table. From their diagonal positions from lower left to upper right, predict their relative electronegativities.

B Arrange the elements in order of increasing electronegativity.

C Classify each element as a metal, a nonmetal, or a semimetal according to its location about the diagonal belt of semimetals running from B to At.

Solution:

A Electronegativity increases from lower left to upper right in the periodic table (Figure 3.2.8). Because Sr lies far to the left of the other elements given, we can predict that it will have the lowest electronegativity. Because Cl lies above and to the right of Se, we can predict that $\chi_{Cl} > \chi_{Se}$. Because Si is located farther from the upper right corner than Se or Cl, its electronegativity should be lower than those of Se and Cl but greater than that of Sr. **B** The overall order is therefore $\chi_{Sr} < \chi_{Si} < \chi_{Se} < \chi_{Cl}$.

C To classify the elements, we note that Sr lies well to the left of the diagonal belt of semimetals running from B to At; while Se and Cl lie to the right and Si lies in the middle. We can predict that Sr is a metal, Si is a semimetal, and Se and Cl are nonmetals.

Exercise

On the basis of their positions in the periodic table, arrange Ge, N, O, Rb, and Zr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a semimetal.

Answer: Rb < Zr < Ge < N < O; metals (Rb, Zr); semimetal (Ge); nonmetal (N, O)

Note the Pattern

Electronegativity values increase from lower left to upper right in the periodic table.

The trends in periodic properties are summarized in Figure 3.2.11. As discussed, atomic radii decrease from lower left to upper right in the periodic table; ionization energies become more positive, electron affinities become more negative, and electronegativities increase from the lower left to the upper right.

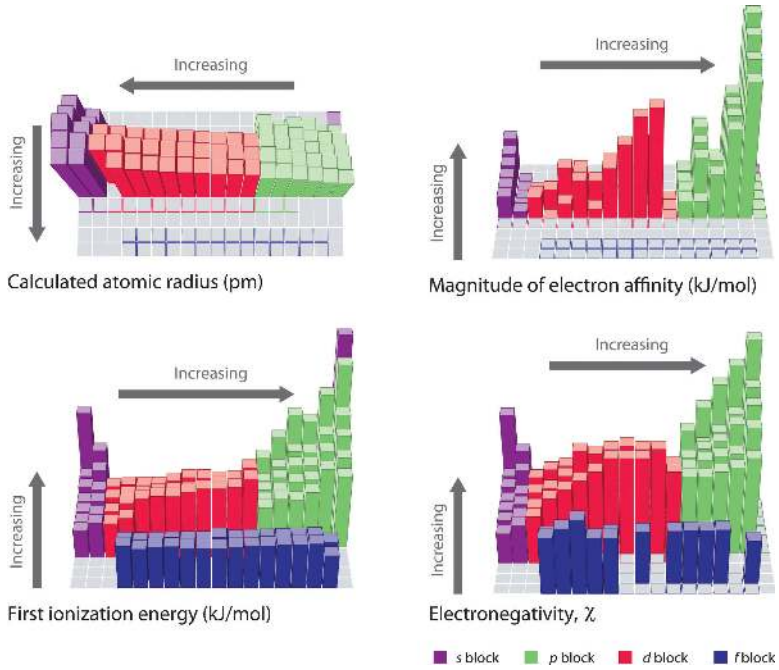


Figure 3.2.11 Summary of Major Periodic Trends*The general trends for the first ionization energy, electron affinity, and electronegativity are opposite to the general trend for covalent atomic radius.*

Summary

The tendency of an element to lose or gain electrons is one of the most important factors in determining the kind of compounds it forms. Periodic behavior is most evident for **ionization energy (*I*)**, the energy required to remove an electron from a gaseous atom. The energy required to remove successive electrons from an atom increases steadily, with a substantial increase occurring with the removal of an electron from a filled inner shell. Consequently, only valence electrons can be removed in chemical reactions, leaving the filled inner shell intact. Ionization energies explain the common oxidation states observed for the elements. Ionization energies increase diagonally from the lower left of the periodic table to the upper right. Minor deviations from this trend can be explained in terms of particularly stable electronic configurations, called **pseudo noble gas configurations**, in either the parent atom or the resulting ion. The **electron affinity (*EA*)** of an element is the energy change that occurs when an electron is added to a gaseous atom to give an anion. In general, elements with the most negative electron affinities (the highest affinity for an added electron) are those with the smallest size and highest ionization energies and are located in the upper right corner of the periodic table. The **electronegativity (χ)** of an element is the relative ability of an atom to attract electrons to itself in a chemical compound and increases diagonally from the lower left of the periodic table to the upper right. The Pauling electronegativity scale is based on measurements of the strengths of covalent bonds between different atoms, whereas the Mulliken electronegativity of an element is the average of its first ionization energy and the absolute value of its electron affinity. Elements with a high electronegativity are generally nonmetals and electrical insulators and tend to behave as oxidants in chemical reactions. Conversely, elements with a low electronegativity are generally metals and good electrical conductors and tend to behave as reductants in chemical reactions.

Key Takeaway

- Generally, the first ionization energy and electronegativity values increase diagonally from the lower left of the periodic table to the upper right, and electron affinities become more negative across a row.

Conceptual Problems

1. Identify each statement as either true or false and explain your reasoning.
    1. Ionization energies increase with atomic radius.
    2. Ionization energies decrease down a group.
    3. Ionization energies increase with an increase in the magnitude of the electron affinity.
    4. Ionization energies decrease diagonally across the periodic table from He to Cs.

5. Ionization energies depend on electron configuration.
6. Ionization energies decrease across a row.

2. Based on electronic configurations, explain why the first ionization energies of the group 16 elements are lower than those of the group 15 elements, which is contrary to the general trend.
3. The first through third ionization energies do not vary greatly across the lanthanides. Why? How does the effective nuclear charge experienced by the *ns* electron change when going from left to right (with increasing atomic number) in this series?
4. Most of the first row transition metals can form at least two stable cations, for example iron(II) and iron(III). In contrast, scandium and zinc each form only a single cation, the Sc^{3+} and Zn^{2+} ions, respectively. Use the electron configuration of these elements to provide an explanation.
5. Of the elements Nd, Al, and Ar, which will readily form(s) +3 ions? Why?
6. Orbital energies can reverse when an element is ionized. Of the ions B^{3+}, Ga^{3+}, Pr^{3+}, Cr^{3+}, and As^{3+}, in which would you expect this reversal to occur? Explain your reasoning.
7. The periodic trends in electron affinities are not as regular as periodic trends in ionization energies, even though the processes are essentially the converse of one another. Why are there so many more exceptions to the trends in electron affinities compared to ionization energies?
8. Elements lying on a lower right to upper left diagonal line cannot be arranged in order of increasing electronegativity according to where they occur in the periodic table. Why?
9. Why do ionic compounds form, if energy is required to form gaseous cations?
10. Why is Pauling's definition of electronegativity considered to be somewhat limited?
11. Based on their positions in the periodic table, arrange Sb, O, P, Mo, K, and H in order of increasing electronegativity.
12. Based on their positions in the periodic table, arrange V, I, B, In, Na, and S in order of decreasing electronegativity.

Answers

1.
2.
3. Both Al and Nd will form a cation with a +3 charge. Aluminum is in Group 13, and loss of all three valence electrons will produce the Al^{3+} ion with a noble gas configuration. Neodymium is a lanthanide, and all of the lanthanides tend to form +3 ions because the ionization potentials do not vary greatly across the row, and a +3 charge can be achieved with many oxidants.
4.
5.
6.
7.
8.
9.
10.
11. K < Mo ≈ Sb < P ≈ H < O
12.

Numerical Problems

1. The following table gives values of the first and third ionization energies for selected elements:

Number of Electrons	Element	I_1 ($E \rightarrow E^+ + e^-$, kJ/mol)	Element	I_3 ($E^{2+} \rightarrow E^{3+} + e^-$, kJ/mol)
11	Na	495.9	Al	2744.8
12	Mg	737.8	Si	3231.6
13	Al	577.6	P	2914.1
14	Si	786.6	S	3357
15	P	1011.9	Cl	3822
16	S	999.6	Ar	3931
17	Cl	1251.2	K	4419.6
18	Ar	1520.6	Ca	4912.4

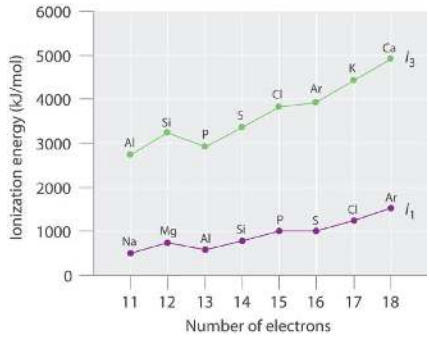
Plot the ionization energies versus number of electrons. Explain why the slopes of the I_1 and I_3 plots are different, even though the species in each row of the table have the same electron configurations.

2. Would you expect the third ionization energy of iron, corresponding to the removal of an electron from a gaseous Fe^{2+} ion, to be larger or smaller than the fourth ionization energy, corresponding to removal of an electron from a gaseous Fe^{3+} ion? Why? How would these ionization energies compare to the first ionization energy of Ca?
3. Which would you expect to have the highest first ionization energy: Mg, Al, or Si? Which would you expect to have the highest third ionization energy. Why?
4. Use the values of the first ionization energies given in Figure 3.3.3 to construct plots of first ionization energy versus atomic number for (a) boron through oxygen in the second period; and (b) oxygen through tellurium in group 16. Which plot shows more variation? Explain the reason for the variation in first ionization energies for this group of elements.
5. Arrange Ga, In, and Zn in order of increasing first ionization energies. Would the order be the same for second and third ionization energies? Explain your reasoning.
6. Arrange each set of elements in order of increasing magnitude of electron affinity.
    1. Pb, Bi, and Te
    2. Na, K, and Rb
    3. P, C, and Ge
7. Arrange each set of elements in order of decreasing magnitude of electron affinity.
    1. As, Bi, and N
    2. O, F, and Ar
    3. Cs, Ba, and Rb
8. Of the species F, O^-, Al^{3+}, and Li^+, which has the highest electron affinity? Explain your reasoning.
9. Of the species O^-, N^{2-}, Hg^{2+}, and H^+, which has the highest electron affinity? Which has the lowest electron affinity? Justify your answers.
10. The Mulliken electronegativity of element A is 542 kJ/mol. If the electron affinity of A is −72 kJ/mol, what is the first ionization energy of element A? Use the data in the following table as a guideline to decide if A is a metal, a nonmetal, or a semimetal. If 1 g of A contains 4.85×10^{21} molecules, what is the identity of element A?

	Na	Al	Si	S	Cl
EA (kJ/mol)	−59.6	−41.8	−134.1	−200.4	−348.6
I (kJ/mol)	495.8	577.5	786.5	999.6	1251.2

11. Based on their valence electron configurations, classify the following elements as either electrical insulators, electrical conductors, or substances with intermediate conductivity: S, Ba, Fe, Al, Te, Be, O, C, P, Sc, W, Na, B, and Rb.
12. Using the data in Problem 10, what conclusions can you draw with regard to the relationship between electronegativity and electrical properties? Estimate the approximate electronegativity of a pure element that is very dense, lustrous, and malleable.

Answers

1. 

   The general features of both plots are roughly the same, with a small peak at 12 electrons and an essentially level region from 15–16 electrons. The slope of the I_3 plot is about twice as large as the slope of the I_1 plot, however, because the I_3 values correspond to removing an electron from an ion with a +2 charge rather than a neutral atom. The greater charge increases the effect of the steady rise in effective nuclear charge across the row.

2.

3. Electron configurations: Mg, $1s^2 2s^2 2p^6 3s^2$; Al, $1s^2 2s^2 2p^6 3s^2 3p^1$; Si, $1s^2 2s^2 2p^6 3s^2 3p^2$; First ionization energies increase across the row due to a steady increase in effective nuclear charge; thus, Si has the highest first ionization energy. The third ionization energy corresponds to removal of a 3*s* electron for Al and Si, but for Mg it involves removing a 2*p* electron from a filled inner shell; consequently, the third ionization energy of Mg is the highest.

4.

5.

6.

7. 1. Bi > As > N
   2. F > O >> Ar
   3. Rb > Cs > Ba

8.

9. $Hg^{2+} > H^+ > O^- > N^{2-}$; Hg^{2+} has the highest positive charge plus a relatively low energy vacant set of orbitals (the 6*p* subshell) to accommodate an added electron, giving it the greatest electron affinity; N^{2-} has a greater negative charge than O^-, so electron–electron repulsions will cause its electron affinity to be even lower (more negative) than that of O^-.

10.

11. insulators: S, O, C (diamond), P; conductors: Ba, Fe, Al, C (graphite), Be, Sc, W, Na, Rb; Te and B are semimetals and semiconductors.

12.

13.

14.
15.
16.

Contributors

- Anonymous

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Chapter 3.3: The Chemical Families

Learning Objectives

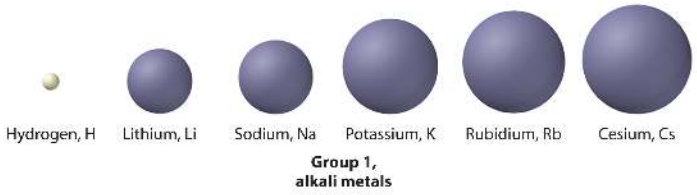
- To understand the correlation between the chemical properties and the reactivity of the elements and their positions in the periodic table.

Periodic trends in properties such as atomic size and ionic size, ionization energy, electron affinity, and electronegativity illustrate the strong connection between the **chemical properties** and the reactivity of the elements and their positions in the periodic table. In this section, we explore that connection by focusing on two periodic properties that correlate strongly with the chemical behavior of the elements: valence electron configurations and Mulliken electronegativities.

The Main Group Elements

We have said that elements with the same valence electron configuration (i.e., elements in the same column of the periodic table) often have similar chemistry. This correlation is particularly evident for the elements of groups 1, 2, 3, 13, 16, 17, and 18. The intervening families in the *p* block (groups 14 and 15) straddle the diagonal line separating metals from nonmetals. The lightest members of these two families are nonmetals, so they react differently compared to the heaviest members, which are metals. We begin our survey with the alkali metals (group 1), which contain only a single electron outside a noble gas electron configuration, and end with the noble gases (group 18), which have full valence electron shells.

Group 1: The Alkali Metals



The elements of group 1 are called the *alkali metals*. *Alkali* (from the Arabic *al-qili*, meaning “ashes of the saltwort plant from salt marshes”) was a general term for substances derived from wood ashes, all of which possessed a bitter taste and were able to neutralize acids. Although oxides of both group 1 and group 2 elements were obtained from wood ashes, the alkali metals had lower melting points.

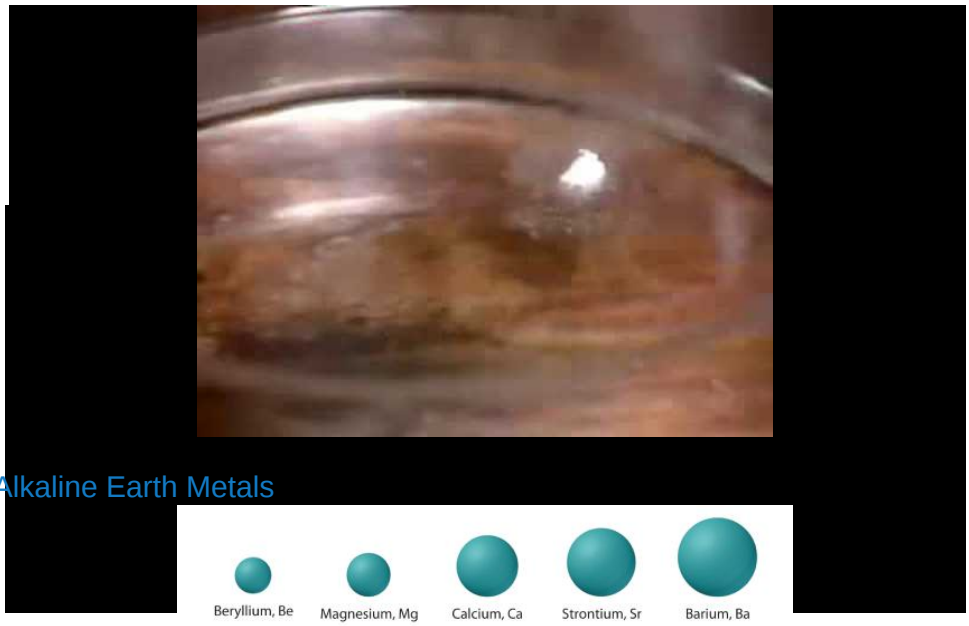
Potassium and sodium were first isolated in 1807 by the British chemist Sir Humphry Davy (1778–1829) by passing an electrical current through molten samples of potash (K_2CO_3) and soda ash (Na_2CO_3). The potassium burst into flames as soon as it was produced because it reacts readily with oxygen at the higher temperature. However, the group 1 elements, like the group 2 elements, become less reactive with air or water as their atomic number decreases. The heaviest element (francium) was not discovered until 1939. It is so radioactive that studying its chemistry is very difficult.

The alkali metals have ns^1 valence electron configurations and the lowest electronegativity of any group; hence they are often referred to as being *electropositive* elements. As a result, they have a strong tendency to lose their single valence electron to form compounds in the +1 oxidation state, producing the EX monohalides and the E_2O oxides.

Reducing agents are species that can lose an electron in a reaction. Alkalai metals with only a single s electron, and very low ionization energies can easily do this and thus are powerful reducing agents. Sodium salts such as common table salt (NaCl), baking soda ($NaHCO_3$), soda ash (Na_2CO_3), and caustic soda (NaOH) are important industrial chemicals. Other compounds of the alkali metals are important in biology. For example, because potassium is required for plant growth, its compounds are used in fertilizers, and lithium salts are used to treat manic-depressive, or bipolar, disorders. The best modern batteries use lithium.

We can watch a video demonstration of the properties of lithium, sodium and potassium. Rubidium and cesium are extremely reactive and difficult to handle in the atmosphere when there is any water vapor present





Group 2: The Alkaline Earth Metals



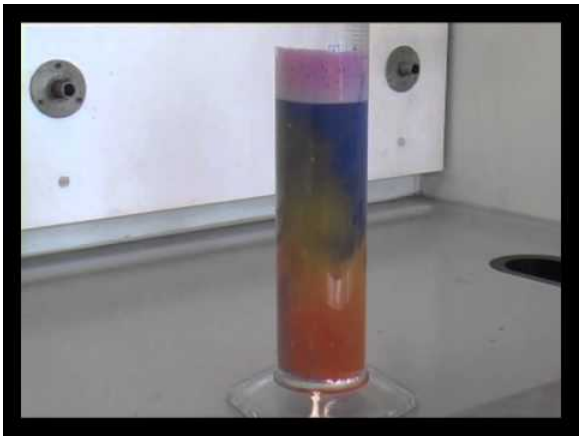
The elements of group 2 are collectively referred to as the *alkaline earth metals*, a name that originated in the Middle Ages, when an “earth” was defined as a substance that did not melt and was not transformed by fire. Alkalis that did not melt easily were called “alkaline earths.”

Recall that the trend in most groups is for the lightest member to have properties that are quite different from those of the heavier members. Consistent with this trend, the properties of the lightest element—in this case, beryllium—tend to be different from those of its heavier *congeners*, the other members of the group. Beryllium is relatively unreactive but forms many covalent compounds, whereas the other group members are much more reactive metals and form ionic compounds. As is the case with the alkali metals, the heaviest element, radium, is highly radioactive, making its size difficult to measure. Radium was discovered in 1902 by Marie Curie (1867–1934; Nobel Prize in Chemistry 1903 and Nobel Prize in Chemistry 1911), who, with her husband, Pierre, isolated 120 mg of radium chloride from tons of residues from uranium mining.

All the alkaline earth metals have ns^2 valence electron configurations, and all have electronegativities less than 1.6. This means that they behave chemically as metals (although beryllium compounds are covalent) and lose the two valence electrons to form compounds in the +2 oxidation state. Examples include the dihalides (EX_2) and the oxides (EO).

Compounds of the group 2 elements have been commercially important since Egyptian and Roman times, when blocks of limestone or marble, which are both $CaCO_3$, were used as building materials, and gypsum ($CaSO_4 \cdot 2\ H_2O$) or lime (CaO) was used as mortar. Calcium sulfate is still used in Portland cement and plaster of Paris. Magnesium and beryllium form lightweight, high-strength alloys that are used in the aerospace, automotive, and other high-tech industries. As you learned in Chapter 2, one of the most impressive uses of these elements is in fireworks; strontium and barium salts, for example, give red or green colors, respectively. Except for beryllium, which is highly toxic when powdered, the group 2 elements are also important biologically. Bone is largely hydroxyapatite [$Ca_5(PO_4)_3OH$], mollusk shells are calcium carbonate, magnesium is part of the chlorophyll molecule in green plants, and calcium is important in hormonal and nerve signal transmission. Because $BaSO_4$ is so insoluble, it is used in “barium milk shakes” to obtain x-rays of the gastrointestinal tract. Reaction of the Alkaline earth metals with water is not quite so. . . .exciting as that of the alkalai metals as seen in this video from the University of Southampton



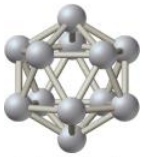


Group 13



Group 13

Of the group 13 elements, only the lightest, boron, lies on the diagonal line that separates nonmetals and metals. Thus boron is a semimetal, whereas the rest of the group 13 elements are metals. Elemental boron has an unusual structure consisting of B_{12} icosahedra covalently bonded to one another; the other elements are typical metallic solids.



B_{12} icosahedron in elemental boron

No group 13 elements were known in ancient times, not because they are scarce—Al is the third most abundant element in Earth's crust—but because they are highly reactive and form extremely stable compounds with oxygen. To isolate the pure elements, potent reducing agents and careful handling were needed.

The elements of group 13 have ns^2np^1 valence electron configurations. Consequently, two oxidation states are important: +3, from losing three valence electrons to give the closed-shell electron configuration of the preceding noble gas; and +1, from losing the single electron in the *np* subshell. Because these elements have small, negative electron affinities (boron's is only −27.0 kJ/mol), they are unlikely to acquire five electrons to reach the next noble gas configuration. In fact, the chemistry of these elements is almost exclusively characterized by +3. Only the heaviest element (Tl) has extensive chemistry in the +1 oxidation state. It loses the single 6*p* electron to produce TlX monohalides and the oxide Tl_2O.

In the 19th century, aluminum was considered a precious metal. In fact, it was considered so precious that aluminum knives and forks were reserved for the French Emperor Louis Napoleon III, while his less important guests had to be content with gold or silver cutlery. Because of the metal's rarity the dedication of the Washington Monument in 1885 was celebrated by placing a 100 oz chunk of pure aluminum at the top. In contrast, today aluminum is used on an enormous scale in aircraft, automobile engines, armor, cookware, and beverage containers. It is valued for its combination of low density, high strength, and corrosion resistance. Aluminum is also found in compounds that are the active ingredients in most antiperspirant deodorants.

Compounds of boron, such as one form of BN, are hard, have a high melting point, and are resistant to corrosion. They are particularly useful in materials that are exposed to extreme conditions, such as aircraft turbines, brake linings, and polishing compounds. Boron is also a major component of many kinds of glasses, and sodium perborate $[Na_2B_2O_4(OH)_4]$ is the active ingredient in many so-called color-safe laundry bleaches.

Gallium, indium, and thallium are less widely used, but gallium arsenide is the red light-emitting diode (LED) in digital readouts in electronics, and $MgGa_2O_4$ produces the green light emitted in many xerographic machines. Compounds of thallium(I) are extremely toxic. Although Tl_2SO_4 is an excellent rat or ant poison, it is so toxic to humans that it is no longer used for this purpose.

Group 14



Group 14

The group 14 elements straddle the diagonal line that divides nonmetals from metals. Of the elements in this group, carbon is a nonmetal, silicon and germanium are semimetals, and tin and lead are metals. As a result of this diversity, the structures of the pure elements vary greatly.

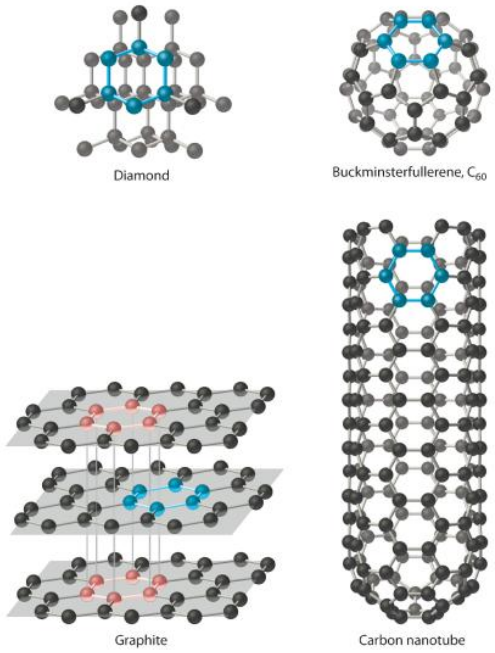
The ns^2np^2 valence electron configurations of group 14 gives rise to three oxidation states: −4, in which four electrons are added to achieve the closed-shell electron configuration of the next noble gas; +4, in which all four valence electrons are lost to give the closed-shell electron configuration of the preceding noble gas; and +2, in which the loss of two np^2 electrons gives a filled ns^2 subshell.

The electronegativity of carbon is only 2.5, placing it in the middle of the electronegativity range, so carbon forms covalent compounds with a wide variety of elements and is the basis of all organic compounds. All of the group 14 elements form compounds in the +4 oxidation state, so all of them are able to form dioxides (from CO_2 to PbO_2) and tetrachlorides (CCl_4 and $PbCl_4$). Only the two metallic elements, Sn and Pb, form an extensive series of compounds in the +2 oxidation state. Tin salts are sprayed onto glass to make an electrically conductive coating, and then the glass is used in the manufacture of frost-free windshields. Lead sulfate is formed when your car battery discharges.

Carbon has at least four allotropes (forms or crystal structures) that are stable at room temperature: graphite; diamond; a group of related cage structures called fullerenesOne of at least four allotropes of carbon comprising a group of related cage structures. (such as C_{60}); nanotubesOne of at least four allotropes of carbon that are cylinders of carbon atoms and are intermediate in structure between graphite and the fullerenes., which are cylinders of carbon atoms (Figure 3.3.1), and graphene which is a single atomic layer of carbon atoms covalently bonded. Graphite consists of extended planes of covalently bonded hexagonal rings. Because the

planes are not linked by covalent bonds, they can slide across one another easily. This makes graphite ideally suited as a lubricant and as the “lead” in lead pencils mixed with a bit of clay as a binder. Graphite also provides the black color in inks and tires, and graphite fibers are used in high-tech items such as golf clubs, tennis rackets, airplanes, and sailboats because of their lightweight, strength, and stiffness.

Figure 3.3.1 Four Allotropes of Carbon



Diamond consists of a rigid three-dimensional array of carbon atoms, making it one of the hardest substances known. In contrast, graphite forms from extended planes of covalently bonded hexagonal rings of carbon atoms that can slide across one another easily. Fullerenes are spherical or ellipsoidal molecules with six- and five-membered rings of carbon atoms, and nanotubes are sheets of graphite rolled up into a cylinder.

In contrast to the layered structure of graphite, each carbon atom in diamond is bonded to four others to form a rigid three-dimensional array, making diamond one of the hardest substances known; consequently, it is used in industry as a cutting tool. Fullerenes, on the other hand, are spherical or ellipsoidal molecules with six- and five-membered rings of carbon atoms; they are volatile substances that dissolve in organic solvents. Fullerenes of extraterrestrial origin have been found in meteorites and have been discovered in a cloud of cosmic dust surrounding a distant star, which makes them the largest molecules ever seen in space. Carbon nanotubes, intermediate in structure between graphite and the fullerenes, can be described as sheets of graphite that have been rolled up into a cylinder or, alternatively, fullerene cages that have been stretched in one direction. Carbon nanotubes are being studied for use in the construction of molecular electronic devices and computers. For example, fabrics that are dipped in an ink of nanotubes and then pressed to thin out the coating are turned into batteries that maintain their flexibility. This creates “wearable electronics” and allows for the possibility of incorporating electronics into flexible surfaces. When applied to a t-shirt, for example, the t-shirt is converted into an “e-shirt.”

Silicon is the second must abundant element in Earth’s crust. Both silicon and germanium have strong, three-dimensional network structures similar to that of diamond. Sand is primarily SiO_2, which is used commercially to make glass and prevent caking in food products. Complex compounds of silicon and oxygen with elements such as aluminum are used in detergents and talcum powder and as industrial catalysts. Because silicon-chip technology laid the foundation for the modern electronics industry, the San Jose region of California, where many of the most important advances in electronics and computers were developed, has been nicknamed “Silicon Valley.”

Elemental tin and lead are metallic solids. Tin is primarily used to make alloys such as bronze, which consists of tin and copper; solder, which is tin and lead; and pewter, which is tin, antimony, and copper.

In ancient times, lead was used for everything from pipes to cooking pots because it is easily hammered into different shapes. In fact, the term *plumbing* is derived from *plumbum*, the Latin name for lead. Lead compounds were used as pigments in paints, and tetraethyllead was an important antiknock agent in gasoline. Now, however, lead has been banned from many uses because of its toxicity, although it is still widely used in lead storage batteries for automobiles. In previous centuries, lead salts were frequently used as medicines. Evidence suggests, for example, that Beethoven's death was caused by the application of various lead-containing medicines by his physician. Beethoven contracted pneumonia and was treated with lead salts, but in addition, he suffered from a serious liver ailment. His physician treated the ailment by repeatedly puncturing his abdominal cavity and then sealing the wound with a lead-laced poultice. It seems that the repeated doses of lead compounds contributed to Beethoven's death.

Group 15: The Pnicogens



The group 15 elements are called the pnicogensThe elements in group 15 of the periodic table.—from the Greek *pnigein*, meaning "to choke," and *genes*, meaning "producing"—ostensibly because of the noxious fumes that many nitrogen and phosphorus compounds produce. This family has five stable elements; one isotope of bismuth (^{209}Bi) is nonradioactive and is the heaviest nonradioactive isotope of any element. Once again, the lightest member of the family has unique properties. Although both nitrogen and phosphorus are nonmetals, nitrogen under standard conditions is a diatomic gas (N_2), whereas phosphorus consists of three allotropes: white, a volatile, low-melting solid consisting of P_4 tetrahedra; a red solid comprised of P_8, P_9, and P_{10} cages linked by P_2 units; and black layers of corrugated phosphorus sheets. The next two elements, arsenic and antimony, are semimetals with extended three-dimensional network structures, and bismuth is a silvery metal with a pink tint.

All of the pnicogens have ns^2np^3 valence electron configurations, leading to three common oxidation states: −3, in which three electrons are added to give the closed-shell electron configuration of the next noble gas; +5, in which all five valence electrons are lost to give the closed-shell electron configuration of the preceding noble gas; and +3, in which only the three *np* electrons are lost to give a filled ns^2 subshell. Because the electronegativity of nitrogen is similar to that of chlorine, nitrogen accepts electrons from most elements to form compounds in the −3 oxidation state (such as in NH_3). Nitrogen has only positive oxidation states when combined with highly electronegative elements, such as oxygen and the halogens (e.g., HNO_3, NF_3). Although phosphorus and arsenic can combine with active metals and hydrogen to produce compounds in which they have a −3 oxidation state (PH_3, for example), they typically attain oxidation states of +3 and +5 when combined with more electronegative elements, such as PCl_3 and H_3PO_4. Antimony and bismuth are relatively unreactive metals, but form compounds with oxygen and the halogens in which their oxidation states are +3 and +5 (as in Bi_2O_3 and SbF_5).

Although it is present in most biological molecules, nitrogen was the last pnicogen to be discovered. Nitrogen compounds such as ammonia, nitric acid, and their salts are used agriculturally in huge quantities; nitrates and nitrites are used as preservatives in meat products such as ham and bacon, and nitrogen is a component of nearly all explosives.

Phosphorus, too, is essential for life, and phosphate salts are used in fertilizers, toothpaste, and baking powder. One, phosphorus sulfide, P_4S_3, is used to ignite modern safety matches. Arsenic, in contrast, is toxic; its compounds are used as pesticides and poisons. Antimony and bismuth are primarily used in metal alloys, but a bismuth compound is the active ingredient in the popular antacid medication Pepto-Bismol.

Group 16: The Chalcogens



The group 16 elements are often referred to as the chalcogensThe elements in group 16 of the periodic table.—from the Greek *chalk*, meaning "copper," and *genes*, meaning "producing"—because the most ancient copper ore, copper sulfide, is also rich in two other group 16 elements: selenium and tellurium. Once again, the lightest member of the family has unique properties. In its

most common pure form, oxygen is a diatomic gas (O_2), whereas sulfur is a volatile solid with S_8 rings, selenium and tellurium are gray or silver solids that have chains of atoms, and polonium is a silvery metal with a regular array of atoms. Like astatine and radon, polonium is a highly radioactive metallic element.

All of the chalcogens have ns^2np^4 valence electron configurations. Their chemistry is dominated by three oxidation states: −2, in which two electrons are added to achieve the closed-shell electron configuration of the *next* noble gas; +6, in which all six valence electrons are lost to give the closed-shell electron configuration of the *preceding* noble gas; and +4, in which only the four *np* electrons are lost to give a filled ns^2 subshell. Oxygen has the second highest electronegativity of any element; its chemistry is dominated by the −2 oxidation state (as in MgO and H_2O). No compounds of oxygen in the +4 or +6 oxidation state are known. In contrast, sulfur can form compounds in all three oxidation states. Sulfur accepts electrons from less electronegative elements to give H_2S and Na_2S, for example, and it donates electrons to more electronegative elements to give compounds such as SO_2, SO_3, and SF_6. Selenium and tellurium, near the diagonal line in the periodic table, behave similarly to sulfur but are somewhat more likely to be found in positive oxidation states.

Oxygen, the second most electronegative element in the periodic table, was not discovered until the late 18th century, even though it constitutes 20% of the atmosphere and is the most abundant element in Earth's crust. Oxygen is essential for life; our metabolism is based on the oxidation of organic compounds by O_2 to produce CO_2 and H_2O. Commercially, oxygen is used in the conversion of pig iron to steel, as the oxidant in oxyacetylene torches for cutting steel, as a fuel for the US space shuttle, and in hospital respirators.

Sulfur is the brimstone in "fire and brimstone" from ancient times. Partly as a result of its long history, it is employed in a wide variety of commercial products and processes. In fact, more sulfuric acid is produced worldwide than any other compound. Sulfur is used to cross-link the polymers in rubber in a process called *vulcanization*, which was discovered by Charles Goodyear in the 1830s and commercialized by Benjamin Goodrich in the 1870s. Vulcanization gives rubber its unique combination of strength, elasticity, and stability.

Selenium, the only other commercially important chalcogen, was discovered in 1817, and today it is widely used in light-sensitive applications. For example, photocopying, or xerography, from the Greek *xèrós*, meaning "dry," and *graphia*, meaning "writing," uses selenium films to transfer an image from one piece of paper to another, while compounds such as cadmium selenide are used to measure light in photographic light meters and automatic streetlights.

Group 17: The Halogens



Group 17, halogens

The term *halogen*, derived from the Greek *háls*, meaning "salt," and *genes*, meaning "producing," was first applied to chlorine because of its tendency to react with metals to form salts. All of the halogens have an ns^2np^5 valence electron configuration, and all but astatine are diatomic molecules in which the two halogen atoms share a pair of electrons. Diatomic F_2 and Cl_2 are pale yellow-green and pale green gases, respectively, while Br_2 is a red liquid, and I_2 is a purple solid. The halogens were not isolated until the 18th and 19th centuries.

Because of their relatively high electronegativities, the halogens are nonmetallic and generally react by gaining one electron per atom to attain a noble gas electron configuration and an oxidation state of −1. *Halides* are produced according to the following equation, in which X denotes a halogen:

$$2\ E + nX_2 \rightarrow 2\ EX_n \quad (3.4.1)$$

If the element E has a low electronegativity (as does Na), the product is typically an ionic halide (NaCl). If the element E is highly electronegative (as P is), the product is typically a covalent halide (PCl_5). Ionic halides tend to be nonvolatile substances with high melting points, whereas covalent halides tend to be volatile substances with low melting points. Fluorine is the most reactive of the halogens, and iodine the least, which is consistent with their relative electronegativities (Figure 3.3.11).As we shall see in subsequent chapters, however, factors such as bond strengths are also important in dictating the reactivities of these elements. In

fact, fluorine reacts with nearly all elements at room temperature. Under more extreme conditions, it combines with all elements except helium, neon, and argon.

The halogens react with hydrogen to form the hydrogen halides (HX):

$$H_2(g) + X_2(g,l,s) \rightarrow 2\ HX(g) \quad (3.4.2)$$

Fluorine is so reactive that any substance containing hydrogen, including coal, wood, and even water, will burst into flames if it comes into contact with pure F_2.

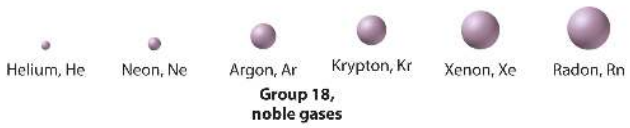
Because it is the most electronegative element known, fluorine never has a positive oxidation state in any compound. In contrast, the other halogens (Cl, Br, I) form compounds in which their oxidation states are +1, +3, +5, and +7, as in the *oxoanions*, XO_n^-, where n = 1–4. Because oxygen has the second highest electronegativity of any element, it stabilizes the positive oxidation states of the halogens in these ions.

All of the halogens except astatine (which is radioactive) are commercially important. NaCl in salt water is purified for use as table salt. Chlorine and hypochlorite (OCl^-) salts are used to sanitize public water supplies, swimming pools, and wastewater, and hypochlorite salts are also used as bleaches because they oxidize colored organic molecules. Organochlorine compounds are used as drugs and pesticides. Fluoride (usually in the form of NaF) is added to many municipal water supplies to help prevent tooth decay, and bromine (in AgBr) is a component of the light-sensitive coating on photographic film. Because iodine is essential to life—it is a key component of the hormone produced by the thyroid gland—small amounts of KI are added to table salt to produce "iodized salt," which prevents thyroid hormone deficiencies. The video shows the (some times explosive) reactions of the halogens





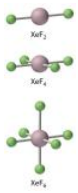
Group 18: The Noble Gases



The noble gases are helium, neon, argon, krypton, xenon, and radon. All have filled valence electron configurations and therefore are unreactive elements found in nature as monatomic gases. The noble gases were long referred to as either “rare gases” or “inert gases,” but they are neither rare nor inert. Argon constitutes about 1% of the atmosphere, which also contains small amounts of the lighter group 18 elements, and helium is found in large amounts in many natural gas deposits. The group’s perceived “rarity” stems in part from the fact that the noble gases were the last major family of elements to be discovered.

The noble gases have $EA \geq 0$, so they do not form compounds in which they have negative oxidation states. Because ionization energies decrease down the column, the only noble gases that form compounds in which they have positive oxidation states are Kr, Xe, and Rn. Of these three elements, only xenon forms an extensive series of compounds. The chemistry of radon is severely limited by its extreme radioactivity, and the chemistry of krypton is limited by its high ionization energy (1350.8 kJ/mol versus 1170.4 kJ/mol for xenon). In essentially all its compounds, xenon is bonded to highly electronegative atoms such as fluorine or oxygen. In fact, the only significant reaction of xenon is with elemental fluorine, which can give XeF_2, XeF_4, or XeF_6. Oxides such as XeO_3 are produced when xenon fluorides react with water, and oxidation with ozone produces the perxenate ion [XeO_6^{4-}], in which xenon acquires a +8 oxidation state by formally donating all eight of its valence electrons to the more electronegative oxygen atoms. In all of its stable compounds, xenon has a positive, even-numbered oxidation state: +2, +4, +6, or +8. The actual stability of these compounds varies greatly. For example, XeO_3 is a shock-sensitive, white crystalline solid with explosive power comparable to that of TNT (trinitrotoluene), whereas another compound, Na_2XeF_8, is stable up to 300°C.

Although none of the noble gas compounds is commercially significant, the elements themselves have important applications. For example, argon is used in incandescent light bulbs, where it provides an inert atmosphere that protects the tungsten filament from oxidation, and in compact fluorescent light bulbs (CFLs). It is also used in arc welding and in the manufacture of reactive elements, such as titanium, or of ultrapure products, such as the silicon used by the electronics industry. Helium, with a boiling point of only 4.2 K, is used as a liquid for studying the properties of substances at very low temperatures. It is also combined in an 80:20 mixture with oxygen used by scuba divers, rather than compressed air, when they descend to great depths. Because helium is less soluble in water than N_2—a component of compressed air—replacing N_2 with He prevents the formation of bubbles in blood vessels, a condition called “the bends” that can occur during rapid ascents. Neon is familiar to all of us as the gas responsible for the red glow in neon lights.



The Transition Metals, the Lanthanides, and the Actinides

As expected for elements with the same valence electron configuration, the elements in each column of the *d* block have vertical similarities in chemical behavior. In contrast to the *s*- and *p*-block elements, however, elements in the *d* block also display strong *horizontal* similarities. The horizontal trends compete with the vertical trends. In further contrast to the *p*-block elements, which tend to have stable oxidation states that are separated by *two* electrons, the transition metalsAny element in groups 3–12 in the periodic table. All of the transition elements are metals. have multiple oxidation states that are separated by only *one* electron.

Note the Pattern

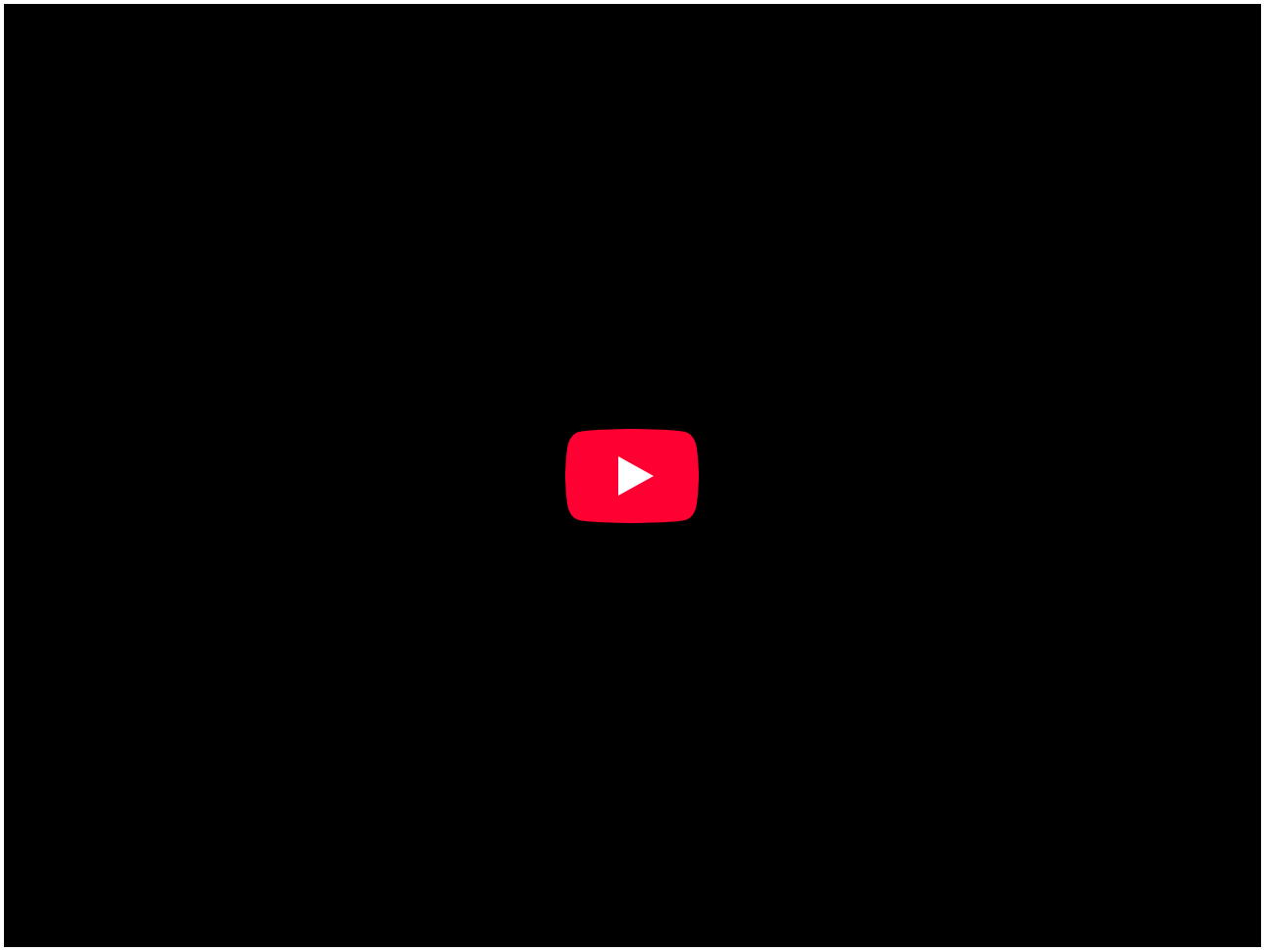
The *p*-block elements form stable compounds in oxidation states that tend to be separated by two electrons, whereas the transition metals have multiple oxidation states that are separated by one electron.

The group 6 elements, chromium, molybdenum, and tungsten, illustrate the competition that occurs between these horizontal and vertical trends. For example, the maximum number of electrons that can be lost for all elements in group 6 is +6, achieved by losing all six valence electrons (recall that Cr has a $4s^1 3d^5$ valence electron configuration), yet nearly all the elements in the first row of the transition metals, including chromium, form compounds with the dication M^{2+}, and many also form the trication M^{3+}. As a result, the transition metals in group 6 have very different tendencies to achieve their maximum oxidation state. The most common oxidation state for chromium is +3, whereas the most common oxidation state for molybdenum and tungsten is +6.

Note the Pattern

The *d*-block elements display both strong vertical and horizontal similarities.

Groups 3 (scandium, lanthanum, actinium), 11 (copper, silver, gold), and 12 (zinc, cadmium, mercury) are the only transition metal groups in which the oxidation state predicted by the valence electron configuration dominates the chemistry of the group. The elements of group 3 have three valence electrons outside an inner closed shell, so their chemistry is almost exclusively that of the M^{3+} ions produced by losing all three valence electrons. The elements of group 11 have 11 valence electrons in an $ns^1(n-1)d^{10}$ valence electron configuration, and so all three lose a single electron to form the monocation M^+ with a closed $(n-1)d^{10}$ electron configuration. Consequently, compounds of Cu^+, Ag^+, and Au^+ are very common, although there is also a great deal of chemistry involving Cu^{2+}. Similarly, the elements of group 12 all have an $ns^2(n-1)d^{10}$ valence electron configuration, so they lose two electrons to form M^{2+} ions with an $(n-1)d^{10}$ electron configuration; indeed, the most important ions for these elements are Zn^{2+}, Cd^{2+}, and Hg^{2+}. Mercury, however, also forms the dimeric mercurous ion (Hg_2^{2+}) because of a subtle balance between the energies needed to remove additional electrons and the energy released when bonds are formed. The +3 oxidation state is the most important for the lanthanidesAny of the 14 elements between Z=58 (cerium) and Z=71 (lutetium) and for most of the actinides (Any of the 14 elements between Z=90 (thorium) and Z=103 (lawrencium).) Why? Here is a brief video on the properties of the Lanthanides





Example 3.3.1

Based on the following information, determine the most likely identities for elements D and E.

1. Element D is a shiny gray solid that conducts electricity only moderately; it forms two oxides (DO_2 and DO_3).
2. Element E is a reddish metallic substance that is an excellent conductor of electricity; it forms two oxides (EO and E_2O) and two chlorides (ECl and ECl_2).

Given: physical and chemical properties of two elements

Asked for: identities

Strategy:

A Based on the conductivity of the elements, determine whether each is a metal, a nonmetal, or a semimetal. Confirm your prediction from its physical appearance.

B From the compounds each element forms, determine its common oxidation states.

C If the element is a nonmetal, it must be located in the *p* block of the periodic table. If a semimetal, it must lie along the diagonal line of semimetals from B to At. Transition metals can have two oxidation states separated by one electron.

D From your classification, the oxidation states of the element, and its physical appearance, deduce its identity.

Solution:

1. **A** The moderate electrical conductivity of element D tells us that it is a semimetal. It must lie in the *p* block of the periodic table because all of the semimetals are located there. **B** The stoichiometry of the oxides tells us that two common oxidation states for D are +4 and +6. **C** Element D must be located in group 16 because the common oxidation states for the chalcogens (group 16) include +6 (by losing all six valence elections) and +4 (by losing the four electrons from the *p* subshell). Thus D is likely to be Se or Te. **D** Additional information is needed to distinguish between the two.
2. **A** Element E is an excellent electrical conductor, so it is a metal. **B** The stoichiometry of the oxides and chlorides, however, tells us that common oxidation states for E are +2 and +1. **C** Metals that can have two oxidation states separated by one electron are usually transition metals. The +1 oxidation state is characteristic of only one group: group 11. Within group 11, copper is the only element with common oxidation states of +1 and +2. **D** Copper also has a reddish hue. Thus element E is probably copper.

Exercise

Based on the following information, determine the most likely identities for elements G and J.

1. Element G is a red liquid that does not conduct electricity. It forms three compounds with fluorine (GF, GF_3, and GF_5) and one with sodium (NaG).
2. Element J is a soft, dull gray solid that conducts electricity well and forms two oxides (JO and JO_2).

Answer:

1. Br
2. Sn or Pb

Summary

The chemical families consist of elements that have the same valence electron configuration and tend to have similar chemistry. The alkali metals (group 1) have ns^1 valence electron configurations and form M^+ ions, while the alkaline earth metals (group 2) have ns^2 valence electron configurations and form M^{2+} ions. Group 13 elements have ns^2np^1 valence electron configurations and have an overwhelming tendency to form compounds in the +3 oxidation state. Elements in group 14 have ns^2np^2 valence electron configurations but exhibit a variety of chemical behaviors because they range from a nonmetal (carbon) to metals (tin/lead). Carbon, the basis of organic compounds, has at least four allotropes with distinct structures: diamond, graphite, **fullerenes**, and carbon **nanotubes**. The **pnicogens** (group 15) all have ns^2np^3 valence electron configurations; they form compounds in oxidation states ranging from −3 to +5. The **chalcogens** (group 16) have ns^2np^4 valence electron configurations and react chemically by either gaining two electrons or by formally losing four or six electrons. The halogens (group 17) all have ns^2np^5 valence electron configurations and are diatomic molecules that tend to react chemically by accepting a single electron. The noble gases (group 18) are monatomic gases that are chemically quite unreactive due to the presence of a filled shell of electrons. The **transition metals** (groups 3–10) contain partially filled sets of *d* orbitals, and the **lanthanides** and the **actinides** are those groups in which *f* orbitals are being filled. These groups exhibit strong horizontal similarities in behavior. Many of the transition metals form M^{2+} ions, whereas the chemistry of the lanthanides and actinides is dominated by M^{3+} ions.

Key Takeaway

- Periodic properties and the chemical behavior of the elements correlate strongly with valence electron configurations and Mulliken electronegativities.

Conceptual Problems

1. Of the group 1 elements, which would you expect to be the best reductant? Why? Would you expect boron to be a good reductant? Why or why not?
2. Classify each element as a metal, a nonmetal, or a semimetal: Hf, I, Tl, S, Si, He, Ti, Li, and Sb. Which would you expect to be good electrical conductors? Why?
3. Classify each element as a metal, a nonmetal, or a semimetal: Au, Bi, P, Kr, V, Na, and Po. Which would you expect to be good electrical insulators? Why?
4. Of the elements Kr, Xe, and Ar, why does only xenon form an extensive series of compounds? Would you expect Xe^{2+} to be a good oxidant? Why or why not?
5. Identify each statement about the halogens as either true or false and explain your reasoning.
    1. Halogens have filled valence electron configurations.
    2. Halogens tend to form salts with metals.
    3. As the free elements, halogens are monatomic.
    4. Halogens have appreciable nonmetallic character.
    5. Halogens tend to have an oxidation state of −1.
    6. Halogens are good reductants.
6. Nitrogen forms compounds in the +5, +4, +3, +2, and −3 oxidation states, whereas Bi forms ions only in the +5 and +3 oxidation states. Propose an explanation for the differences in behavior.
7. Of the elements Mg, Al, O, P, and Ne, which would you expect to form covalent halides? Why? How do the melting points of covalent halides compare with those of ionic halides?
8. Of the elements Li, Ga, As, and Xe, would you expect to form ionic chlorides? Explain your reasoning. Which are usually more volatile—ionic or covalent halides? Why?
9. Predict the relationship between the oxidative strength of the oxoanions of bromine—BrO_n^- (n = 1–4)—and the number of oxygen atoms present (n). Explain your reasoning.
10. The stability of the binary hydrides of the chalcogens decreases in the order $H_2O > H_2S > H_2Se > H_2Te$. Why?
11. Of the elements O, Al, H, and Cl, which will form a compound with nitrogen in a positive oxidation state? Write a reasonable chemical formula for an example of a binary compound with each element.
12. How do you explain the differences in chemistry observed for the group 14 elements as you go down the column? Classify each group 14 element as a metal, a nonmetal, or a semimetal. Do you expect the group 14 elements to form covalent or ionic compounds? Explain your reasoning.
13. Why is the chemistry of the group 13 elements less varied than the chemistry of the group 15 elements? Would you expect the chemistry of the group 13 elements to be more or less varied than that of the group 17 elements? Explain your reasoning.
14. If you needed to design a substitute for $BaSO_4$, the barium milkshake used to examine the large and small intestine by x-rays, would $BeSO_4$ be an inappropriate substitute? Explain your reasoning.
15. The alkali metals have an ns^1 valence electron configuration, and consequently they tend to lose an electron to form ions with +1 charge. Based on their valence electron configuration, what other kind of ion can the alkali metals form? Explain your answer.
16. Would Mo or W be the more appropriate biological substitute for Cr? Explain your reasoning.

Answer

1.
2.
3.
4.

5.
6.
7.
8.
9.
10.
11. Nitrogen will have a positive oxidation state in its compounds with O and Cl, because both O and Cl are more electronegative than N. Reasonable formulas for binary compounds are: N_2O_5 or N_2O_3 and NCl_3.
12.
13.
14.
15.
16.

Numerical Problems

1. Write a balanced equation for formation of XeO_3 from elemental Xe and O_2. What is the oxidation state of Xe in XeO_3? Would you expect Ar to undergo an analogous reaction? Why or why not?
2. Which of the *p*-block elements exhibit the greatest variation in oxidation states? Why? Based on their valence electron configurations, identify these oxidation states.
3. Based on its valence electron configuration, what are the three common oxidation states of selenium? In a binary compound, what atoms bonded to Se will stabilize the highest oxidation state? the lowest oxidation state?
4. Would you expect sulfur to be readily oxidized by HCl? Why or why not? Would you expect phosphorus to be readily oxidized by sulfur? Why or why not?
5. What are the most common oxidation states for the pnicogens? What factors determine the relative stabilities of these oxidation states for the lighter and the heavier pnicogens? What is likely to be the most common oxidation state for phosphorus and arsenic? Why?
6. Of the compounds NF_3, NCl_3, and NI_3, which would be the least stable? Explain your answer. Of the ions BrO^-, ClO^-, or FO^-, which would be the least stable? Explain your answer.
7. In an attempt to explore the chemistry of the superheavy element ununquadium, $Z = 114$, you isolated two distinct salts by exhaustively oxidizing metal samples with chlorine gas. These salts are found to have the formulas MCl_2 and MCl_4. What would be the name of ununquadium using Mendeleev's *eka*-notation?
8. Would you expect the compound CCl_2 to be stable? $SnCl_2$? Why or why not?
9. A newly discovered element (Z) is a good conductor of electricity and reacts only slowly with oxygen. Reaction of 1 g of Z with oxygen under three different sets of conditions gives products with masses of 1.333 g, 1.668 g, and 1.501 g, respectively. To what family of elements does Z belong? What is the atomic mass of the element?
10. An unknown element (Z) is a dull, brittle powder that reacts with oxygen at high temperatures. Reaction of 0.665 gram of Z with oxygen under two different sets of conditions forms gaseous products with masses of 1.328 g and 1.660 g. To which family of elements does Z belong? What is the atomic mass of the element?
11. Why are the alkali metals such powerful reductants? Would you expect Li to be able to reduce H_2? Would Li reduce V? Why or why not?
12. What do you predict to be the most common oxidation state for Au, Sc, Ag, and Zn? Give the valence electron configuration for each element in its most stable oxidation state.
13. Complete the following table.

	Mg	C	Ne	Fe	Br
Valence Electron Configuration					
Common Oxidation States					
Oxidizing Strength					

14. Use the following information to identify elements T, X, D, and Z. Element T reacts with oxygen to form at least three compounds: TO, T_2O_3, and TO_2. Element X reacts with oxygen to form XO_2, but X is also known to form compounds in the +2 oxidation state. Element D forms D_2O_3, and element Z reacts vigorously and forms Z_2O. Electrical conductivity measurements showed that element X exhibited electrical conductivity intermediate between metals and insulators, while elements T, D, and Z were good conductors of electricity. Element T is a hard, lustrous, silvery metal, element X is a blue-gray metal, element D is a light, silvery metal, and element Z is a soft, low-melting metal.
15. Predict whether Cs, F_2, Al, and He will react with oxygen. If a reaction will occur, identify the products.
16. Predict whether K, Ar, O, and Al will react with Cl_2. If a reaction will occur, identify the products.
17. Use the following information to identify elements X, T, and Z.
    1. Element X is a soft, silvery-white metal that is flammable in air and reacts vigorously with water. Its first ionization energy is less than 500 kJ/mol, but the second ionization energy is greater than 3000 kJ/mol.
    2. Element T is a gas that reacts with F_2 to form a series of fluorides ranging from TF_2 to TF_6. It is inert to most other chemicals.
    3. Element Z is a deep red liquid that reacts with fluorine to form ZF_3 and with chlorine to form ZCl and ZCl_3, and with iodine to form ZI. Element Z also reacts with the alkali metals and alkaline earth metals.
18. Adding a reactive metal to water in the presence of oxygen results in a fire. In the absence of oxygen, the addition of 551 mg of the metal to water produces 6.4 mg of hydrogen gas. Treatment of 2.00 g of this metal with 6.3 g of Br_2 results in the formation of 3.86 g of an ionic solid. To which chemical family does this element belong? What is the identity of the element? Write and balance the chemical equation for the reaction of water with the metal to form hydrogen gas.

Answers

1. $2\ Xe + 3\ O_2 \rightarrow 2\ XeO_3$

   The oxidation state of xenon in XeO_3 is +6. No, Ar is much more difficult to oxidize than Xe.

2.

3. The valence electron configuration of Se is $[Ar]4s^23d^{10}4p^4$. Its common oxidation states are: +6, due to loss of all six electrons in the 4*s* and 4*p* subshells; +4, due to loss of only the four 4*p* electrons; and −2, due to addition of two electrons to give an $[Ar]4s^23d^{10}4p^6$ electron configuration, which is isoelectronic with the following noble gas, Kr. The highest oxidation state (+6) will be stabilized by bonds to highly electronegative atoms such as F (SeF_6) and O (SeO_3), while the lowest oxidation state will be stabilized in covalent compounds by bonds to less electronegative atoms such as H (H_2Se) or C [$(CH_3)_2Se$], or in ionic compounds with cations of electropositive metals (Na_2Se).

4.

5. All of the pnicogens have ns^2np^3 valence electron configurations. The pnicogens therefore tend to form compounds in three oxidation states: +5, due to loss of all five valence electrons; +3, due to loss of the three np^3 electrons; and −3, due to addition of three electrons to give a closed shell electron configuration. Bonds to highly electronegative atoms such as F and O will stabilize the higher oxidation states, while bonds to less electronegative atoms such as H and C will stabilize the lowest oxidation state, as will formation of an ionic compound with the cations of electropositive metals. The most common oxidation state for phosphorus and arsenic is +5.

6.

7. Uuq = *eka*-lead
8.
9. The ratios of the masses of the element to the mass of oxygen give empirical formulas of ZO, Z_2O_3, and ZO_2. The high electrical conductivity of the element immediately identifies it as a metal, and the existence of three oxides of the element with oxidation states separated by only one electron identifies it as a transition metal. If 1 g of Z reacts with 0.33 g O_2 to give ZO, the balanced equation for the reaction must be 2 Z + O_2 → 2 ZO. Using M to represent molar mass, the ratio of the molar masses of ZO and Z is therefore:

   $M_{ZO}:M_Z = (M_Z + M_O): M_Z = (M_Z + 16.0): M_Z = 1.33:1 = 1.33$.

   Solving for M_Z gives a molar mass of 48 g/mol and an atomic mass of 48 amu for Z, which identifies it as titanium.
10.
11. Alkali metals are powerful reductants because they have a strong tendency to lose their ns^1 valence electron, as reflected in their low first ionization energies and electronegativities. Lithium has a more positive electron affinity than hydrogen and a substantially lower first ionization energy, so we expect lithium to reduce hydrogen. Transition metals have low electron affinities and do not normally form compounds in negative oxidation states. Therefore, we do not expect lithium to reduce vanadium.
12.
13.

	Mg	C	Ne	Fe	Br
Valence Electron Configuration	$3s^2$	$2s^22p^2$	$2s^22p^6$	$4s^23d^6$	$4s^24p^5$
Common Oxidation States	+2	−4, +4	0	+2, +3	−1, +1, +3, +5, +7
Oxidizing Strength	None	Weak	None	None	Strong

14.
15. 4 Cs(s) + O_2(g) → 2 Cs_2O(s) 2 F_2(g) + O_2(g) → OF_2(g) 4 Al(s) + 3 O_2(g) → 2 Al_2O_3(s) He + O_2(g) → no reaction
16.
17. 1. sodium or potassium
    2. xenon
    3. bromine
18.

Contributors

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Chapter 3.4: The History of the Periodic Table

Learning Objectives

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

The modern periodic table has evolved through a long history of attempts by chemists to arrange the elements according to their reactivity and other properties as an aid in predicting chemical behavior. Now that we have arranged the table according to electronic structure, it makes sense to go back and look at earlier efforts in the light of what we know about electronic structure

One of the first to suggest such an arrangement was the German chemist Johannes Dobereiner (1780–1849), who noticed that many of the known elements could be grouped in triadsA set of three elements that have similar properties., sets of three elements that have similar properties—for example, chlorine, bromine, and iodine; or copper, silver, and gold. Dobereiner proposed that all elements could be grouped in such triads, but subsequent attempts to expand his concept were unsuccessful. We now know that portions of the periodic table—the *d* block in particular—contain triads of elements with substantial similarities. The middle three members of most of the other columns, such as sulfur, selenium, and tellurium in group 16 or aluminum, gallium, and indium in group 13, also have remarkably similar chemistry.

By the mid-19th century, the atomic masses of many of the elements had been determined. The English chemist John Newlands (1838–1898), hypothesizing that the chemistry of the elements might be related to their masses, arranged the known elements in order of increasing atomic mass and discovered that every seventh element had similar properties (Figure 3.4.1). (The noble gases were still unknown.) Newlands therefore suggested that the elements could be classified into octaves. A group of seven elements, corresponding to the horizontal rows in the main group elements (not counting the noble gases, which were unknown at the time)., corresponding to the *horizontal* rows in the main group elements. Unfortunately, Newlands's "law of octaves" did not seem to work for elements heavier than calcium, and his idea was publicly ridiculed. At one scientific meeting, Newlands was asked why he didn't arrange the elements in alphabetical order instead of by atomic mass, since that would make just as much sense! Actually, Newlands was on the right track—with only a few exceptions, atomic mass does increase with atomic number, and similar properties occur every time a set of ns^2np^6 subshells is filled. Despite the fact that Newlands's table had no logical place for the *d*-block elements, he was honored for his idea by the Royal Society of London in 1887.

John Newlands (1838–1898)

Newlands noticed that elemental properties repeated every seventh (or multiple of seven) element, as musical notes repeat every eighth note.

No.	No.	No.	No.	No.	No.	No.	No.
H 1	F 8	Cl 15	Co & Ni 22	Br 29	Pd 36	I 42	Pt & Ir 50
Li 2	Na 9	K 16	Cu 23	Rb 30	Ag 37	Cs 44	Tl 51
G 3	Mg 10	Ca 17	Zn 25	Sr 31	Bd [sic-Cd] 38	Ba & V 45	Pb 54
Bo 4	Al 11	Cr 19	Y 24	Ce & La 33	U 40	Ta 46	Th 56
C 5	Si 12	Ti 18	In 26	Zr 32	Sn 39	W 47	Hg 52
N 6	**P 13**	Mn 20	**As 27**	Di & Mo 34	**Sb 41**	Nb 48	**Bi 55**
O 7	S 14	Fe 21	Se 28	Ro & Ru 35	Te 43	Au 49	Os 51

NOTE. Where two elements happen to have the same equivalent, both are designated by the same number.

Figure 3.4.1 The Arrangement of the Elements into Octaves as Proposed by Newlands *The table shown here accompanied a letter from a 27-year-old Newlands to the editor of the journal Chemical News in which he wrote: "If the elements are arranged in the order of their equivalents, with a few slight transpositions, as in the accompanying table, it will be observed that elements belonging to the same group usually appear on the same horizontal line. It will also be seen that the numbers of analogous elements generally differ either by 7 or by some multiple of seven; in other words, members of the same group stand to each other in the same relation as the extremities of one or more octaves in music. Thus, in the nitrogen group, between nitrogen and phosphorus there are 7 elements; between phosphorus and arsenic, 14; between arsenic and antimony, 14; and lastly, between antimony and bismuth, 14 also. This peculiar relationship I propose to provisionally term the Law of Octaves. I am, &c. John A. R. Newlands, F.C.S. Laboratory, 19, Great St. Helen's, E.C., August 8, 1865."*

The periodic table achieved its modern form through the work of the German chemist Julius Lothar Meyer (1830–1895) and the Russian chemist Dimitri Mendeleev (1834–1907), both of whom focused on the relationships between atomic mass and various

physical and chemical properties. In 1869, they independently proposed essentially identical arrangements of the elements. Meyer aligned the elements in his table according to periodic variations in simple atomic properties, such as “atomic volume” (Figure 3.4.2), which he obtained by dividing the atomic mass (molar mass) in grams per mole by the density of the element in grams per cubic centimeter. This property is equivalent to what is today defined as molar volumeThe molar mass of an element divided by its density. (measured in cubic centimeters per mole):

$$\frac{molar\ mass\ \left(g/mol\right)}{density\ \left(g/cm^3\right)} = molar\ volume\ \left(cm^3/mol\right)$$

As shown in Figure 3.4.2 , the alkali metals have the highest molar volumes of the solid elements. In Meyer’s plot of atomic volume versus atomic mass, the nonmetals occur on the rising portion of the graph, and metals occur at the peaks, in the valleys, and on the downslopes.

Dimitri Mendeleev (1834–1907)

When his family’s glass factory was destroyed by fire, Mendeleev moved to St. Petersburg, Russia, to study science. He became ill and was not expected to recover, but he finished his PhD with the help of his professors and fellow students. In addition to the periodic table, another of Mendeleev’s contributions to science was an outstanding textbook, *The Principles of Chemistry*, which was used for many years.

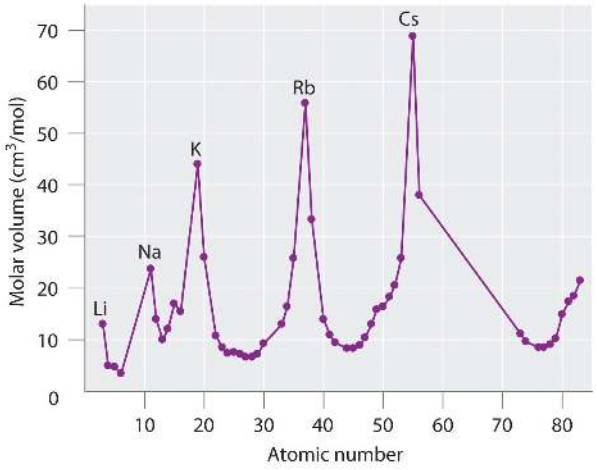


Figure 3.4.2 Variation of Atomic Volume with Atomic Number, Adapted from Meyer’s Plot of 1870 *Note the periodic increase and decrease in atomic volume. Because the noble gases had not yet been discovered at the time this graph was formulated, the peaks correspond to the alkali metals (group 1).*

Mendeleev’s Periodic Table

Mendeleev, who first published his periodic table in 1869 (Figure 3.4.3), is usually credited with the origin of the modern periodic table. The key difference between his arrangement of the elements and that of Meyer and others is that Mendeleev did not assume that all the elements had been discovered (actually, only about two-thirds of the naturally occurring elements were known at the time). Instead, he deliberately left blanks in his table at atomic masses 44, 68, 72, and 100, in the expectation that elements with those atomic masses would be discovered. Those blanks correspond to the elements we now know as scandium, gallium, germanium, and technetium.

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

Figure 3.4.3 Mendeleev's Periodic Table, as Published in the German Journal *Annalen der Chemie und Pharmacie* in 1872
The column headings "Reihen" and "Gruppe" are German for "row" and "group." Formulas indicate the type of compounds formed by each group, with "R" standing for "any element" and superscripts used where we now use subscripts. Atomic masses are shown after equal signs and increase across each row from left to right.

The groups in Mendeleev's table are determined by how many oxygen or hydrogen atoms are needed to form compounds with each element. For example, in Group I, two atoms of hydrogen, lithium, Li, sodium, Na, and potassium form compounds with one atom of oxygen. In Group VII, one atom of fluorine, F, chlorine, Cl, and bromine, Br, react with one atom of hydrogen. Notice how this approach has trouble with the transition metals. Until roughly 1960, a rectangular table developed from Mendeleev's table and based on reactivity was standard at the front of chemistry lecture halls.

The most convincing evidence in support of Mendeleev's arrangement of the elements was the discovery of two previously unknown elements whose properties closely corresponded with his predictions (Table 3.4.1). Two of the blanks Mendeleev had left in his original table were below aluminum and silicon, awaiting the discovery of two as-yet-unknown elements, *eka*-aluminum and *eka*-silicon (from the Sanskrit *eka*, meaning "one," as in "one beyond aluminum"). The observed properties of gallium and germanium matched those of *eka*-aluminum and *eka*-silicon so well that once they were discovered, Mendeleev's periodic table rapidly gained acceptance.



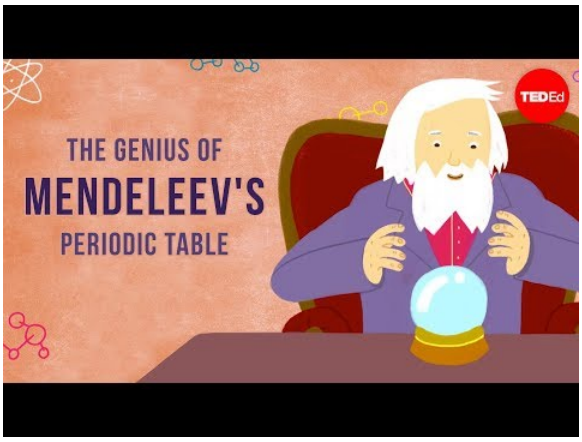


Table 3.4.1 Comparison of the Properties Predicted by Mendeleev in 1869 for *eka*-Aluminum and *eka*-Silicon with the Properties of Gallium (Discovered in 1875) and Germanium (Discovered in 1886)

Property	*eka*-Aluminum (predicted)	Gallium (observed)	*eka*-Silicon (predicted)	Germanium (observed)
atomic mass	68	69.723	72	72.64
element	metal	metal	dirty-gray metal	gray-white metal
	low mp*	mp = 29.8°C	high mp	mp = 938°C
	d = 5.9 g/cm^3	d = 5.91 g/cm^3	d = 5.5 g/cm^3	d = 5.323 g/cm^3
oxide	E_2O_3	Ga_2O_3	EO_2	GeO_2
	d = 5.5 g/cm^3	d = 6.0 g/cm^3	d = 4.7 g/cm^3	d = 4.25 g/cm^3
chloride	ECl_3	$GaCl_3$	ECl_4	$GeCl_4$
	volatile	mp = 78°C bp* = 201°C	bp < 100°C	bp = 87°C

*mp = melting point; bp = boiling point.

When the chemical properties of an element suggested that it might have been assigned the wrong place in earlier tables, Mendeleev carefully reexamined its atomic mass. He discovered, for example, that the atomic masses previously reported for beryllium, indium, and uranium were incorrect. The atomic mass of indium had originally been reported as 75.6, based on an assumed stoichiometry of InO for its oxide. If this atomic mass were correct, then indium would have to be placed in the middle of the nonmetals, between arsenic (atomic mass 75) and selenium (atomic mass 78). Because elemental indium is a silvery-white *metal*, however, Mendeleev postulated that the stoichiometry of its oxide was really In_2O_3 rather than InO. This would mean that indium's atomic mass was actually 113, placing the element between two other metals, cadmium and tin.

One group of elements that absent from Mendeleev's table is the noble gases, all of which were discovered more than 20 years later, between 1894 and 1898, by Sir William Ramsay (1852–1916; Nobel Prize in Chemistry 1904). Initially, Ramsay did not know where to place these elements in the periodic table. Argon, the first to be discovered, had an atomic mass of 40. This was greater than chlorine's and comparable to that of potassium, so Ramsay, using the same kind of reasoning as Mendeleev, decided to place the noble gases between the halogens and the alkali metals.

The Role of the Atomic Number in the Periodic Table

Despite its usefulness, Mendeleev's periodic table was based entirely on empirical observation supported by very little understanding. It was not until 1913, when a young British physicist, H. G. J. Moseley (1887–1915), while analyzing the frequencies of x-rays emitted by the elements, discovered that the underlying foundation of the order of the elements was by the

atomic number, not the atomic mass. Moseley hypothesized that the placement of each element in his series corresponded to its atomic number *Z*, which is the number of positive charges (protons) in its nucleus. Argon, for example, although having an atomic mass greater than that of potassium (39.9 amu versus 39.1 amu, respectively), was placed *before* potassium in the periodic table. While analyzing the frequencies of the emitted x-rays, Moseley noticed that the atomic number of argon is 18, whereas that of potassium is 19, which indicated that they were indeed placed correctly. Moseley also noticed three gaps in his table of x-ray frequencies, so he predicted the existence of three unknown elements: technetium (Z = 43), discovered in 1937; promethium (Z = 61), discovered in 1945; and rhenium (Z = 75), discovered in 1925.

H. G. J. Moseley (1887–1915)

Moseley left his research work at the University of Oxford to join the British army as a telecommunications officer during World War I. He was killed during the Battle of Gallipoli in Turkey.

Example 3.4.1

Before its discovery in 1999, some theoreticians believed that an element with a Z of 114 existed in nature. Use Mendeleev's reasoning to name element 114 as *eka*-_____; then identify the known element whose chemistry you predict would be most similar to that of element 114.

Given: atomic number

Asked for: name using prefix *eka*-

Strategy:

A Using the periodic table locate the n = 7 row. Identify the location of the unknown element with Z = 114; then identify the known element that is directly above this location.

B Name the unknown element by using the prefix *eka*- before the name of the known element.

Solution:

A The n = 7 row can be filled in by assuming the existence of elements with atomic numbers greater than 112, which is underneath mercury (Hg). Counting three boxes to the right gives element 114, which lies directly below lead (Pb). **B** If Mendeleev were alive today, he would call element 114 *eka*-lead.

Exercise

Use Mendeleev's reasoning to name element 112 as *eka*-_____; then identify the known element whose chemistry you predict would be most similar to that of element 112.

Answer: *eka*-mercury

Summary

The periodic table arranges the elements according to their electron configurations, such that elements in the same column have the same valence electron configurations. Periodic variations in size and chemical properties are important factors in dictating the types of chemical reactions the elements undergo and the kinds of chemical compounds they form. The modern periodic table was based on empirical correlations of properties such as atomic mass; early models using limited data noted the existence of **triads** and **octaves** of elements with similar properties. The periodic table achieved its current form through the work of Dimitri Mendeleev and Julius Lothar Meyer, who both focused on the relationship between atomic mass and chemical properties. Meyer arranged the elements by their atomic volume, which today is equivalent to the **molar volume**, defined as molar mass divided by molar density. The correlation with the electronic structure of atoms was made when H. G. J. Moseley showed that the periodic arrangement of the elements was determined by atomic number, not atomic mass.

Key Takeaway

- The elements in the periodic table are arranged according to their properties, and the periodic table serves as an aid in predicting chemical behavior.

Conceptual Problems

1. Johannes Dobereiner is credited with developing the concept of chemical triads. Which of the group 15 elements would you expect to compose a triad? Would you expect B, Al, and Ga to act as a triad? Justify your answers.
2. Despite the fact that Dobereiner, Newlands, Meyer, and Mendeleev all contributed to the development of the modern periodic table, Mendeleev is credited with its origin. Why was Mendeleev's periodic table accepted so rapidly?
3. How did Moseley's contribution to the development of the periodic table explain the location of the noble gases?
4. The *eka*- naming scheme devised by Mendeleev was used to describe undiscovered elements.
    1. Use this naming method to predict the atomic number of *eka*-mercury, *eka*-astatine, *eka*-thallium, and *eka*-hafnium.
    2. Using the *eka*-prefix, identify the elements with these atomic numbers: 79, 40, 51, 117, and 121.

Numerical Problem

1. Based on the data given, complete the table.

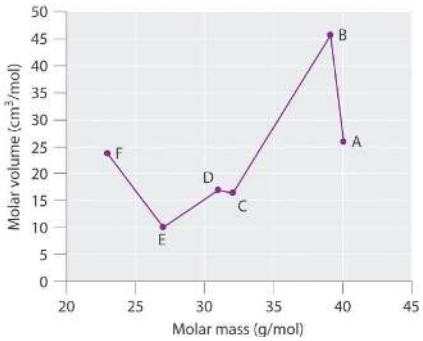
Species	Molar Mass (g/mol)	Density (g/cm^3)	Molar Volume (cm^3/mol)
A	40.078		25.85
B	39.09	0.856	
C	32.065		16.35
D		1.823	16.98
E	26.98		9.992
F	22.98	0.968	

Plot molar volume versus molar mass for these substances. According to Meyer, which would be considered metals and which would be considered nonmetals?

Answer

1.

Species	Molar Mass (g/mol)	Density (g/cm^3)	Molar Volume (cm^3/mol)
A	**40.078**	1.550	**25.85**
B	**39.09**	**0.856**	45.67
C	**32.065**	1.961	**16.35**
D	30.95	**1.823**	**16.98**
E	**26.98**	2.700	**9.992**
F	**22.98**	**0.968**	23.7



Meyer found that the alkali metals had the highest molar volumes, and that molar volumes decreased steadily with increasing atomic mass, then leveled off, and finally rose again. The elements located on the rising portion of a plot of molar volume versus molar mass were typically nonmetals. If we look at the plot of the data in the table, we can immediately identify those elements with the largest molar volumes (A, B, F) as metals located on the left side of the periodic table. The element with the smallest molar volume (E) is aluminum. The plot shows that the subsequent elements (C, D) have molar volumes that are larger than that of E, but smaller than those of A and B. Thus, C and D are most likely to be nonmetals (which is the case: C = sulfur, D = phosphorus).

Contributors

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Chapter 3.5: End of Chapter Material

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APPLICATION PROBLEMS

Problems marked with a ♦ involve multiple concepts.

1. Titanium is currently used in the aircraft industry and is now used in ships, which operate in a highly corrosive environment. Interest in this metal is due to the fact that titanium is strong, light, and corrosion resistant. The densities of selected elements are given in the following table. Why can an element with an even lower density such as calcium not be used to produce an even lighter structural material?

Element	Density (g/cm^3)	Element	Density (g/cm^3)
K	0.865	Cr	7.140
Ca	1.550	Mn	7.470
Sc	2.985	Fe	7.874
Ti	4.507	Co	8.900
V	6.110	Ni	8.908

2. ♦ The compound Fe_3O_4 was called lodestone in ancient times because it responds to Earth's magnetic field and can be used to construct a primitive compass. Today Fe_3O_4 is commonly called magnetite because it contains both Fe^{2+} and Fe^{3+}, and the unpaired electrons on these ions align to form tiny magnets. How many unpaired electrons does each ion have? Would you expect to observe magnetic behavior in compounds containing Zn^{2+}? Why or why not? Would you expect Fe or Zn to have the lower third ionization energy? Why?
3. ♦ Understanding trends in periodic properties allows us to predict the properties of individual elements. For example, if we need to know whether francium is a liquid at room temperature (approximately 20°C), we could obtain this information by plotting the melting points of the other alkali metals versus atomic number. Based on the data in the following table, would you predict francium to be a solid, a liquid, or a gas at 20°C?

	Li	Na	K	Rb	Cs
Melting Point (°C)	180	97.8	63.7	39.0	28.5

Francium is found in minute traces in uranium ores. Is this consistent with your conclusion? Why or why not? Why would francium be found in these ores, but only in small quantities?

ANSWERS

1.
2. Iron(II) has four unpaired electrons, and iron(III) has five unpaired electrons. Compounds of Zn^{2+} do not exhibit magnetic behavior, because the Zn^{2+} ion has no unpaired electrons. The third ionization potential of zinc is larger than that of iron, because removing a third electron from zinc requires breaking into the closed $3d^{10}$ subshell.
3.

Contributors

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SECTION OVERVIEW

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- Chapter 4.1: Ionic Bonding
- Chapter 4.2: Lattice Energies in Ionic Solids
- Chapter 4.3: Lewis Electron Dot Symbols
- Chapter 4.4: Lewis Structures and Covalent Bonding
- Chapter 4.5: Exceptions to the Octet Rule
- Chapter 4.6: Properties of Covalent Bonds
- Chapter 4.7: Properties of Polar Covalent Bonds
- Chapter 4.8: Metallic Bonding
- Chapter 4.9: End of Chapter Material

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CHAPTER OVERVIEW

Chapter 4: Chemical Bonding

- Chapter 4.0: What is a Chemical Bond?
- Chapter 4.1: Ionic Bonding
- Chapter 4.2: Lattice Energies in Ionic Solids
- Chapter 4.3: Lewis Electron Dot Symbols
- Chapter 4.4: Lewis Structures and Covalent Bonding
- Chapter 4.5: Exceptions to the Octet Rule
- Chapter 4.6: Properties of Covalent Bonds
- Chapter 4.7: Properties of Polar Covalent Bonds
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Chapter 4.0: What is a Chemical Bond?

Learning Objectives

- To present three common features of chemical bonding.

A **chemical bond** is the force that holds atoms together in a chemical compound. There are three idealized types of bonding: covalent bondingA type of chemical bonding in which electrons are shared between atoms in a molecule or polyatomic ion., in which electrons are shared between atoms in a molecule or polyatomic ion, ionic bondingA type of chemical bonding in which positively and negatively charged ions are held together by electrostatic forces., in which positively and negatively charged ions are held together by electrostatic forces and **metallic bonding**, where all of the atoms in the metal share a few of their electrons which are free to circulate. One can relate the properties of materials to the type of bonding. Ionic compounds, for example, typically dissolve in water to form aqueous solutions that conduct electricity as the ions separate into solution. Solid ionic compounds do not conduct eletricity or heat. In contrast, most covalent compounds that dissolve in water form solutions that do not conduct electricity because they go into the solvent as neutral molecules. The solids or liquids are not conductors. In metals, of course, the free electrons conduct electricity, and what is not obvious, also heat. Metals are good conductors of both. Further, in general, covalent compounds are volatile because the forces holding the neutral molecules together are relatively weak, whereas ionic compounds are not because the individual ions are strongly attracted to each other.

Despite the differences in the distribution of electrons between these idealized types of bonding, all models of chemical bonding have three features in common:

1. Atoms interact with one another to form aggregates such as molecules, compounds, and crystals because doing so lowers the total energy of the system; that is, the aggregates are more stable than the isolated atoms.
2. The type of bonding is determined by how the outermost electrons of an atom, the so called **valence** electrons of one atom interact with neighboring atoms. In ionic materials electrons are fully transferred. Covalent materials share electrons with neighboring atoms and metals share electrons over a wide region.
3. Energy is required to dissociate bonded atoms or ions into isolated atoms or ions. For ionic solids, in which the ions form a three-dimensional array called a *lattice*, this energy is called the lattice energyThe enthalpy change that occurs when a solid ionic compound (whose ions form a three-dimensional array called a lattice) is transformed into gaseous ions., the change that occurs when a solid ionic compound is transformed into gaseous ions. For covalent compounds, this energy is called the bond energyThe enthalpy change that occurs when a given bond in a gaseous molecule is broken., which is the change that occurs when a given bond in a gaseous molecule is broken. The details of these processes will be discussed at the end of this semester when we study thermochemistry.
4. Each chemical bond is characterized by a particular optimal internuclear distance called the bond distance(r_0)The optimal internuclear distance between two bonded atoms..

Note the Pattern

Energy is required to dissociate bonded atoms or ions.

We explore these characteristics further, after briefly describing the energetic factors involved in the formation of an ionic bond.

Summary

Chemical bonding is the general term used to describe the forces that hold atoms together in molecules and ions. Three idealized types of bonding are **ionic bonding**, in which positively and negatively charged ions are held together by electrostatic forces, **covalent bonding**, in which electron pairs are shared between atoms and metallic bonding where electrons are shared across large volumes of metal atoms ionic cores. All models of chemical bonding have three common features: atoms form bonds because the products are more stable than the isolated atoms; bonding interactions are characterized by a particular energy (the **bond energy** or **lattice energy**), which is the amount of energy required to dissociate the substance into its components; and bonding interactions have an optimal internuclear distance, the **bond distance**.

Key Takeaway

- Forming bonds lowers the total energy of the system, energy is required to dissociate bonded atoms or ions, and there is an optimal bond distance.

Conceptual Problems

1. Describe the differences between covalent bonding and ionic bonding. Which best describes the bonding in $MgCl_2$ and PF_5?
2. What three features do all chemical bonds have in common?

Contributors

- Anonymous

Modified by Joshua Halpern, Scott Sinex and Scott Johnson

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Chapter 4.1: Ionic Bonding

Learning Objectives

- To quantitatively describe the energetic factors involved in the formation of an ionic bond.

Ionic bonds are formed when positively and negatively charged ions are held together by electrostatic forces. The energy of the electrostatic attraction (E), a measure of the force's strength, is inversely proportional to the internuclear distance between the charged particles (r):

$$E \propto \frac{Q_1 Q_2}{r} \qquad E = k\frac{Q_1 Q_2}{r}$$

where each ion's charge is represented by the symbol Q. The proportionality constant k is equal to 2.31×10^{-28} J·m.This value of k includes the charge of a single electron (1.6022×10^{-19} C) for each ion. The equation can also be written using the charge of each ion, expressed in coulombs (C), incorporated in the constant. In this case, the proportionality constant, k, equals 8.999×10^{9} J·m/C^2. In the example given, $Q_1 = +1(1.6022 \times 10^{-19}$ C) and $Q_2 = -1(1.6022 \times 10^{-19}$ C). If Q_1 and Q_2 have opposite signs (as in NaCl, for example, where Q_1 is +1 for Na^+ and Q_2 is −1 for Cl^-), then E is negative, which means that energy is released when oppositely charged ions are brought together from an infinite distance to form an isolated ion pair. As shown by the green curve in the lower half of Figure 4.1.1 predicts that the maximum energy is released when the ions are infinitely close to each other, at $r = 0$. Because ions occupy space and have a structure with the positive nucleus being surrounded by electrons, however, they cannot be infinitely close together. At very short distances, repulsive electron–electron interactions between electrons on adjacent ions become stronger than the attractive interactions between ions with opposite charges, as shown by the red curve in the upper half of Figure 4.1.1. The total energy of the system is a balance between the attractive and repulsive interactions. The purple curve in Figure 4.1.1 shows that the total energy of the system reaches a minimum at r_0, the point where the electrostatic repulsions and attractions are exactly balanced. This distance is the same as the experimentally measured bond distance.

Note the Pattern

Energy is released when a bond is formed.

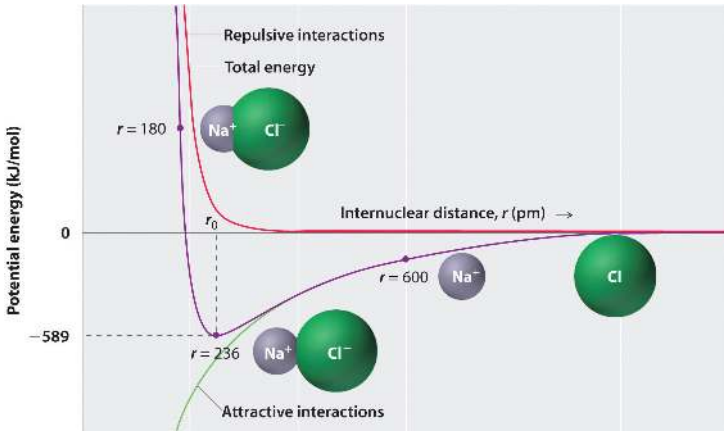
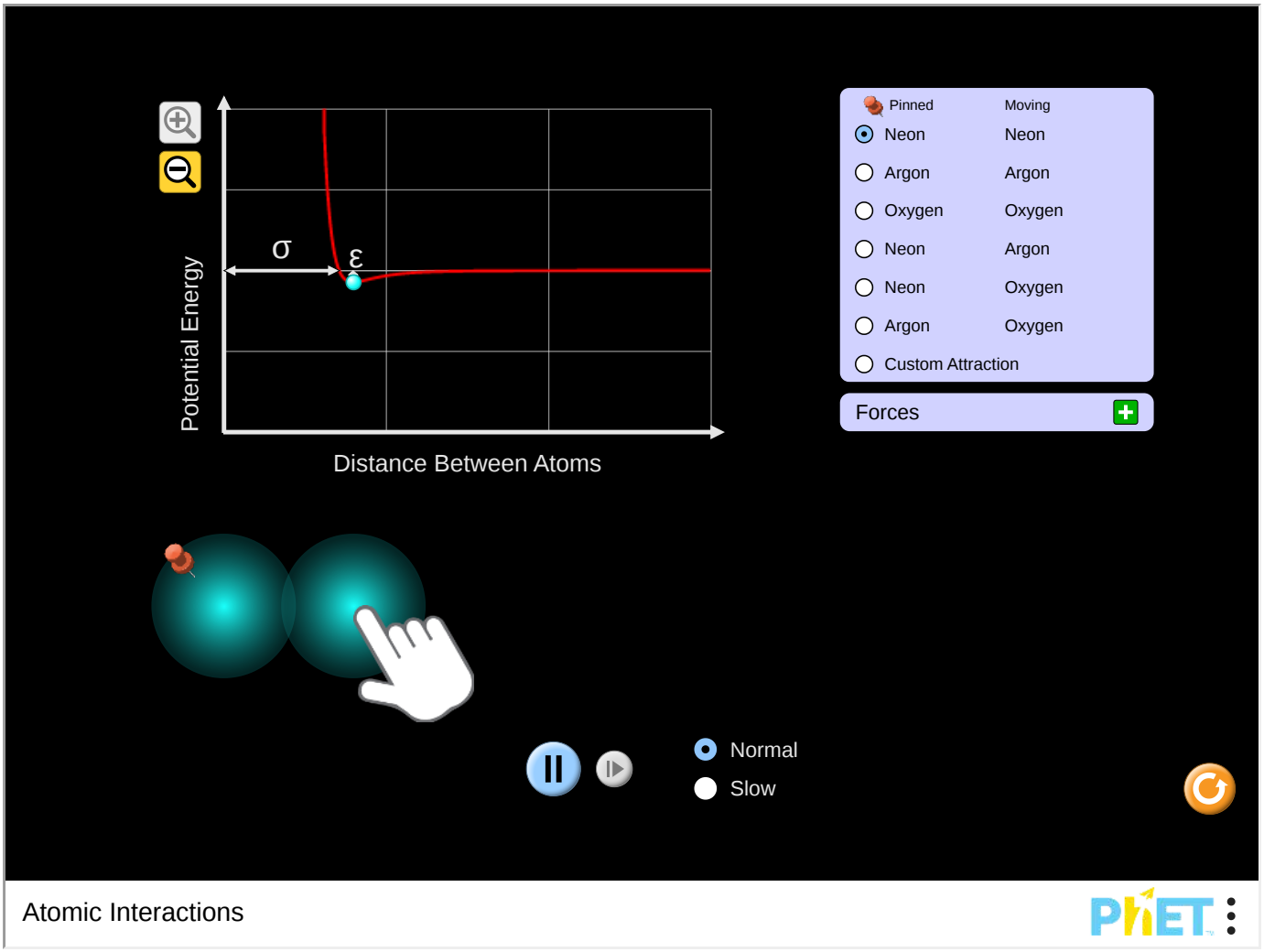


Figure 4.1.1 A Plot of Potential Energy versus Internuclear Distance for the Interaction between Ions With Different Charges: A Gaseous Na^+ Ion and a Gaseous Cl^- Ion *The energy of the system reaches a minimum at a particular distance (r_0) when the attractive and repulsive interactions are balanced.*



Let's consider the energy released when a gaseous Na^+ ion and a gaseous Cl^- ion are brought together from $r = \infty$ to $r = r_0$. Given that the observed gas-phase internuclear distance is 236 pm, the energy change associated with the formation of an ion pair from an $Na^+(g)$ ion and a $Cl^-(g)$ ion is as follows:

$$E = k\frac{Q_1Q_2}{r_0} = (2.31 \times 10^{-28}\,\text{J} \cdot \cancel{\text{m}})\left(\frac{(+1)(-1)}{236\ \cancel{\text{pm}} \times 10^{-12}\ \cancel{\text{m/pm}}}\right) = -9.79 \times 10^{-19}\ \text{J/ion pair}$$

The negative value indicates that energy is released. Our convention is that if a chemical process provides energy to the outside world, the energy change is negative. If it requires energy, the energy change is positive, energy has to be given to the atoms. To calculate the energy change in the formation of a mole of NaCl pairs, we need to multiply the energy per ion pair by Avogadro's number:

$$E = \left(-9.79 \times 10^{-19}\ J/\cancel{ionpair}\right)\left(6.022 \times 10^{23}\ \cancel{ion\text{-}pair}\ /mol\right) = -589\ kJ/mol$$

This is the energy released when 1 mol of gaseous ion pairs is formed, *not* when 1 mol of positive and negative ions condenses to form a crystalline lattice. Because of long-range interactions in the lattice structure, this energy does not correspond directly to the lattice energy of the crystalline solid. However, the large negative value indicates that bringing positive and negative ions together is energetically very favorable, whether an ion pair or a crystalline lattice is formed.

We summarize the important points about ionic bonding:

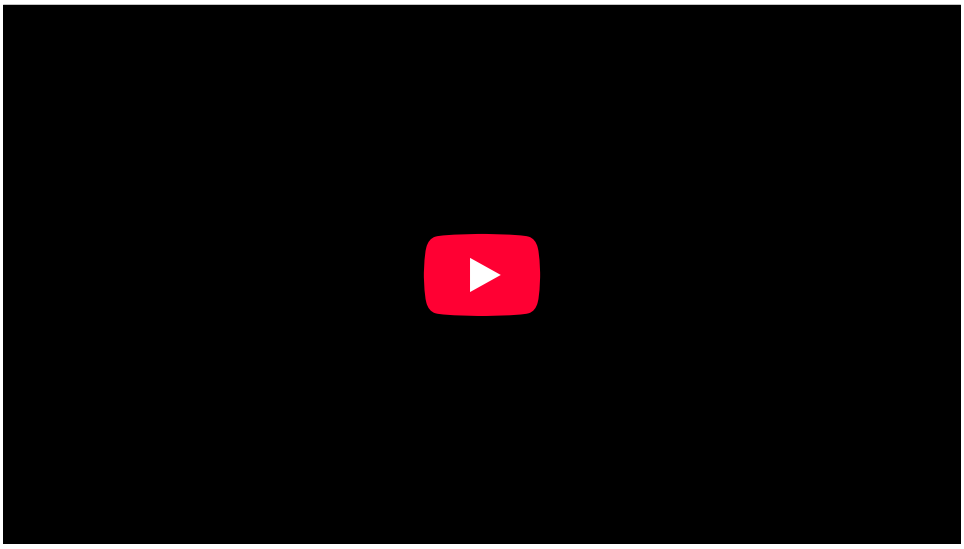
- At r_0, the ions are more stable (have a lower potential energy) than they are at an infinite internuclear distance. When oppositely charged ions are brought together from $r = \infty$ to $r = r_0$, the energy of the system is lowered (energy is released).
- Because of the low potential energy at r_0, energy must be added to the system to separate the ions. The amount of energy needed is the bond energy.
- The energy of the system reaches a minimum at a particular internuclear distance (the bond distance).

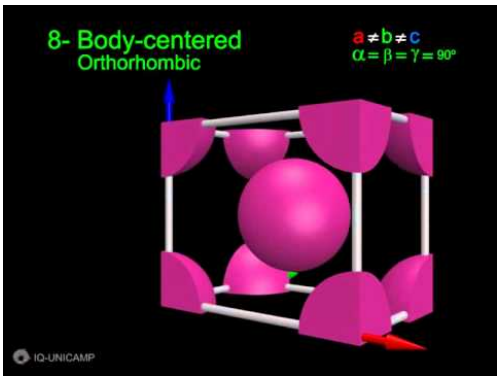
Ionic Crystal Lattices

An ionic solid is formed out of endlessly repeating patterns of ionic pairs. Because we want to establish the basics about ionic bonding and not get involved in detail we will continue to use table salt, NaCl, to discuss ionic bonding.

In NaCl, of course, an electron is transferred from each sodium atom to a chlorine atom leaving Na^+ and Cl^-. The size of the lattice depends on the physical size of the crystal which can be microscopic, a few nm on a side to macroscopic, centimeters or even more. Salt crystals that you buy at the store can range in size from a few tenths of a mm in finely ground table salt to a few mm for coarsely ground salt used in cooking. Given that the spacing between the Na^+ and Cl^- ions, is ~240 pm, a 2.4 mm on edge crystal has 10^{+7} Na^+ - Cl^- units, and a cube of salt 2mm on edge will have about 2 x 10^{21} atoms.

The ions arrange themselves into an extended lattice. The distinguishing feature of these lattices is that they are space filling, there are no voids. Thinking about this in three dimensions this turns out to be a bit complex. In nature, there are only 14 such lattices, called Bravais lattices after August Bravais who first classified them in 1850. If interested, you can view a video visualization of the 14 lattices by Manuel Moreira Baptista





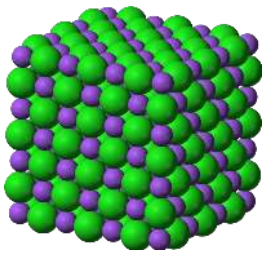


Figure 4.1.2 Small section of the arrangment of ions in an NaCl crystal *The relative positions of the sodium ions are shown in blue, the chlorine in green*

The repeating pattern is called the unit cell.

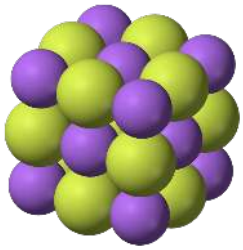


Figure 4.1.3 The unit cell for an NaCl crystal lattice. *If you look at the diagram carefully, you will see that the sodium ions and chloride ions alternate with each other in each of the three dimensions.*

This diagram is easy enough to draw with a computer, but extremely difficult to draw convincingly by hand. We normally draw an "exploded" version which looks like this:

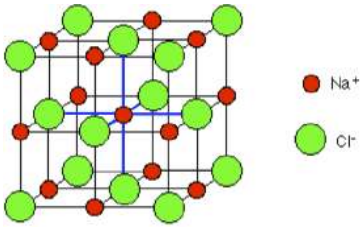


Figure 4.1.4 An "exploded" view of the unit cell for an NaCl crystal lattice. *The sodium ion in the center is being touched by 6 chloride ions as indicated by the blue lines.*

By chance we might just as well have centered the diagram around a chloride ion - that, of course, would be touched by 6 sodium ions. Sodium chloride is described as being 6:6-coordinated. This diagram represents only a tiny part of the whole sodium chloride crystal; the pattern repeats in this way over countless ions.

Sodium chloride has a high melting and boiling point

There are strong electrostatic attractions between the positive and negative ions, and it takes a lot of heat energy to overcome them. Ionic substances all have high melting and boiling points. Differences between ionic substances will depend on things like:

- **The number of charges on the ions**: Magnesium oxide has exactly the same structure as sodium chloride, but a much higher melting and boiling point. The 2+ and 2- ions attract each other more strongly than 1+ attracts 1-.
- **The sizes of the ions**: If the ions are smaller they get closer together and so the electrostatic attractions are greater. Rubidium iodide, for example, melts and boils at slightly lower temperatures than sodium chloride, because both rubidium and iodide ions are bigger than sodium and chloride ions. The attractions are less between the bigger ions and so less heat energy is needed to separate them.

Sodium chloride crystals are brittle

Brittleness is again typical of ionic substances. Imagine what happens to the crystal if a stress is applied which shifts the ion layers slightly.

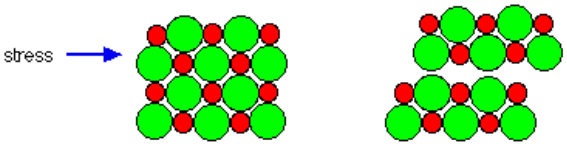


Figure 4.1.5 Cleving an ionic crystal *When an ionic crystal is cleved, a sharp tool such as a knife, displaces adjourning layers of the crystal, pushing ions of the same charge on top of each other. At that point the two pieces repel each other, shattering the crystal.*

The electrical behavior of sodium chloride

Solid sodium chloride does not conduct electricity, because there are no electrons which are free to move. When it melts, at a very high temperature of course, the sodium and chloride ions can move freely when a voltage is placed across the liquid. The positive sodium ions move towards the negatively charged electrode (the cathode). When they get there, each sodium ion picks up an electron from the electrode to form a sodium atom. These float to the top of the melt as molten sodium metal. (And assuming you are doing this open to the air, this immediately catches fire and burns with an orange flame.)

The power source (the battery or whatever) moves electrons along the wire in the external circuit so that the number of electrons is the same. That flow of electrons would be seen as an electric current (the external circuit is all the rest of the circuit apart from the molten sodium chloride.) Thus, in the process called electrolysis, sodium and chlorine are produced. This is a chemical change rather than a physical process.

$$\mathbf{Na^+ + e^- \rightarrow Na}$$

Meanwhile, chloride ions are attracted to the positive electrode (the anode). When they get there, each chloride ion loses an electron to the anode to form an atom. These then pair up to make chlorine molecules. Chlorine gas is produced. Overall, the change is . . .

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

The new electrons deposited on the anode are pumped off around the external circuit by the power source, eventually ending up on the cathode where they will be transferred to sodium ions. Molten sodium chloride conducts electricity because of the movement of the ions in the melt, and the discharge of the ions at the electrodes. Both of these have to happen if you are to get electrons flowing in the external circuit. In solid sodium chloride, of course, that ion movement can not happen and that stops any possibility of any current flow in the circuit.

Acknowlegement: The discussion of the NaCl lattice is a slightly modified version of the Jim Clark's article in LibreTexts

Example 4.1.1

Calculate the amount of energy released when 1 mol of gaseous Li^+F^- ion pairs is formed from the separated ions. The observed internuclear distance in the gas phase is 156 pm.

Given: cation and anion, amount, and internuclear distance

Asked for: energy released from formation of gaseous ion pairs

Strategy:

Substitute the appropriate values into Equation 4.1.1 to obtain the energy released in the formation of a single ion pair and then multiply this value by Avogadro's number to obtain the energy released per mole.

Solution:

Inserting the values for Li^+F^- into Equation 4.1.1 (where $Q_1 = +1$, $Q_2 = -1$, and $r = 156$ pm), we find that the energy associated with the formation of a single pair of Li^+F^- ions is

$$E = k\frac{Q_1Q_2}{r_0} = (2.31 \times 10^{-28}\,\text{J} \cdot \cancel{\text{m}}) \left(\frac{(+1)(-1)}{156\ \cancel{\text{pm}} \times 10^{-12}\ \cancel{\text{m/pm}}} \right) = -1.48 \times 10^{-18}\ \text{J/ion pair}$$

Then the energy released per mole of Li^+F^- ion pairs is

$$E = \left(-1.48 \times 10^{-18}\ J/\cancel{ion pair}\right)\left(6.022 \times 10^{23}\ \cancel{ion\ pair}/mol\right) = -891\ kJ/mol$$

Because Li^+ and F^- are smaller than Na^+ and Cl^- (see Figure 3.2.7), the internuclear distance in LiF is shorter than in NaCl. Consequently, in accordance with Equation 4.1.1, much more energy is released when 1 mol of gaseous Li^+F^- ion pairs is formed (−891 kJ/mol) than when 1 mol of gaseous Na^+Cl^- ion pairs is formed (−589 kJ/mol).

Exercise

Calculate the amount of energy released when 1 mol of gaseous MgO ion pairs is formed from the separated ions. The internuclear distance in the gas phase is 175 pm.

Answer: −3180 kJ/mol = -3.18×10^3 kJ/mol

Summary

The strength of the electrostatic attraction between ions with opposite charges is directly proportional to the magnitude of the charges on the ions and inversely proportional to the internuclear distance. The total energy of the system is a balance between the repulsive interactions between electrons on adjacent ions and the attractive interactions between ions with opposite charges.

Key Takeaway

- The amount of energy needed to separate a gaseous ion pair is its bond energy.

Conceptual Problems

1. Describe the differences in behavior between NaOH and CH_3OH in aqueous solution. Which solution would be a better conductor of electricity? Explain your reasoning.
2. What is the relationship between the strength of the electrostatic attraction between oppositely charged ions and the distance between the ions? How does the strength of the electrostatic interactions change as the size of the ions increases?
3. Which will result in the release of more energy: the interaction of a gaseous sodium ion with a gaseous oxide ion or the interaction of a gaseous sodium ion with a gaseous bromide ion? Why?
4. Which will result in the release of more energy: the interaction of a gaseous chloride ion with a gaseous sodium ion or a gaseous potassium ion? Explain your answer.
5. What are the predominant interactions when oppositely charged ions are
    1. far apart?

2. at internuclear distances close to r_0?
3. very close together (at a distance that is *less* than the sum of the ionic radii)?

6. Several factors contribute to the stability of ionic compounds. Describe one type of interaction that *destabilizes* ionic compounds. Describe the interactions that *stabilize* ionic compounds.
7. What is the relationship between the electrostatic attractive energy between charged particles and the distance between the particles?

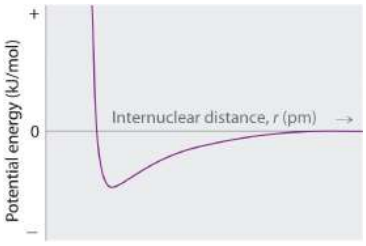
Answer

1.
2.
3. The interaction of a sodium ion and an oxide ion. The electrostatic attraction energy between ions of opposite charge is directly proportional to the charge on each ion (Q_1 and Q_2 in Equation 4.1.1). Thus, more energy is released as the charge on the ions increases (assuming the internuclear distance does not increase substantially). A sodium ion has a +1 charge; an oxide ion, a −2 charge; and a bromide ion, a −1 charge. For the interaction of a sodium ion with an oxide ion, $Q_1 = +1$ and $Q_2 = −2$, whereas for the interaction of a sodium ion with a bromide ion, $Q_1 = +1$ and $Q_2 = −1$. The larger value of $Q_1 \times Q_2$ for the sodium ion–oxide ion interaction means it will release more energy.
4.
5.
6.
7.

Numerical Problems

1. How does the energy of the electrostatic interaction between ions with charges +1 and −1 compare to the interaction between ions with charges +3 and −1 if the distance between the ions is the same in both cases? How does this compare with the magnitude of the interaction between ions with +3 and −3 charges?
2. How many grams of gaseous $MgCl_2$ are needed to give the same electrostatic attractive energy as 0.5 mol of gaseous LiCl? The ionic radii are $Li^+ = 76$ pm, $Mg^{+2} = 72$ pm, and $Cl^- = 181$ pm.
3. Sketch a diagram showing the relationship between potential energy and internuclear distance (from $r = \infty$ to $r = 0$) for the interaction of a bromide ion and a potassium ion to form gaseous KBr. Explain why the energy of the system increases as the distance between the ions decreases from $r = r_0$ to $r = 0$.
4. Calculate the magnitude of the electrostatic attractive energy (E, in kilojoules) for 85.0 g of gaseous SrS ion pairs. The observed internuclear distance in the gas phase is 244.05 pm.
5. What is the electrostatic attractive energy (E, in kilojoules) for 130 g of gaseous HgI_2? The internuclear distance is 255.3 pm.

Answers

1. According to Equation 4.1.1, in the first case $Q_1Q_2 = (+1)(−1) = −1$; in the second case, $Q_1Q_2 = (+3)(−1) = −3$. Thus, E will be three times larger for the +3/−1 ions. For +3/−3 ions, $Q_1Q_2 = (+3)(−3) = −9$, so E will be nine times larger than for the +1/−1 ions.
2.
3. 

   At $r < r_0$, the energy of the system increases due to electron–electron repulsions between the overlapping electron distributions on *adjacent* ions. At very short internuclear distances, electrostatic repulsions between adjacent *nuclei* also become important.
4.
5.

Contributors

- Anonymous

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Chapter 4.2: Lattice Energies in Ionic Solids

Learning Objectives

- To understand the relationship between the lattice energy and physical properties of an ionic compound.

The reaction of a metal with a nonmetal usually produces an ionic compound; that is, electrons are transferred from the metal to the nonmetal. Metal ores are commonly combinations of metal atoms with oxygen atoms, and this combination is produced when metals rust, so the process where electrons are transferred to the oxygen atoms from the metal atoms is known as **oxidation** of the metal and the reverse process, where pure metals are produced is called **reduction** of the ore to the metal.

Ionic compounds are usually rigid, brittle, crystalline substances with flat surfaces that intersect at characteristic angles. They are not easily deformed, and they melt at relatively high temperatures. NaCl, for example, melts at 801°C. These properties result from the regular arrangement of the ions in the crystalline lattice and from the strong electrostatic attractive forces between ions with opposite charges.

While Equation 4.1.1 has demonstrated that the formation of ion pairs from isolated ions releases large amounts of energy, even more energy is released when these ion pairs condense to form an ordered three-dimensional array. In such an arrangement each cation in the lattice is surrounded by more than one anion (typically four, six, or eight) and vice versa, so it is more stable than a system consisting of separate pairs of ions, in which there is only one cation–anion interaction in each pair. Note that r_0 may differ between the gas-phase dimer and the lattice.

Note the Pattern

An ionic lattice is more stable than a system consisting of separate ion pairs.

Calculating Lattice Energies

The lattice energy of nearly any ionic solid can be calculated rather accurately using a modified form of Equation 4.2.1:

$$U = -k' \frac{Q_1 Q_2}{r_0}, \ where \ U > 0$$

U, which is always a positive number, represents the amount of energy required to dissociate 1 mol of an ionic solid into the gaseous ions. As before, Q_1 and Q_2 are the charges on the ions and r_0 is the internuclear distance. We see from Equation 4.2.1 that lattice energy is directly related to the product of the ion charges and inversely related to the internuclear distance. The value of the constant k' depends on the specific arrangement of ions in the solid lattice and their valence electron configurations, topics that will be discussed in more detail in the second semester. Representative values for calculated lattice energies, which range from about 600 to 10,000 kJ/mol, are listed in Table 4.2.1. Energies of this magnitude can be decisive in determining the chemistry of the elements.

Table 4.2.1 Representative Calculated Lattice Energies

Substance	U (kJ/mol)
NaI	682
CaI_2	1971
MgI_2	2293
NaOH	887
Na_2O	2481
$NaNO_3$	755
$Ca_3(PO_4)_2$	10,602
$CaCO_3$	2804

Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

Because the lattice energy depends on the *product* of the charges of the ions, a salt having a metal cation with a +2 charge (M^{2+}) and a nonmetal anion with a −2 charge (X^{2-}) will have a lattice energy four times greater than one with M^+ and X^-, assuming the ions are of comparable size (and have similar internuclear distances). For example, the calculated value of U for NaF is 910 kJ/mol, whereas U for MgO (containing Mg^{2+} and O^{2-} ions) is 3795 kJ/mol.

Because lattice energy is *inversely* related to the internuclear distance, it is also inversely proportional to the size of the ions. This effect is illustrated in Figure 4.2.2, which shows that lattice energy decreases for the series LiX, NaX, and KX as the radius of X^- increases. Because r_0 in Equation 4.2.1 is the sum of the ionic radii of the cation and the anion ($r_0 = r^+ + r^-$), r_0 increases as the cation becomes larger in the series, so the magnitude of U decreases. A similar effect is seen when the anion becomes larger in a series of compounds with the same cation.

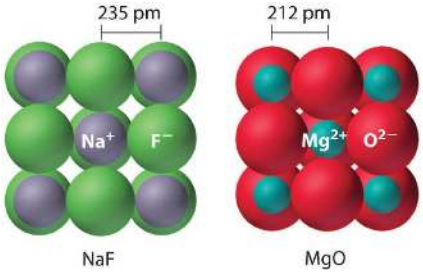


Figure 4.2.1 Unit cells for NaF and MgO

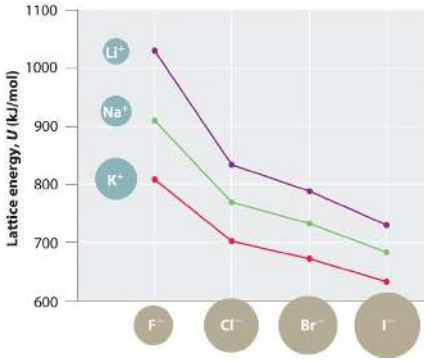


Figure 4.2.2 A Plot of Lattice Energy versus the Identity of the Halide for the Lithium, Sodium, and Potassium Halides *Because the ionic radii of the cations decrease in the order $K^+ > Na^+ > Li^+$ for a given halide ion, the lattice energy decreases smoothly from Li^+ to K^+. Conversely, for a given alkali metal ion, the fluoride salt always has the highest lattice energy and the iodide salt the lowest.*

Note the Pattern

Lattice energies are highest for substances with small, highly charged ions.

Example 4.2.1

Arrange GaP, BaS, CaO, and RbCl in order of increasing lattice energy.

Given: four compounds

Asked for: order of increasing lattice energy

Strategy:

Using Equation 4.2.1, predict the order of the lattice energies based on the charges on the ions. For compounds with ions with the same charge, use the relative sizes of the ions to make this prediction.

Solution:

The compound GaP, which is used in semiconductor electronics, contains Ga^{3+} and $P^{3−}$ ions; the compound BaS contains Ba^{2+} and $S^{2−}$ ions; the compound CaO contains Ca^{2+} and $O^{2−}$ ions; and the compound RbCl has Rb^{+} and $Cl^{−}$ ions. We know from Equation 4.2.1 that lattice energy is directly proportional to the product of the ionic charges. Consequently, we expect RbCl, with a (−1)(+1) term in the numerator, to have the lowest lattice energy, and GaP, with a (+3)(−3) term, the highest. To decide whether BaS or CaO has the greater lattice energy, we need to consider the relative sizes of the ions because both compounds contain a +2 metal ion and a −2 chalcogenide ion. Because Ba^{2+} lies below Ca^{2+} in the periodic table, Ba^{2+} is larger than Ca^{2+}. Similarly, $S^{2−}$ is larger than $O^{2−}$. Because the cation and the anion in BaS are both larger than the corresponding ions in CaO, the internuclear distance is greater in BaS and its lattice energy will be lower than that of CaO. The order of increasing lattice energy is RbCl < BaS < CaO < GaP.

Exercise

Arrange InAs, KBr, LiCl, SrSe, and ZnS in order of decreasing lattice energy.

Answer: InAs > ZnS > SrSe > LiCl > KBr

The Relationship between Lattice Energies and Physical Properties

The magnitude of the forces that hold an ionic substance together has a dramatic effect on many of its properties. The melting pointThe temperature at which the individual ions in a lattice or the individual molecules in a covalent compound have enough kinetic energy to overcome the attractive forces that hold them together in the solid., for example, is the temperature at which the individual ions have enough kinetic energy to overcome the attractive forces that hold them in place. At the melting point, the ions can move freely, and the substance becomes a liquid. Thus melting points vary with lattice energies for ionic substances that have similar structures. The melting points of the sodium halides (Figure 4.2.3), for example, decrease smoothly from NaF to NaI, following the same trend as seen for their lattice energies (Figure 4.2.2). Similarly, the melting point of MgO is 2825°C, compared with 996°C for NaF, reflecting the higher lattice energies associated with higher charges on the ions. In fact, because of its high melting point, MgO is used as an electrical insulator in heating elements for electric stoves.

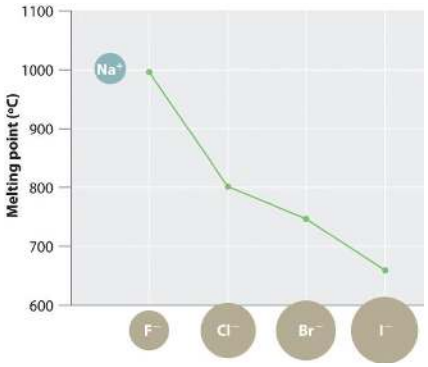


Figure 4.2.3 A Plot of Melting Point versus the Identity of the Halide for the Sodium Halides The melting points follow the same trend as the magnitude of the lattice energies in Figure 4.2.2.

The hardnessThe resistance of ionic materials to scratching or abrasion. of ionic materials—that is, their resistance to scratching or abrasion—is also related to their lattice energies. Hardness is directly related to how tightly the ions are held together electrostatically, which, as we saw, is also reflected in the lattice energy. As an example, MgO is harder than NaF, which is consistent with its higher lattice energy.

In addition to determining melting point and hardness, lattice energies affect the solubilities of ionic substances in water. In general, *the higher the lattice energy, the less soluble a compound is in water*. For example, the solubility of NaF in water at 25°C is 4.13 g/100 mL, but under the same conditions, the solubility of MgO is only 0.65 mg/100 mL, meaning that it is essentially insoluble.

Note the Pattern

High lattice energies lead to hard, insoluble compounds with high melting points.

Summary

Ionic compounds have strong electrostatic attractions between oppositely charged ions in a regular array. The lattice energy (U) of an ionic substance is defined as the energy required to dissociate the solid into gaseous ions; U can be calculated from the charges on the ions, the arrangement of the ions in the solid, and the internuclear distance. Because U depends on the product of the ionic charges, substances with di- or tripositive cations and/or di- or trinegative anions tend to have higher lattice energies than their singly charged counterparts. Higher lattice energies typically result in higher **melting points** and increased **hardness** because more thermal energy is needed to overcome the forces that hold the ions together.

Key Takeaway

- The lattice energy is usually the most important energy factor in determining the stability of an ionic compound.

Key Equation

Lattice energy

Equation 4.2.1: $U = -k' \frac{Q_1 Q_2}{r_0}$

Conceptual Problems

1. If a great deal of energy is required to form gaseous ions, why do ionic compounds form at all?
2. What are the general physical characteristics of ionic compounds?
3. Ionic compounds consist of crystalline lattices rather than discrete ion pairs. Why?
4. What factors affect the magnitude of the lattice energy of an ionic compound? What is the relationship between ionic size and lattice energy?
5. Which would have the larger lattice energy—an ionic compound consisting of a large cation and a large anion or one consisting of a large anion and a small cation? Explain your answer and any assumptions you made.
6. How would the lattice energy of an ionic compound consisting of a monovalent cation and a divalent anion compare with the lattice energy of an ionic compound containing a monovalent cation and a monovalent anion, if the internuclear distance was the same in both compounds? Explain your answer.
7. Which would have the larger lattice energy—$CrCl_2$ or $CrCl_3$—assuming similar arrangements of ions in the lattice? Explain your answer.
8. Which cation in each pair would be expected to form a chloride salt with the larger lattice energy, assuming similar arrangements of ions in the lattice? Explain your reasoning.
    1. Na^+, Mg^{2+}
    2. Li^+, Cs^+
    3. Cu^+, Cu^{2+}
9. Which cation in each pair would be expected to form an oxide with the higher melting point, assuming similar arrangements of ions in the lattice? Explain your reasoning.
    1. Mg^{2+}, Sr^{2+}
    2. Cs^+, Ba^{2+}
    3. Fe^{2+}, Fe^{3+}

Numerical Problems

1. Arrange SrO, PbS, and PrI_3 in order of decreasing lattice energy.
2. Compare BaO and MgO with respect to each of the following properties.
    1. enthalpy of sublimation
    2. ionization energy of the metal
    3. lattice energy

4. enthalpy of formation

3.

Contributors

- Anonymous

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Chapter 4.3: Lewis Electron Dot Symbols

Learning Objectives

- To use Lewis electron dot symbols to predict the number of bonds an element will form.

At the beginning of the 20th century, the American chemist G. N. Lewis (1875–1946) devised a system of symbols—now called Lewis electron dot symbols, often shortened to *Lewis dot symbols*—that can be used for predicting the number of bonds formed by most elements in their compounds (Figure 4.3.1). Each Lewis dot symbol consists of the chemical symbol for an element surrounded by dots that represent its valence electrons, the total number of *s* and *p* electrons in the outermost shell available for bonding. Lewis symbols do not easily capture the involvement of *d* electrons in bonding, but are incredibly useful for describing bonding of the first three periods and indicating which atoms are bonded to which ones. They are how organic molecular structures are drawn. As a simple example, Cesium, has the electron configuration $[Xe]6s^1$, which indicates one valence electron outside a closed shell. In the Lewis dot symbol, this single electron is represented as a single dot:

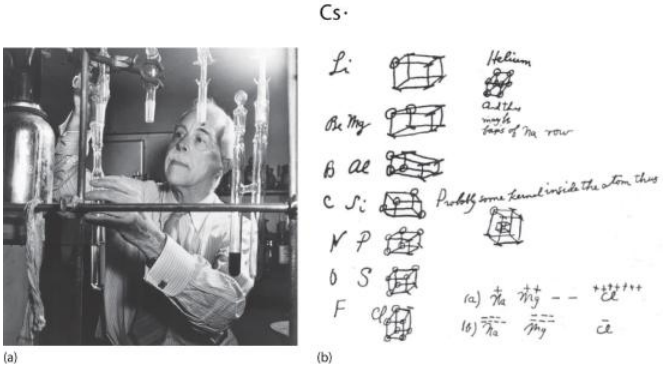
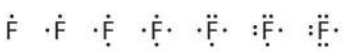


Figure 4.3.1 G. N. Lewis and the Octet Rule *(a) Lewis is working in the laboratory. (b) In Lewis's original sketch for the octet rule, he initially placed the electrons at the corners of a cube rather than placing them as we do now.*

Creating a Lewis Dot Symbol

To write an element's Lewis dot symbol, we place dots representing its valence electrons, one at a time, around the element's chemical symbol. Up to four dots are placed above, below, to the left, and to the right of the symbol (in any order, as long as elements with four or fewer valence electrons have no more than one dot in each position). The next dots, for elements with more than four valence electrons, are again distributed one at a time, each paired with one of the first four. Fluorine, for example, with the electron configuration $[He]2s^22p^5$, has seven valence electrons, so its Lewis dot symbol is constructed as follows:



The number of dots in the Lewis dot symbol is the same as the number of valence electrons, which is the same as the last digit of the element's group number in the periodic table. Lewis dot symbols for the elements in period 2 are given in Figure 4.3.2.

Lewis used the unpaired dots to predict the number of bonds that an element will form in a compound. Consider the symbol for nitrogen in Figure 4.3.2. The Lewis dot symbol explains why nitrogen, with three unpaired valence electrons, tends to form compounds in which it shares the unpaired electrons to form three bonds. Boron, which also has three unpaired valence electrons in its Lewis dot symbol, also tends to form compounds with three bonds, whereas carbon, with four unpaired valence electrons in its Lewis dot symbol, tends to share all of its unpaired valence electrons by forming compounds in which it has four bonds.

Group	1	2	13	14	15	16	17	18
Electron Configuration	$[He]2s^1$	$[He]2s^2$	$[He]2s^22p^1$	$[He]2s^22p^2$	$[He]2s^22p^3$	$[He]2s^22p^4$	$[He]2s^22p^5$	$[He]2s^22p^6$
Lewis Dot Symbol	Li·	·Be·	·B·	·Ċ·	·N̈·	:Ö·	:F̈·	:N̈e:

Figure 4.3.2 Lewis Dot Symbols for the Elements in Period 2

The Octet Rule

Lewis's major contribution to bonding theory was to recognize that atoms tend to lose, gain, or share electrons to reach a total of eight valence electrons, called an *octet*. This so-called octet rule The tendency for atoms to lose, gain, or share electrons to reach a total of eight valence electrons. explains the stoichiometry of most compounds in the *s* and *p* blocks of the periodic table. We now know from quantum mechanics that the number eight corresponds to having one *ns* and three *np* valence orbitals filled, which together can accommodate a total of eight electrons. We also know that the configuration ns^2np^6 is the one in a period which with the highest ionization energy and the lowest electron affinity. This level is the most difficult to take a valence electron away from or add one to. Atoms which can achieve an ns^2np^6 by sharing, borrowing or lending electrons to another atom which also achieves this configuration in the exchange will form a bond.

Remarkably, though, Lewis's insight was made nearly a decade before Rutherford proposed the nuclear model of the atom and more than two before Schrodinger had explained the electronic structure of hydrogen.

For some time helium was treated as an exception to the octet rule. Today we know that helium's $1s^2$ electron configuration gives it a full $n = 1$ shell, and why hydrogen gains its one electron to achieve the electron configuration of helium. We understand this as a consequence of only two electrons being able to fit in the $n = 1$ shell. In Lewis' time this was a mystery, something that was simply accepted. It is the ability to understand the atomic orbital basis of *ad hoc* rules developed in the past that motivates our atoms first approach to chemistry.

Lewis dot symbols can also be used to represent the ions in ionic compounds. The reaction of cesium with fluorine, for example, to produce the ionic compound CsF can be written as follows:



No dots are shown on Cs^+ in the product because cesium has lost its single valence electron to fluorine. The transfer of this electron produces the Cs^+ ion, which has the valence electron configuration of Xe, and the F^- ion, which has a total of eight valence electrons (an octet) and the Ne electron configuration. This description is consistent with the statement in Chapter 3 that among the main group elements, ions in simple binary ionic compounds generally have the electron configurations of the nearest noble gas. The charge of each ion is written in the product, and the anion and its electrons are enclosed in brackets. This notation emphasizes that the ions are associated electrostatically; no electrons are shared between the two elements.

As you might expect for such a qualitative approach to bonding, there are exceptions to the octet rule, which we describe in Section 4.5. These include molecules in which one or more atoms contain fewer or more than eight electrons. In Section 4.4 , however, we explain how to form molecular compounds by completing octets.

Summary

One convenient way to predict the number and basic arrangement of bonds in compounds is by using **Lewis electron dot symbols**, which consist of the chemical symbol for an element surrounded by dots that represent its valence electrons, grouped into pairs often placed above, below, and to the left and right of the symbol. The structures reflect the fact that the elements in period 2 and beyond tend to gain, lose, or share electrons to reach a total of eight valence electrons in their compounds, the so-called **octet rule**. Hydrogen, with only two valence electrons, does not obey the octet rule.

Key Takeaway

- Lewis dot symbols can be used to predict the number of bonds formed by most elements in their compounds.

Conceptual Problems

1. The Lewis electron system is a simplified approach for understanding bonding in covalent and ionic compounds. Why do chemists still find it useful?
2. Is a Lewis dot symbol an exact representation of the valence electrons in an atom or ion? Explain your answer.
3. How can the Lewis electron dot system help to predict the stoichiometry of a compound and its chemical and physical properties?

4. How is a Lewis dot symbol consistent with the quantum mechanical model of the atom described in Chapter 2 ? How is it different?

Answer

1.
2.
3. Lewis dot symbols allow us to predict the number of bonds atoms will form, and therefore the stoichiometry of a compound. The Lewis structure of a compound also indicates the presence or absence of lone pairs of electrons, which provides information on the compound's chemical reactivity and physical properties.
4.

Contributors

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Chapter 4.4: Lewis Structures and Covalent Bonding

Learning Objectives

- To use Lewis dot symbols to explain the stoichiometry of a compound.
- To understand the concept of resonance.

We begin our discussion of the relationship between structure and bonding in covalent compounds by describing the interaction between two identical neutral atoms—for example, the H_2 molecule, which contains a purely covalent bond. Each hydrogen atom in H_2 contains one electron and one proton, with the electron attracted to the proton by electrostatic forces. As the two hydrogen atoms are brought together, additional interactions must be considered (Figure 4.4.1):

- The electrons in the two atoms repel each other because they have the same charge ($E > 0$).
- Similarly, the protons in adjacent atoms repel each other ($E > 0$).
- The electron in one atom is attracted to the oppositely charged proton in the other atom and vice versa ($E < 0$).Recall from Chapter 2 that it is impossible to specify precisely the position of the electron in either hydrogen atom. Hence the quantum mechanical probability distributions must be used.

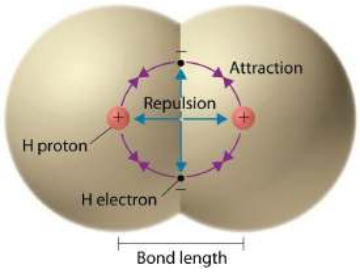


Figure 4.4.1 Attractive and Repulsive Interactions between Electrons and Nuclei in the Hydrogen Molecule *Electron–electron and proton–proton interactions are repulsive; electron–proton interactions are attractive. At the observed bond distance, the repulsive and attractive interactions are balanced.*

A plot of the potential energy of the system as a function of the internuclear distance (Figure 4.4.2) shows that the system becomes more stable (the energy of the system decreases) as two hydrogen atoms move toward each other from $r = \infty$, until the energy reaches a minimum at $r = r_0$ (the observed internuclear distance in H_2 is 74 pm). Thus at intermediate distances, proton–electron attractive interactions dominate, but as the distance becomes very short, electron–electron and proton–proton repulsive interactions cause the energy of the system to increase rapidly. Notice the similarity between Figure 4.4.2 and Figure 4.4.1 , which described a system containing two oppositely charged *ions*. The shapes of the energy versus distance curves in the two figures are similar because they both result from attractive and repulsive forces between charged entities.

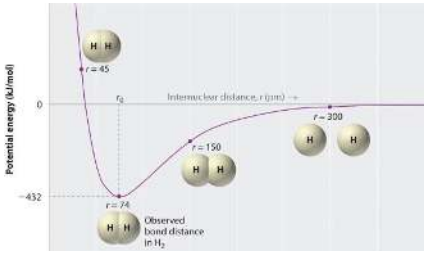
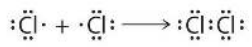


Figure 4.4.2 A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen Atoms *At long distances, both attractive and repulsive interactions are small. As the distance between the atoms decreases, the attractive electron–proton interactions dominate, and the energy of the system decreases. At the observed bond distance, the repulsive electron–electron and proton–proton interactions just balance the attractive interactions, preventing a further decrease in the internuclear distance. At very short internuclear distances, the repulsive interactions dominate, making the system less stable than the isolated atoms.*

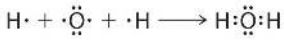
Using Lewis Dot Symbols to Describe Covalent Bonding

This sharing of electrons allowing atoms to "stick" together is the basis of covalent bonding. There is some intermediate distant, generally a bit longer than 0.1 nm, or if you prefer 100 pm, at which the attractive forces significantly outweigh the repulsive forces and a bond will be formed if both atoms can achieve a completen s^2np^6 configuration. It is this behavior that Lewis captured in his octet rule. The valence electron configurations of the constituent atoms of a covalent compound are important factors in determining its structure, stoichiometry, and properties. For example, chlorine, with seven valence electrons, is one electron short of an octet. If two chlorine atoms share their unpaired electrons by making a covalent bond and forming Cl_2, they can each complete their valence shell:



Each chlorine atom now has an octet. The electron pair being shared by the atoms is called a bonding pair A pair of electrons in a Lewis structure that is shared by two atoms, thus forming a covalent bond.; the other three pairs of electrons on each chlorine atom are called lone pairsA pair of electrons in a Lewis structure that is not involved in covalent bonding.. Lone pairs are not involved in covalent bonding. If both electrons in a covalent bond come from the same atom, the bond is called a coordinated covalent bondA covalent bond in which both electrons come from the same atom.. Examples of this type of bonding are presented in Section 4.5 when we discuss atoms with less than an octet of electrons.

We can illustrate the formation of a water molecule from two hydrogen atoms and an oxygen atom using Lewis dot symbols:



The structure on the right is the *Lewis electron structure*, or *Lewis structure*, for H_2O. With two bonding pairs and two lone pairs, the oxygen atom has now completed its octet. Moreover, by sharing a bonding pair with oxygen, each hydrogen atom now has a full valence shell of two electrons. Chemists usually indicate a bonding pair by a single line, as shown here for our two examples:



The following procedure can be used to construct Lewis electron structures for more complex molecules and ions:

1. **Arrange the atoms to show specific connections.** When there is a central atom, it is usually the least electronegative element in the compound. Chemists usually list this central atom first in the chemical formula (as in CCl_4 and CO_3^{2-}, which both have C as the central atom), which is another clue to the compound's structure. Hydrogen and the halogens are almost always connected to only one other atom, so they are usually *terminal* rather than central.

Note the Pattern

The central atom is usually the least electronegative element in the molecule or ion; hydrogen and the halogens are usually terminal.

2. **Determine the total number of valence electrons in the molecule or ion.** Add together the valence electrons from each atom. (Recall from Chapter 2 that the number of valence electrons is indicated by the position of the element in the periodic table.) If the species is a polyatomic ion, remember to add or subtract the number of electrons necessary to give the total charge on the ion. For CO_3^{2-}, for example, we add two electrons to the total because of the −2 charge.

3. **Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond.** In H_2O, for example, there is a bonding pair of electrons between oxygen and each hydrogen.

4. **Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).** These electrons will usually be lone pairs.

5. **If any electrons are left over, place them on the central atom.** We explain in Section 4.6 that some atoms are able to accommodate more than eight electrons.

6. **If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.** This will not change the number of electrons on the terminal atoms.

Now let's apply this procedure to some particular compounds, beginning with one we have already discussed.

H_2O

1. Because H atoms are almost always terminal, the arrangement within the molecule must be HOH.

2. Each H atom (group 1) has 1 valence electron, and the O atom (group 16) has 6 valence electrons, for a total of 8 valence electrons.

3. Placing one bonding pair of electrons between the O atom and each H atom gives H:O:H, with 4 electrons left over.

4. Each H atom has a full valence shell of 2 electrons.

5. Adding the remaining 4 electrons to the oxygen (as two lone pairs) gives the following structure:



This is the Lewis structure we drew earlier. Because it gives oxygen an octet and each hydrogen two electrons, we do not need to use step 6.

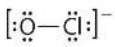
OCl^-

1. With only two atoms in the molecule, there is no central atom.

2. Oxygen (group 16) has 6 valence electrons, and chlorine (group 17) has 7 valence electrons; we must add one more for the negative charge on the ion, giving a total of 14 valence electrons.

3. Placing a bonding pair of electrons between O and Cl gives O:Cl, with 12 electrons left over.

4. If we place six electrons (as three lone pairs) on each atom, we obtain the following structure:



Each atom now has an octet of electrons, so steps 5 and 6 are not needed. The Lewis electron structure is drawn within brackets as is customary for an ion, with the overall charge indicated outside the brackets, and the bonding pair of electrons is indicated by a solid line. OCl^- is the hypochlorite ion, the active ingredient in chlorine laundry bleach and swimming pool disinfectant.

CH_2O

1. Because carbon is less electronegative than oxygen and hydrogen is normally terminal, C must be the central atom. One possible arrangement is as follows:



2. Each hydrogen atom (group 1) has one valence electron, carbon (group 14) has 4 valence electrons, and oxygen (group 16) has 6 valence electrons, for a total of [(2)(1) + 4 + 6] = 12 valence electrons.

3. Placing a bonding pair of electrons between each pair of bonded atoms gives the following:



Six electrons are used, and 6 are left over.

4. Adding all 6 remaining electrons to oxygen (as three lone pairs) gives the following:



Although oxygen now has an octet and each hydrogen has 2 electrons, carbon has only 6 electrons.

5. There are no electrons left to place on the central atom.

6. To give carbon an octet of electrons, we use one of the lone pairs of electrons on oxygen to form a carbon–oxygen double bond:



Both the oxygen and the carbon now have an octet of electrons, so this is an acceptable Lewis electron structure. The O has two bonding pairs and two lone pairs, and C has four bonding pairs. This is the structure of formaldehyde, which is used in embalming fluid.

An alternative structure can be drawn with one H bonded to O. *Formal charges*, discussed later in this section, suggest that such a structure is less stable than that shown previously.

Example 4.4.1

Write the Lewis electron structure for each species.

1. NCl_3
2. S_2^{2-}
3. NOCl

Given: chemical species

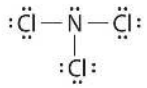
Asked for: Lewis electron structures

Strategy:

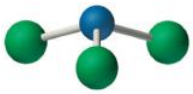
Use the six-step procedure to write the Lewis electron structure for each species.

Solution:

1. Nitrogen is less electronegative than chlorine, and halogen atoms are usually terminal, so nitrogen is the central atom. The nitrogen atom (group 15) has 5 valence electrons and each chlorine atom (group 17) has 7 valence electrons, for a total of 26 valence electrons. Using 2 electrons for each N–Cl bond and adding three lone pairs to each Cl account for (3 × 2) + (3 × 2 × 3) = 24 electrons. Rule 5 leads us to place the remaining 2 electrons on the central N:

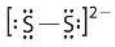


   Nitrogen trichloride is an unstable oily liquid once used to bleach flour; this use is now prohibited in the United States.

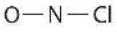


Nitrogen trichloride

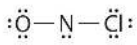
2. In a diatomic molecule or ion, we do not need to worry about a central atom. Each sulfur atom (group 16) contains 6 valence electrons, and we need to add 2 electrons for the −2 charge, giving a total of 14 valence electrons. Using 2 electrons for the S–S bond, we arrange the remaining 12 electrons as three lone pairs on each sulfur, giving each S atom an octet of electrons:



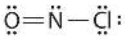
3. Because nitrogen is less electronegative than oxygen or chlorine, it is the central atom. The N atom (group 15) has 5 valence electrons, the O atom (group 16) has 6 valence electrons, and the Cl atom (group 17) has 7 valence electrons, giving a total of 18 valence electrons. Placing one bonding pair of electrons between each pair of bonded atoms uses 4 electrons and gives the following:



   Adding three lone pairs each to oxygen and to chlorine uses 12 more electrons, leaving 2 electrons to place as a lone pair on nitrogen:



Because this Lewis structure has only 6 electrons around the central nitrogen, a lone pair of electrons on a terminal atom must be used to form a bonding pair. We could use a lone pair on either O or Cl. Because we have seen many structures in which O forms a double bond but none with a double bond to Cl, it is reasonable to select a lone pair from O to give the following:



All atoms now have octet configurations. This is the Lewis electron structure of nitrosyl chloride, a highly corrosive, reddish-orange gas.

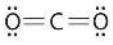


Nitrosyl chloride

Exercise

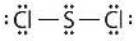
Write Lewis electron structures for CO_2 and SCl_2, a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

Answer:

1. 



Carbon dioxide

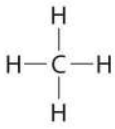
2. 



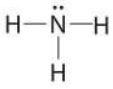
Sulfur dichloride

Using Lewis Electron Structures to Explain Stoichiometry

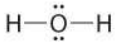
Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries. In the Lewis model, the number of bonds formed by an element in a neutral compound is the same as the number of unpaired electrons it must share with other atoms to complete its octet of electrons. For the elements of group 17 (the halogens), this number is one; for the elements of group 16 (the chalcogens), it is two; for group 15, three; and for group 14, four. These requirements are illustrated by the following Lewis structures for the hydrides of the lightest members of each group:



Group 14



Group 15

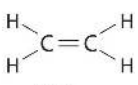


Group 16



Group 17

Elements may form multiple bonds to complete an octet. In ethylene, for example, each carbon contributes two electrons to the double bond, giving each carbon an octet (two electrons/bond × four bonds = eight electrons). Neutral structures with fewer or more bonds exist, but they are unusual and violate the octet rule.



Ethylene

Allotropes of an element can have very different physical and chemical properties because of different three-dimensional arrangements of the atoms; the number of bonds formed by the component atoms, however, is always the same. As noted at the beginning of the chapter, diamond is a hard, transparent solid; graphite is a soft, black solid; and the fullerenes have open cage structures. Despite these differences, the carbon atoms in all three allotropes form four bonds, in accordance with the octet rule. Elemental phosphorus also exists in three forms: white phosphorus, a toxic, waxy substance that initially glows and then spontaneously ignites on contact with air; red phosphorus, an amorphous substance that is used commercially in safety matches, fireworks, and smoke bombs; and black phosphorus, an unreactive crystalline solid with a texture similar to graphite (Figure 4.4.3). Nonetheless, the phosphorus atoms in all three forms obey the octet rule and form three bonds per phosphorus atom.

Note the Pattern

Lewis structures explain why the elements of groups 14–17 form neutral compounds with four, three, two, and one bonded atom(s), respectively.

Figure 4.4.3 The Three Allotropes of Phosphorus: White, Red, and Black

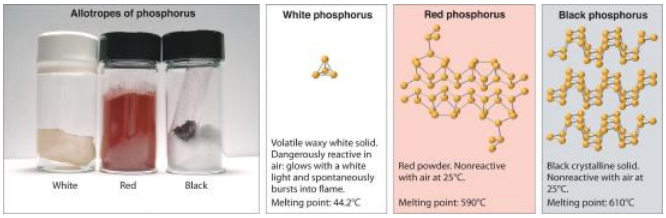


Figure 4.4.3 The Three Allotropes of Phosphorus: White, Red, and Black *All three forms contain only phosphorus atoms, but they differ in the arrangement and connectivity of their atoms. White phosphorus contains P_4 tetrahedra, red phosphorus is a network of linked P_8 and P_9 units, and black phosphorus forms sheets of six-membered rings. As a result, their physical and chemical properties differ dramatically.*

Formal Charges

It is sometimes possible to write more than one Lewis structure for a substance that does not violate the octet rule, as we saw for CH_2O, but not every Lewis structure may be equally reasonable. In these situations, we can choose the most stable Lewis structure by considering the formal chargeThe difference between the number of valence electrons in a free atom and the number of electrons assigned to it in a particular Lewis electron structure. on the atoms, which is the difference between the number of valence electrons in the free atom and the number assigned to it in the Lewis electron structure. The formal charge is a way of computing the charge distribution within a Lewis structure; the sum of the formal charges on the atoms within a molecule or an ion must equal the overall charge on the molecule or ion. A formal charge does *not* represent a true charge on an atom in a covalent bond but is simply used to predict the most likely structure when a compound has more than one valid Lewis structure.

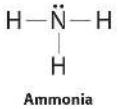
To calculate formal charges, we assign electrons in the molecule to individual atoms according to these rules:

- Nonbonding electrons are assigned to the atom on which they are located
- Bonding electrons are divided equally between the bonded atoms, one to each

For each atom, we then compute a formal charge:

$$\textit{formal charge} = \underset{(\textit{free atom})}{\textit{valence } e^-} - \underset{(\textit{atom in Lewis structure})}{\left(\textit{non} - \textit{bonding } e^- + \frac{\textit{bonding } e^-}{2}\right)}$$

To illustrate this method, let's calculate the formal charge on the atoms in ammonia (NH_3) whose Lewis electron structure is as follows:



Ammonia

A neutral nitrogen atom has five valence electrons (it is in group 15). From its Lewis electron structure, the nitrogen atom in ammonia has one lone pair and shares three bonding pairs with hydrogen atoms, so nitrogen itself is assigned a total of five electrons [2 nonbonding e^- + (6 bonding $e^-/2$)]. Substituting into Equation 4.4.1, we obtain

$$formal\ charge\,(N) = 5\ valence\ e^- - \left(2\ non-bonding\ e^- + \frac{6\ bonding\ e^-}{2}\right) = 0$$

A neutral hydrogen atom has one valence electron. Each hydrogen atom in the molecule shares one pair of bonding electrons and is therefore assigned one electron [0 nonbonding e^- + (2 bonding $e^-/2$)]. Using Equation 4.4.1 to calculate the formal charge on hydrogen, we obtain

$$formal\ charge\,(H) = 1\ valence\ e^- - \left(0\ non-bonding\ e^- + \frac{2\ bonding\ e^-}{2}\right) = 0$$

The hydrogen atoms in ammonia have the same number of electrons as neutral hydrogen atoms, and so their formal charge is also zero. Adding together the formal charges should give us the overall charge on the molecule or ion. In this example, the nitrogen and each hydrogen has a formal charge of zero. When summed the overall charge is zero, which is consistent with the overall charge on the NH_3 molecule.

Typically, the structure with the most charges on the atoms closest to zero is the more stable Lewis structure. In cases where there are positive or negative formal charges on various atoms, stable structures generally have negative formal charges on the more electronegative atoms and positive formal charges on the less electronegative atoms. The next example further demonstrates how to calculate formal charges.

Example 4.4.2

Calculate the formal charges on each atom in the NH_4^+ ion.

Given: chemical species

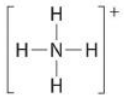
Asked for: formal charges

Strategy:

Identify the number of valence electrons in each atom in the NH_4^+ ion. Use the Lewis electron structure of NH_4^+ to identify the number of bonding and nonbonding electrons associated with each atom and then use Equation 4.4.1 to calculate the formal charge on each atom.

Solution:

The Lewis electron structure for the NH_4^+ ion is as follows:



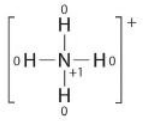
The nitrogen atom shares four bonding pairs of electrons, and a neutral nitrogen atom has five valence electrons. Using Equation 4.4.1, the formal charge on the nitrogen atom is therefore

$$formal\ charge\,(N) = 5 - \left(0 + \frac{8}{2}\right) = 0$$

Each hydrogen atom in has one bonding pair. The formal charge on each hydrogen atom is therefore

$$formal\ charge\,(H) = 1 - \left(0 + \frac{2}{2}\right) = 0$$

The formal charges on the atoms in the NH_4^+ ion are thus

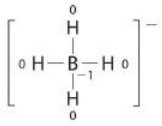


Adding together the formal charges on the atoms should give us the total charge on the molecule or ion. In this case, the sum of the formal charges is 0 + 1 + 0 + 0 + 0 = +1.

Exercise

Write the formal charges on all atoms in BH_4^-.

Answer:



If an atom in a molecule or ion has the number of bonds that is typical for that atom (e.g., four bonds for carbon), its formal charge is zero.

Note the Pattern

An atom, molecule, or ion has a formal charge of zero if it has the number of bonds that is typical for that species.

Using Formal Charges to Distinguish between Lewis Structures

As an example of how formal charges can be used to determine the most stable Lewis structure for a substance, we can compare two possible structures for CO_2. Both structures conform to the rules for Lewis electron structures.

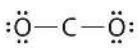
CO_2

1. C is less electronegative than O, so it is the central atom.

2. C has 4 valence electrons and each O has 6 valence electrons, for a total of 16 valence electrons.

3. Placing one electron pair between the C and each O gives O–C–O, with 12 electrons left over.

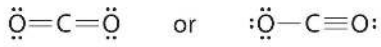
4. Dividing the remaining electrons between the O atoms gives three lone pairs on each atom:



This structure has an octet of electrons around each O atom but only 4 electrons around the C atom.

5. No electrons are left for the central atom.

6. To give the carbon atom an octet of electrons, we can convert two of the lone pairs on the oxygen atoms to bonding electron pairs. There are, however, two ways to do this. We can either take one electron pair from each oxygen to form a symmetrical structure or take both electron pairs from a single oxygen atom to give an asymmetrical structure:



Both Lewis electron structures give all three atoms an octet. How do we decide between these two possibilities? The formal charges for the two Lewis electron structures of CO_2 are as follows:



Both Lewis structures have a net formal charge of zero, but the structure on the right has a +1 charge on the more electronegative atom (O). Thus the symmetrical Lewis structure on the left is predicted to be more stable, and it is, in fact, the structure observed experimentally. Remember, though, that formal charges do *not* represent the actual charges on atoms in a molecule or ion. They are used simply as a bookkeeping method for predicting the most stable Lewis structure for a compound.

Note the Pattern

The Lewis structure with the set of formal charges closest to zero is usually the most stable.

Example 4.4.3

The thiocyanate ion (SCN^-), which is used in printing and as a corrosion inhibitor against acidic gases, has at least two possible Lewis electron structures. Draw two possible structures, assign formal charges on all atoms in both, and decide which is the preferred arrangement of electrons.

Given: chemical species

Asked for: Lewis electron structures, formal charges, and preferred arrangement

Strategy:

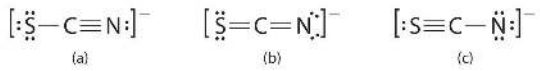
A Use the step-by-step procedure to write two plausible Lewis electron structures for SCN^-.

B Calculate the formal charge on each atom using Equation 4.4.1.

C Predict which structure is preferred based on the formal charge on each atom and its electronegativity relative to the other atoms present.

Solution:

A Possible Lewis structures for the SCN^- ion are as follows:



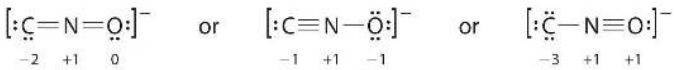
B We must calculate the formal charges on each atom to identify the more stable structure. If we begin with carbon, we notice that the carbon atom in each of these structures shares four bonding pairs, the number of bonds typical for carbon, so it has a formal charge of zero. Continuing with sulfur, we observe that in (a) the sulfur atom shares one bonding pair and has three lone pairs and has a total of six valence electrons. The formal charge on the sulfur atom is therefore $6-\left(6+\frac{2}{2}\right)=-1.5-\left(4+\frac{4}{2}\right)=-1$ In (c), nitrogen has a formal charge of −2.

C Which structure is preferred? Structure (b) is preferred because the negative charge is on the more electronegative atom (N), and it has lower formal charges on each atom as compared to structure (c): 0, −1 versus +1, −2.

Exercise

Salts containing the fulminate ion (CNO^-) are used in explosive detonators. Draw three Lewis electron structures for CNO^- and use formal charges to predict which is more stable. (Note: N is the central atom.)

Answer:



The second structure is predicted to be more stable.

Resonance Structures

Sometimes, even when formal charges are considered, the bonding in some molecules or ions cannot be described by a single Lewis structure. 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°.

O_3

1. We know that ozone has a V-shaped structure, so one O atom is central:



2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.

3. Assigning one bonding pair of electrons to each oxygen–oxygen bond gives



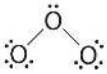
with 14 electrons left over.

4. If we place three lone pairs of electrons on each terminal oxygen, we obtain

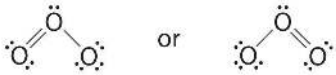


and have 2 electrons left over.

5. At this point, both terminal oxygen atoms have octets of electrons. We therefore place the last 2 electrons on the central atom:



6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons —but which one? Depending on which one we choose, we obtain either



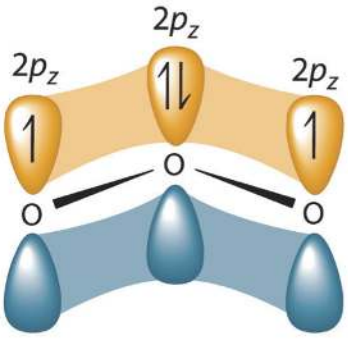
Which is correct? In fact, neither is correct. Both predict one O–O single bond and one O=O double bond. As you will learn in Section 4.6, if the bonds were of different types (one single and one double, for example), they would have different lengths. It turns out, however, that both O–O bond distances are identical, 127.2 pm, which is shorter than a typical O–O single bond (148 pm) and longer than the O=O double bond in O_2 (120.7 pm).

Equivalent Lewis dot structures, such as those of ozone, are called resonance structures A Lewis electron structure that has different arrangements of electrons around atoms whose positions do not change.. 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:



Before the development of quantum chemistry it was thought that the double-headed arrow indicates that the actual electronic structure is an *average* of those shown, or that the molecule oscillates between the two structures. Today we know that the electrons involved in the double bonds occupy an orbital that extends over all three oxygen molecules, combining *p* orbitals on all three.

Figure 4.4.4 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.

We will discuss the formation of these molecular orbitals in the next chapter but it is important to understand that resonance structures are based on molecular orbitals not averages of different bonds between atoms. We describe the electrons in such molecular orbitals as being delocalized, that is they cannot be assigned to a bond between two atoms.

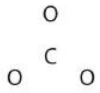
Note the Pattern

When it is possible to write more than one equivalent resonance structure for a molecule or ion, the actual structure involves a molecular orbital which is a linear combination of atomic orbitals from each of the atoms.

CO_3^{2-}

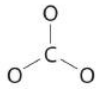
Like ozone, the electronic structure of the carbonate ion cannot be described by a single Lewis electron structure. Unlike O_3, though, the Lewis structures describing CO_3^{2-} has *three* equivalent representations.

1. Because carbon is the least electronegative element, we place it in the central position:

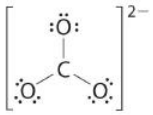


2. Carbon has 4 valence electrons, each oxygen has 6 valence electrons, and there are 2 more for the −2 charge. This gives 4 + (3 × 6) + 2 = 24 valence electrons.

3. Six electrons are used to form three bonding pairs between the oxygen atoms and the carbon:

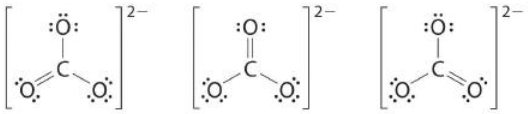


4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the −2 charge:

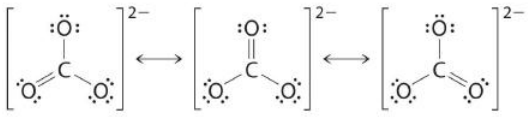


5. No electrons are left for the central atom.

6. At this point, the carbon atom has only 6 valence electrons, so we must take one lone pair from an oxygen and use it to form a carbon–oxygen double bond. In this case, however, there are *three* possible choices:



As with ozone, none of these structures describes the bonding exactly. Each predicts one carbon–oxygen double bond and two carbon–oxygen single bonds, but experimentally all C–O bond lengths are identical. We can write resonance structures (in this case, three of them) for the carbonate ion:



As the case for ozone, 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.

Example 4.4.4

Benzene is a common organic solvent that was previously used in gasoline; it is no longer used for this purpose, however, because it is now known to be a carcinogen. The benzene molecule (C_6H_6) consists of a regular hexagon of carbon atoms, each of which is also bonded to a hydrogen atom. Use resonance structures to describe the bonding in benzene.

Given: molecular formula and molecular geometry

Asked for: resonance structures

Strategy:

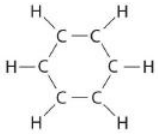
A Draw a structure for benzene illustrating the bonded atoms. Then calculate the number of valence electrons used in this drawing.

B Subtract this number from the total number of valence electrons in benzene and then locate the remaining electrons such that each atom in the structure reaches an octet.

C Draw the resonance structures for benzene.

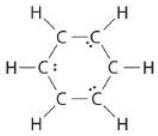
Solution:

A Each hydrogen atom contributes 1 valence electron, and each carbon atom contributes 4 valence electrons, for a total of (6 × 1) + (6 × 4) = 30 valence electrons. If we place a single bonding electron pair between each pair of carbon atoms and between each carbon and a hydrogen atom, we obtain the following:



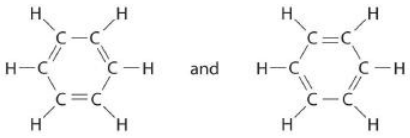
Each carbon atom in this structure has only 6 electrons and has a formal charge of +1, but we have used only 24 of the 30 valence electrons.

B If the 6 remaining electrons are uniformly distributed pairwise on alternate carbon atoms, we obtain the following:

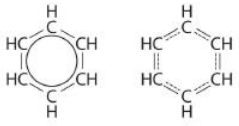


Three carbon atoms now have an octet configuration and a formal charge of −1, while three carbon atoms have only 6 electrons and a formal charge of +1. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of electrons and a formal charge of 0, by making three C=C double bonds.

C There are, however, two ways to do this:



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:



This combination of *p* orbitals for benzene can be visualized as a ring with a node in the plane of the carbon atoms.

Exercise

The sodium salt of nitrite is used to relieve muscle spasms. Draw two resonance structures for the nitrite ion (NO_2^-).

Answer:



Resonance structures are particularly common in oxoanions of the *p*-block elements, such as sulfate and phosphate, and in aromatic hydrocarbons, such as benzene and naphthalene.

Summary

A plot of the overall energy of a covalent bond as a function of internuclear distance is identical to a plot of an ionic pair because both result from attractive and repulsive forces between charged entities. In Lewis electron structures, we encounter **bonding pairs**, which are shared by two atoms, and **lone pairs**, which are not shared between atoms. If both electrons in a covalent bond come from the same atom, the bond is called a **coordinate covalent bond**. Lewis structures are an attempt to rationalize why certain stoichiometries are commonly observed for the elements of particular families. Neutral compounds of group 14 elements typically contain four bonds around each atom (a double bond counts as two, a triple bond as three), whereas neutral compounds of group 15 elements typically contain three bonds. In cases where it is possible to write more than one Lewis electron structure with octets around all the nonhydrogen atoms of a compound, the **formal charge** on each atom in alternative structures must be considered to decide which of the valid structures can be excluded and which is the most reasonable. The formal charge is the difference between the number of valence electrons of the free atom and the number of electrons assigned to it in the compound, where bonding electrons are divided equally between the bonded atoms. The Lewis structure with the lowest formal charges on the atoms is almost always the most stable one. Some molecules have two or more chemically equivalent Lewis electron structures, called **resonance structures**. These structures are written with a double-headed arrow between them, indicating that *none* of the Lewis structures accurately describes the bonding but that the actual structure is an *average* of the individual resonance structures.

Key Takeaway

- Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries.

Key Equation

Formal charge on an atom

Equation 4.4.1: $$formal\ charge = valence\ e^- - \left(non-bonding\ e^- + \frac{bonding\ e^-}{2}\right)$$

Conceptual Problems

1. Compare and contrast covalent and ionic compounds with regard to
    1. volatility.
    2. melting point.
    3. electrical conductivity.
    4. physical appearance.
2. What are the similarities between plots of the overall energy versus internuclear distance for an ionic compound and a covalent compound? Why are the plots so similar?
3. Which atom do you expect to be the central atom in each of the following species?
    1. SO_4^{2-}
    2. NH_4^+
    3. BCl_3
    4. SO_2Cl_2?
4. Which atom is the central atom in each of the following species?

1. PCl_3
2. $CHCl_3$
3. SO_2
4. IF_3?

5. What is the relationship between the number of bonds typically formed by the period 2 elements in groups 14, 15, and 16 and their Lewis electron structures?
6. Although formal charges do not represent actual charges on atoms in molecules or ions, they are still useful. Why?
7. Why are resonance structures important?
8. In what types of compounds are resonance structures particularly common?

Numerical Problems

1. Give the electron configuration and the Lewis dot symbol for the following. How many more electrons can each atom accommodate?
    1. Se
    2. Kr
    3. Li
    4. Sr
    5. H
2. Give the electron configuration and the Lewis dot symbol for the following. How many more electrons can each atom accommodate?
    1. Na
    2. Br
    3. Ne
    4. C
    5. Ga
3. Based on Lewis dot symbols, predict the preferred oxidation state of Be, F, B, and Cs.
4. Based on Lewis dot symbols, predict the preferred oxidation state of Br, Rb, O, Si, and Sr.
5. Based on Lewis dot symbols, predict how many bonds gallium, silicon, and selenium will form in their neutral compounds.
6. Determine the total number of valence electrons in the following.
    1. Cr
    2. Cu^+
    3. NO^+
    4. XeF_2
    5. Br_2
    6. CH_2Cl_2
    7. NO_3^-
    8. H_3O^+
7. Determine the total number of valence electrons in the following.
    1. Ag
    2. Pt^{2+}
    3. H_2S
    4. OH^-
    5. I_2
    6. CH_4
    7. SO_4^{2-}

8. NH_4^+.

8. Draw Lewis electron structures for the following.

    1. F_2
    2. SO_2
    3. $AlCl_4^-$
    4. SO_3^{2-}
    5. BrCl
    6. XeF_4
    7. NO^+
    8. PCl_3

9. Draw Lewis electron structures for the following.

    1. Br_2
    2. CH_3Br
    3. SO_4^{2-}
    4. O_2
    5. S_2^{2-}
    6. BF_3

10. Draw Lewis electron structures for CO_2, NO_2^-, SO_2, and NO_2^+. From your diagram, predict which pair(s) of compounds have similar electronic structures.

11. Write Lewis dot symbols for each pair of elements. For a reaction between each pair of elements, predict which element is the oxidant, which element is the reductant, and the final stoichiometry of the compound formed.

    1. K, S
    2. Sr, Br
    3. Al, O
    4. Mg, Cl

12. Write Lewis dot symbols for each pair of elements. For a reaction between each pair of elements, predict which element is the oxidant, which element is the reductant, and the final stoichiometry of the compound formed.

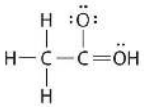
    1. Li, F
    2. Cs, Br
    3. Ca, Cl
    4. B, F

13. Use Lewis dot symbols to predict whether ICl and NO_4^- are chemically reasonable formulas.

14. Draw a plausible Lewis electron structure for a compound with the molecular formula Cl_3PO.

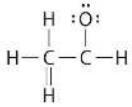
15. Draw a plausible Lewis electron structure for a compound with the molecular formula CH_4O.

16. While reviewing her notes, a student noticed that she had drawn the following structure in her notebook for acetic acid:



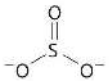
    Why is this structure not feasible? Draw an acceptable Lewis structure for acetic acid. Show the formal charges of all nonhydrogen atoms in both the correct and incorrect structures.

17. A student proposed the following Lewis structure shown for acetaldehyde.



Why is this structure not feasible? Draw an acceptable Lewis structure for acetaldehyde. Show the formal charges of all nonhydrogen atoms in both the correct and incorrect structures.

18. Draw the most likely structure for HCN based on formal charges, showing the formal charge on each atom in your structure. Does this compound have any plausible resonance structures? If so, draw one.
19. Draw the most plausible Lewis structure for NO_3^-. Does this ion have any other resonance structures? Draw at least one other Lewis structure for the nitrate ion that is not plausible based on formal charges.
20. At least two Lewis structures can be drawn for BCl_3. Using arguments based on formal charges, explain why the most likely structure is the one with three B–Cl single bonds.
21. Using arguments based on formal charges, explain why the most feasible Lewis structure for SO_4^{2-} has two sulfur–oxygen double bonds.
22. At least two distinct Lewis structures can be drawn for N_3^-. Use arguments based on formal charges to explain why the most likely structure contains a nitrogen–nitrogen double bond.
23. Is H–O–N=O a reasonable structure for the compound HNO_2? Justify your answer using Lewis electron dot structures.
24. Is H–O=C–H a reasonable structure for a compound with the formula CH_2O? Use Lewis electron dot structures to justify your answer.
25. Explain why the following Lewis structure for SO_3^{2-} is or is not reasonable.



26. Draw all the resonance structures for each ion.
    1. HSO_4^-
    2. HSO_3^-

Answers

1. 1. $[Ar]4s^2 3d^{10} 4p^4$



Selenium can accommodate two more electrons, giving the Se^{2-} ion.

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



Krypton has a closed shell electron configuration, so it cannot accommodate any additional electrons.

3. $1s^2 2s^1$



Lithium can accommodate one additional electron in its 2*s* orbital, giving the Li^- ion.

4. $[Kr]5s^2$



Strontium has a filled 5*s* subshell, and additional electrons would have to be placed in an orbital with a higher energy. Thus strontium has no tendency to accept an additional electron.

5. $1s^1$



Hydrogen can accommodate one additional electron in its 1*s* orbital, giving the H^- ion.

2.

3. Be^{2+}, F^-, B^{3+}, Cs^+

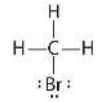
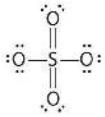
4.

5.

6.

7. 1. 11
   2. 8
   3. 8
   4. 8
   5. 14
   6. 8
   7. 32
   8. 8

8.

9. 1. 
   2. 
   3. 
   4. 
   5. 
   6. 

10.

11. 1. 

    K is the reductant; S is the oxidant. The final stoichiometry is K_2S.

    2. 

    Sr is the reductant; Br is the oxidant. The final stoichiometry is $SrBr_2$.

    3. 

    Al is the reductant; O is the oxidant. The final stoichiometry is Al_2O_3.

    4. 

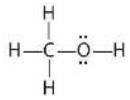
Mg is the reductant; Cl is the oxidant. The final stoichiometry is $MgCl_2$.

12.

13.

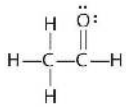
14.

15. The only structure that gives both oxygen and carbon an octet of electrons is the following:

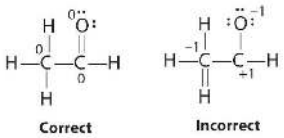


16.

17. The student's proposed structure has two flaws: the hydrogen atom with the double bond has four valence electrons (H can only accommodate two electrons), and the carbon bound to oxygen only has six valence electrons (it should have an octet). An acceptable Lewis structure is

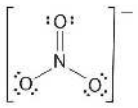


The formal charges on the correct and incorrect structures are as follows:



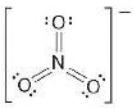
18.

19. The most plausible Lewis structure for NO_3^- is:



There are three equivalent resonance structures for nitrate (only one is shown), in which nitrogen is doubly bonded to one of the three oxygens. In each resonance structure, the formal charge of N is +1; for each singly bonded O, it is −1; and for the doubly bonded oxygen, it is 0.

The following is an example of a Lewis structure that is *not* plausible:



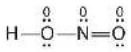
This structure nitrogen has six bonds (nitrogen can form only four bonds) and a formal charge of –1.

20.

21. With four S–O single bonds, each oxygen in SO_4^{2-} has a formal charge of −1, and the central sulfur has a formal charge of +2. With two S=O double bonds, only two oxygens have a formal charge of –1, and sulfur has a formal charge of zero. Lewis structures that minimize formal charges tend to be lowest in energy, making the Lewis structure with two S=O double bonds the most probable.

22.

23. Yes. This is a reasonable Lewis structure, because the formal charge on all atoms is zero, and each atom (except H) has an octet of electrons.



24.
25.
26.

Contributors

- Anonymous

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Chapter 4.5: Exceptions to the Octet Rule

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Learning Objective

To assign a Lewis dot symbol to elements not having an octet of electrons in their compounds.

Lewis dot structures provide a simple model for rationalizing the bonding in most known compounds. However, there are four general exceptions to the octet rule: (1) molecules, such as NO, with an *odd* number of electrons; (2) molecules in which one or more atoms possess *more* than eight electrons, such as SF_6; (3) molecules such as BCl_3, in which one or more atoms possess *less* than eight electrons and (4) molecules where electrons in bonds are not localized. These are each historical artifacts resulting from the ad hoc nature of the octet rule which predates quantum theory. In discussing these exceptions we will explain how the quantum theory provides a simple explanation for each

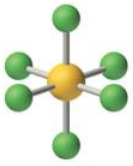
Odd Number of Electrons

Because most molecules or ions that consist of *s*- and *p*-block elements contain even numbers of electrons, their bonding can be described using a model that assigns every electron to either a bonding pair or a lone pair. Molecules or ions containing *d*-block elements frequently contain an odd number of electrons, and their bonding cannot adequately be described using the simple approach we have developed so far. There are, however, a few molecules containing only *p*-block elements that have an odd number of electrons. Some important examples are nitric oxide (NO); nitrogen dioxide (NO_2), an oxidizing agent in rocket propulsion; and chlorine dioxide (ClO_2), which is used in water purification plants. Consider NO, for example. With 5 + 6 = 11 valence electrons, there is no way to draw a Lewis structure that gives each atom an octet of electrons. Molecules such as NO, NO_2, and ClO_2 require a more sophisticated treatment of bonding, which will be developed in Chapter 5. Even without such a treatment, we notice that such odd electron species are extremely reactive.

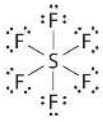
More Than an Octet of Electrons

The most common exception to the octet rule is a molecule or an ion with at least one atom that possesses more than an octet of electrons. Such compounds are found for elements of period 3 and beyond and involve the participation of a *d* orbital in the bonding. Examples from the *p*-block elements include SF_6, a substance used by the electric power industry to insulate high-voltage lines, and the SO_4^{2-} and PO_4^{3-} ions.

Let's look at sulfur hexafluoride (SF_6), whose Lewis structure must accommodate a total of 48 valence electrons [6 + (6 × 7) = 48]. If we arrange the atoms and electrons symmetrically, we obtain a structure with six bonds to sulfur; that is, it is *six-coordinate*. Each fluorine atom has an octet, but the sulfur atom has 12 electrons surrounding it rather than 8.The third step in our procedure for writing Lewis electron structures, in which we place an electron pair between each pair of bonded atoms, requires that an atom have more than 8 electrons whenever it is bonded to more than 4 other atoms.



Sulfur hexafluoride

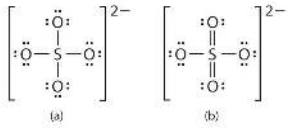


The octet rule is based on the fact that each valence orbital (typically, one *ns* and three *np* orbitals) can accommodate only two electrons. To accommodate more than eight electrons, sulfur must be using not only the *ns* and *np* valence orbitals but additional orbitals as well. Sulfur has an $[Ne]3s^23p^43d^0$ electron configuration, so in principle it could accommodate more than eight valence electrons by using one or more *d* orbitals. Thus species such as SF_6 are often called expanded-valence molecules A compound with

more than an octet of electrons around an atom.. This model explains why compounds exist with more than an octet of electrons around an atom.

There is no correlation between the stability of a molecule or an ion and whether or not it has an expanded valence shell. Some species with expanded valences, such as PF_5, are highly reactive, whereas others, such as SF_6, are very unreactive. In fact, SF_6 is so inert that it has many commercial applications. In addition to its use as an electrical insulator, it is used as the coolant in some nuclear power plants, and it was used as the pressurizing gas in “unpressurized” tennis balls. However, because it is an extremely strong and long lived greenhouse gas, its use is being phased out.

An expanded valence shell is often written for oxoanions of the heavier *p*-block elements, such as sulfate (SO_4^{2-}) and phosphate (PO_4^{3-}). Sulfate, for example, has a total of 32 valence electrons [6 + (4 × 6) + 2]. If we use a single pair of electrons to connect the sulfur and each oxygen, we obtain the four-coordinate Lewis structure (a). We know that sulfur can accommodate more than eight electrons by using its empty valence *d* orbitals, just as in SF_6. An alternative structure (b) can be written with S=O double bonds, making the sulfur again six-coordinate. We can draw five other resonance structures equivalent to (b) that vary only in the arrangement of the single and double bonds. In fact, experimental data show that the S-to-O bonds in the SO_4^{2-} ion are intermediate in length between single and double bonds, as expected for a system whose resonance structures all contain two S–O single bonds and two S=O double bonds. When calculating the formal charges on structures (a) and (b), we see that the S atom in (a) has a formal charge of +2, whereas the S atom in (b) has a formal charge of 0. Thus by using an expanded octet, a +2 formal charge on S can be eliminated.

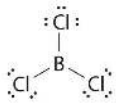


Note the Pattern

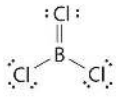
In oxoanions of the heavier *p*-block elements, the central atom often has an expanded valence shell.

Less Than an Octet of Electrons

Molecules with atoms that possess less than an octet of electrons generally contain the lighter *s*- and *p*-block elements, especially beryllium, typically with just four electrons around the central atom, and boron, typically with six. One example, boron trichloride (BCl_3) is used to produce fibers for reinforcing high-tech tennis rackets and golf clubs. The compound has 24 valence electrons and the following Lewis structure:



The boron atom has only six valence electrons, while each chlorine atom has eight. A reasonable solution might be to use a lone pair from one of the chlorine atoms to form a B-to-Cl double bond:



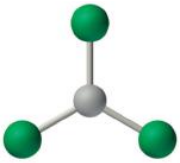
This resonance structure, however, results in a formal charge of +1 on the doubly bonded Cl atom and −1 on the B atom. The high electronegativity of Cl makes this separation of charge unlikely and suggests that this is not the most important resonance structure for BCl_3. This conclusion is shown to be valid based on the three equivalent B–Cl bond lengths of 173 pm that have no double bond character. Electron-deficient compounds such as BCl_3 have a strong tendency to gain an additional pair of electrons by reacting with species with a lone pair of electrons.

Note the Pattern

Molecules with atoms that have fewer than an octet of electrons generally contain the lighter *s*- and *p*-block elements.

Note the Pattern

Electron-deficient compounds have a strong tendency to gain electrons in their reactions.



Boron trichloride

Example 4.5.1

Draw Lewis dot structures for each compound.

1. $BeCl_2$ gas, a compound used to produce beryllium, which in turn is used to produce structural materials for missiles and communication satellites
2. SF_4, a compound that reacts violently with water

Include resonance structures where appropriate.

Given: two compounds

Asked for: Lewis electron structures

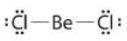
Strategy:

A Use the procedure given earlier to write a Lewis electron structure for each compound. If necessary, place any remaining valence electrons on the element most likely to be able to accommodate more than an octet.

B After all the valence electrons have been placed, decide whether you have drawn an acceptable Lewis structure.

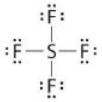
Solution:

1. **A** Because it is the least electronegative element, Be is the central atom. The molecule has 16 valence electrons (2 from Be and 7 from each Cl). Drawing two Be–Cl bonds and placing three lone pairs on each Cl gives the following structure:

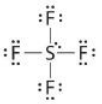


   B Although this arrangement gives beryllium only 4 electrons, it is an acceptable Lewis structure for $BeCl_2$. Beryllium is known to form compounds in which it is surrounded by less than an octet of electrons.

2. **A** Sulfur is the central atom because it is less electronegative than fluorine. The molecule has 34 valence electrons (6 from S and 7 from each F). The S–F bonds use 8 electrons, and another 24 are placed around the F atoms:



   The only place to put the remaining 2 electrons is on the sulfur, giving sulfur 10 valence electrons:

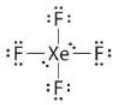


   B Sulfur can accommodate more than an octet, so this is an acceptable Lewis structure.

Exercise

Draw Lewis dot structures for XeF_4.

Answer:



Summary

Molecules with an odd number of electrons are relatively rare in the *s* and *p* blocks but rather common among the *d*- and *f*-block elements. Compounds with more than an octet of electrons around an atom are called **expanded-valence molecules**. One model to explain their existence uses one or more *d* orbitals in bonding in addition to the valence *ns* and *np* orbitals. Such species are known for only atoms in period 3 or below, which contain *nd* subshells in their valence shell.

Key Takeaway

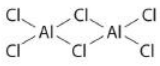
- General exceptions to the octet rule include molecules that have an odd number of electrons and molecules in which one or more atoms possess more or fewer than eight electrons.

Conceptual Problems

1. What regions of the periodic table contain elements that frequently form molecules with an odd number of electrons? Explain your answer.
2. How can atoms expand their valence shell? What is the relationship between an expanded valence shell and the stability of an ion or a molecule?
3. What elements are known to form compounds with less than an octet of electrons? Why do electron-deficient compounds form?
4. List three elements that form compounds that do not obey the octet rule. Describe the factors that are responsible for the stability of these compounds.

Numerical Problems

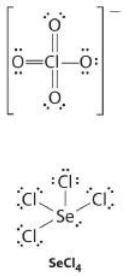
1. What is the major weakness of the Lewis system in predicting the electron structures of PCl_6^- and other species containing atoms from period 3 and beyond?
2. The compound aluminum trichloride consists of Al_2Cl_6 molecules with the following structure (lone pairs of electrons removed for clarity):

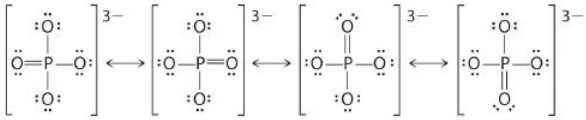


   Does this structure satisfy the octet rule? What is the formal charge on each atom? Given the chemical similarity between aluminum and boron, what is a plausible explanation for the fact that aluminum trichloride forms a dimeric structure rather than the monomeric trigonal planar structure of BCl_3?
3. Draw Lewis electron structures for ClO_4^-, IF_5, $SeCl_4$, and SbF_5.
4. Draw Lewis electron structures for ICl_3, Cl_3PO, Cl_2SO, and AsF_6^-.
5. Draw plausible Lewis structures for the phosphate ion, including resonance structures. What is the formal charge on each atom in your structures?
6. Draw an acceptable Lewis structure for PCl_5, a compound used in manufacturing a form of cellulose. What is the formal charge of the central atom? What is the oxidation number of the central atom?
7. Using Lewis structures, draw all of the resonance structures for the BrO_3^- ion.
8. Draw an acceptable Lewis structure for xenon trioxide (XeO_3), including all resonance structures.

Answers

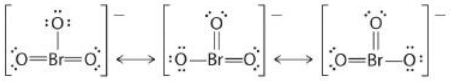
1.
2.
3. ClO_4^- (one of four equivalent resonance structures)

4. 

5. 

   The formal charge on phosphorus is 0, while three oxygen atoms have a formal charge of −1 and one has a formal charge of zero.

6.

7. 

8.

Contributors

- Anonymous

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Chapter 4.6: Properties of Covalent Bonds

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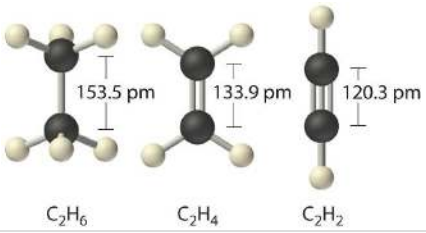
LEARNING OBJECTIVE

To understand the relationship between bond order, bond length, and bond energy.

In proposing his theory that octets can be completed by two atoms sharing electron pairs, Lewis provided scientists with the first description of covalent bonding. In this section, we expand on this and describe some of the properties of covalent bonds.

Bond Order

When we draw Lewis structures, we place one, two, or three pairs of electrons between adjacent atoms. In the Lewis bonding model, the number of electron pairs that hold two atoms together is called the bond order . For a single bond, such as the C–C bond in $H_3C–CH_3$, the bond order is one. For a double bond (such as $H_2C=CH_2$), the bond order is two. For a triple bond, such as HC≡CH, the bond order is three.



When analogous bonds in similar compounds are compared, bond length decreases as bond order increases. The bond length data in Table 4.6.1 for example, show that the C–C distance in $H_3C–CH_3$ (153.5 pm) is longer than the distance in $H_2C=CH_2$ (133.9 pm), which in turn is longer than that in HC≡CH (120.3 pm). Additionally, as noted in Section 4.5, molecules or ions whose bonding must be described using resonance structures usually have bond distances that are intermediate between those of single and double bonds, as we demonstrated with the C–C distances in benzene. The relationship between bond length and bond order is not linear, however. A double bond is not half as long as a single bond, and the length of a C=C bond is not the average of the lengths of C≡C and C–C bonds. Nevertheless, as bond orders increase, bond lengths generally decrease.

Table 4.6.1 Bond Lengths and Bond Dissociation Energies for Bonds with Different Bond Orders in Selected Gas-Phase Molecules at 298 K

Compound	Bond Order	Bond Length (pm)	Bond Dissociation Energy (kJ/mol)	Compound	Bond Order	Bond Length (pm)	Bond Dissociation Energy (kJ/mol)
$H_3C–CH_3$	1	153.5	376	$H_3C–NH_2$	1	147.1	331
$H_2C=CH_2$	2	133.9	728	$H_2C=NH$	2	127.3	644
HC≡CH	3	120.3	965	HC≡N	3	115.3	937
$H_2N–NH_2$	1	144.9	275.3	$H_3C–OH$	1	142.5	377
HN=NH	2	125.2	456	$H_2C=O$	2	120.8	732
N≡N	3	109.8	945.3	O=C=O	2	116.0	799
HO–OH	1	147.5	213	C≡O	3	112.8	1076.5
O=O	2	120.7	498.4				

Sources: Data from *CRC Handbook of Chemistry and Physics* (2004); *Lange's Handbook of Chemistry* (2005); http://cccbdb.nist.gov.

The Relationship between Bond Order and Bond Energy

As shown in Table 4.6.1, triple bonds between like atoms are shorter than double bonds, and because more energy is required to completely break all three bonds than to completely break two, a triple bond is also stronger than a double bond. Similarly, double bonds between like atoms are stronger and shorter than single bonds. Bonds of the same order between *different* atoms show a wide range of bond energies, however. Table 4.6.2 lists the average values for some commonly encountered bonds. Although the values shown vary widely, we can observe four trends:

Table 4.6.2 Average Bond Energies (kJ/mol) for Commonly Encountered Bonds at 273 K

Single Bonds										Multiple Bonds	
H–H	432	C–C	346	N–N	≈167	O–O	≈142	F–F	155	C=C	602
H–C	411	C–Si	318	N–O	201	O–F	190	F–Cl	249	C≡C	835
H–Si	318	C–N	305	N–F	283	O–Cl	218	F–Br	249	C=N	615
H–N	386	C–O	358	N–Cl	313	O–Br	201	F–I	278	C≡N	887
H–P	≈322	C–S	272	N–Br	243	O–I	201	Cl–Cl	240	C=O	749
H–O	459	C–F	485	P–P	201	S–S	226	Cl–Br	216	C≡O	1072
H–S	363	C–Cl	327			S–F	284	Cl–I	208	N=N	418
H–F	565	C–Br	285			S–Cl	255	Br–Br	190	N≡N	942
H–Cl	428	C–I	213			S–Br	218	Br–I	175	N=O	607
H–Br	362	Si–Si	222					I–I	149	O=O	494
H–I	295	Si–O	452							S=O	532

Source: Data from J. E. Huheey, E. A. Keiter, and R. L. Keiter, Inorganic Chemistry, 4th ed. (1993).

1. Bonds between hydrogen and atoms in the same column of the periodic table decrease in strength as we go down the column. Thus an H–F bond is stronger than an H–I bond, H–C is stronger than H–Si, H–N is stronger than H–P, H–O is stronger than H–S, and so forth. The reason for this is that the region of space in which electrons are shared between two atoms becomes proportionally smaller as one of the atoms becomes larger (part (a) in Figure 4.6.1).

2. Bonds between like atoms usually become *weaker* as we go down a column (important exceptions are noted later). For example, the C–C single bond is stronger than the Si–Si single bond, which is stronger than the Ge–Ge bond, and so forth. As two bonded atoms become larger, the region between them occupied by bonding electrons becomes *proportionally* smaller, as illustrated in part (b) in Figure 4.6.1. Noteworthy exceptions are single bonds between the period 2 atoms of groups 15, 16, and 17 (i.e., N, O, F), which are unusually weak compared with single bonds between their larger congeners. It is likely that the N–N, O–O, and F–F single bonds are weaker than might be expected due to strong repulsive interactions between lone pairs of electrons on *adjacent* atoms. The trend in bond energies for the halogens is therefore

$$\text{Cl–Cl} > \text{Br–Br} > \text{F–F} > \text{I–I}$$

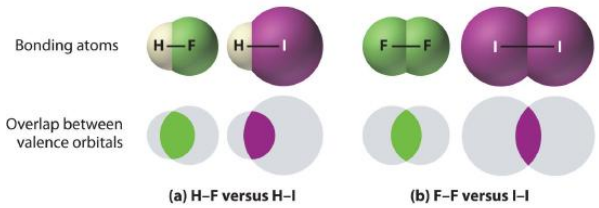
Similar effects are also seen for the O–O versus S–S and for N–N versus P–P single bonds.

Note the Pattern

Bonds between hydrogen and atoms in a given column in the periodic table are weaker down the column; bonds between like atoms usually become weaker down a column.

3. Because elements in periods 3 and 4 rarely form multiple bonds with themselves, their multiple bond energies are not accurately known. Nonetheless, they are presumed to be significantly weaker than multiple bonds between lighter atoms of the same families. Compounds containing an Si=Si double bond, for example, have only recently been prepared, whereas compounds containing C=C double bonds are one of the best-studied and most important classes of organic compounds.

Figure 4.6.1 *The Strength of Covalent Bonds Depends on the Overlap between the Valence Orbitals of the Bonded Atoms*



The relative sizes of the region of space in which electrons are shared between (a) a hydrogen atom and lighter (smaller) vs. heavier (larger) atoms in the same periodic group; and (b) two lighter versus two heavier atoms in the same group. Although the absolute amount of shared space increases in both cases on going from a light to a heavy atom, the amount of space relative to the size of the bonded atom decreases; that is, the percentage of total orbital volume decreases with increasing size. Hence the strength of the bond decreases.

4. Multiple bonds between carbon, oxygen, or nitrogen and a period 3 element such as phosphorus or sulfur tend to be unusually strong. In fact, multiple bonds of this type dominate the chemistry of the period 3 elements of groups 15 and 16. Multiple bonds to phosphorus or sulfur occur as a result of *d*-orbital interactions, as we discussed for the SO_4^{2-} ion in Section 4.5. In contrast, silicon in group 14 has little tendency to form discrete silicon–oxygen double bonds. Consequently, SiO_2 has a three-dimensional network structure in which each silicon atom forms four Si–O single bonds, which makes the physical and chemical properties of SiO_2 very different from those of CO_2.

Note the Pattern

Bond strengths increase as bond order increases, while bond distances decrease.

The Relationship between Molecular Structure and Bond Energy

Bond energy is defined as the energy required to break a particular bond in a molecule in the gas phase. Its value depends on not only the identity of the bonded atoms but also their environment. Thus the bond energy of a C–H single bond is *not* the same in all organic compounds. For example, the energy required to break a C–H bond in methane varies by as much as 25% depending on how many other bonds in the molecule have already been broken (Table 4.6.3); that is, the C–H bond energy depends on its molecular environment. Except for diatomic molecules, the bond energies listed in Table 4.6.2 are *average* values for all bonds of a given type in a range of molecules. Even so, they are not likely to differ from the actual value of a given bond by more than about 10%.

Table 4.6.3 Energies for the Dissociation of Successive C–H Bonds in Methane

Reaction	*D* (kJ/mol)
$CH_4(g) \rightarrow CH_3(g) + H(g)$	439
$CH_3(g) \rightarrow CH_2(g) + H(g)$	462
$CH_2(g) \rightarrow CH(g) + H(g)$	424
$CH(g) \rightarrow C(g) + H(g)$	338

Source: Data from *CRC Handbook of Chemistry and Physics* (2004).

Summary

Bond order is the number of electron pairs that hold two atoms together. Single bonds have a bond order of one, and multiple bonds with bond orders of two (a double bond) and three (a triple bond) are quite common. In closely related compounds with bonds between the same kinds of atoms, the bond with the highest bond order is both the shortest and the strongest. In bonds with the same bond order between different atoms, trends are observed that, with few exceptions, result in the strongest single bonds being formed between the smallest atoms. Tabulated values of average bond energies can be used to calculate the enthalpy change of many chemical reactions. If the bonds in the products are stronger than those in the reactants, the reaction is exothermic and vice versa.

KEY TAKEAWAY

- The strength of a covalent bond depends on the overlap between the valence orbitals of the bonded atoms.

CONCEPTUAL PROBLEMS

1. Which would you expect to be stronger—an S–S bond or an Se–Se bond? Why?
2. Which element—nitrogen, phosphorus, or arsenic—will form the strongest multiple bond with oxygen? Why?
3. Why do multiple bonds between oxygen and period 3 elements tend to be unusually strong?
4. What can bond energies tell you about reactivity?
5. Bond energies are typically reported as average values for a range of bonds in a molecule rather than as specific values for a single bond? Why?

6. If the bonds in the products are weaker than those in the reactants, is a reaction exothermic or endothermic? Explain your answer.
7. A student presumed that because heat was required to initiate a particular reaction, the reaction product would be stable. Instead, the product exploded. What information might have allowed the student to predict this outcome?

NUMERICAL PROBLEMS

1. What is the bond order about the central atom(s) of hydrazine (N_2H_4), nitrogen, and diimide (N_2H_2)? Draw Lewis electron structures for each compound and then arrange these compounds in order of increasing N–N bond distance. Which of these compounds would you expect to have the largest N–N bond energy? Explain your answer.
2. What is the carbon–carbon bond order in ethylene (C_2H_4), BrH_2CCH_2Br, and FCCH? Arrange the compounds in order of increasing C–C bond distance. Which would you expect to have the largest C–C bond energy? Why?
3. From each pair of elements, select the one with the greater bond strength? Explain your choice in each case.
    a. P–P, Sb–Sb
    b. Cl–Cl, I–I
    c. O–O, Se–Se
    d. S–S, Cl–Cl
    e. Al–Cl, B–Cl
4. From each pair of elements, select the one with the greater bond strength? Explain your choice in each case.
    a. Te–Te, S–S
    b. C–H, Ge–H
    c. Si–Si, P–P
    d. Cl–Cl, F–F
    e. Ga–H, Al–H

ANSWER

1. N_2H_4, bond order 1; N_2H_2, bond order 2; N_2, bond order 3; N–N bond distance: $N_2 < N_2H_2 < N_2H_4$; Largest bond energy: N_2; Highest bond order correlates with strongest and shortest bond.
2.
3.
4.
5.
6.
7.

Contributors

- Anonymous

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Chapter 4.7: Properties of Polar Covalent Bonds

Learning Objectives

- To calculate the percent ionic character of a covalent polar bond.

In Chapter 4 , we described the two idealized extremes of chemical bonding: (1) ionic bonding—in which one or more electrons are transferred completely from one atom to another, and the resulting ions are held together by purely electrostatic forces—and (2) covalent bonding, in which electrons are shared equally between two atoms. Most compounds, however, have polar covalent bonds A covalent bond in which the electrons are shared unequally between the bonded atoms., which means that electrons are shared *unequally* between the bonded atoms. Figure 4.7.1 compares the electron distribution in a polar covalent bond with those in an ideally covalent and an ideally ionic bond. A lowercase Greek delta δ is used to indicate that a bonded atom possesses a partial positive charge, indicated by δ^+ or a partial negative charge, indicated by δ^- and a bond between two atoms that possess partial charges is a *polar bond*.

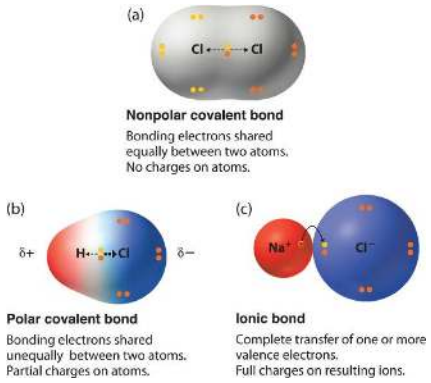


Figure 4.7.1 The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures

In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely from one atom to the other. A polar covalent bond (b) is intermediate between the two extremes: the bonding electrons are shared unequally between the two atoms, and the electron distribution is asymmetrical with the electron density being greater around the more electronegative atom. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.

Bond Polarity

The polarity of a bond—the extent to which it is polar—is determined largely by the relative electronegativities of the bonded atoms. In Chapter 3, electronegativity (χ) was defined as the ability of an atom in a molecule or an ion to attract electrons to itself. Thus there is a direct correlation between electronegativity and bond polarity. A bond is *nonpolar* if the bonded atoms have equal electronegativities. If the electronegativities of the bonded atoms are not equal, however, the bond is *polarized* toward the more electronegative atom. A bond in which the electronegativity of B (χ_B) is greater than the electronegativity of A (χ_A), for example, is indicated with the partial negative charge on the more electronegative atom:

$$\underset{\delta^+}{\overset{\textit{less electronegative}}{A}} - \underset{\delta^-}{\overset{\textit{more electronegative}}{B}}$$

One way of estimating the ionic character of a bond—that is, the magnitude of the charge separation in a polar covalent bond—is to calculate the difference in electronegativity between the two atoms: $\Delta\chi = \chi_B - \chi_A$.

To predict the polarity of the bonds in Cl_2, HCl, and NaCl, for example, we look at the electronegativities of the relevant atoms: $\chi_{Cl} = 3.16$, $\chi_H = 2.20$, and $\chi_{Na} = 0.93$ (see Figure 3.2.2). Cl_2 must be nonpolar because the electronegativity difference ($\Delta\chi$) is zero; hence the two chlorine atoms share the bonding electrons equally. In NaCl, $\Delta\chi$ is 2.23. This high value is typical of an ionic compound ($\Delta\chi \geq \approx 1.5$) and means that the valence electron of sodium has been completely transferred to chlorine to form Na^+ and

Cl^- ions. In HCl, however, Δχ is only 0.96. The bonding electrons are more strongly attracted to the more electronegative chlorine atom, and so the charge distribution is

$$\overset{\delta+}{H} - \overset{\delta-}{Cl}$$

Remember that electronegativities are difficult to measure precisely and different definitions produce slightly different numbers. In practice, the polarity of a bond is usually estimated rather than calculated.

Note the Pattern

Bond polarity and ionic character increase with an increasing difference in electronegativity.

As with bond energies, the electronegativity of an atom depends to some extent on its chemical environment. It is therefore unlikely that the reported electronegativities of a chlorine atom in NaCl, Cl_2, ClF_5, and $HClO_4$ would be exactly the same.

Dipole Moments

The asymmetrical charge distribution in a polar substance such as HCl produces a dipole moment where Qr in meters (m). is abbreviated by the Greek letter mu (μ). The dipole moment is defined as the product of the partial charge Q on the bonded atoms and the distance r between the partial charges:

$$\mu = Qr$$

where Q is measured in coulombs (C) and r in meters. The unit for dipole moments is the debye (D):

$$1\ D = 3.3356 \times 10^{-30}\ C \cdot m$$

When a molecule with a dipole moment is placed in an electric field, it tends to orient itself with the electric field because of its asymmetrical charge distribution (Figure 4.7.2).

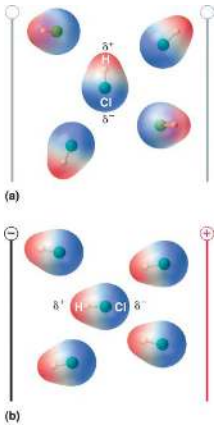


Figure 4.7.2 Molecules That Possess a Dipole Moment Partially Align Themselves with an Applied Electric Field *In the absence of a field (a), the HCl molecules are randomly oriented. When an electric field is applied (b), the molecules tend to align themselves with the field, such that the positive end of the molecular dipole points toward the negative terminal and vice versa.*

We can measure the partial charges on the atoms in a molecule such as HCl using Equation 4.7.2 If the bonding in HCl were purely ionic, an electron would be transferred from H to Cl, so there would be a full +1 charge on the H atom and a full −1 charge on the Cl atom. The dipole moment of HCl is 1.109 D, as determined by measuring the extent of its alignment in an electric field, and the reported gas-phase H–Cl distance is 127.5 pm. Hence the charge on each atom is

$$Q = \frac{\mu}{r} = 1.109\ \cancel{D}\left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}}\right)\left(\frac{1}{127.8\ \cancel{pm}}\right)\left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}}\right) = 2.901 \times 10^{-20}\ C$$

By dividing this calculated value by the charge on a single electron (1.6022×10^{-19} C), we find that the electron distribution in HCl is asymmetric and that effectively it appears that there is a net negative charge on the Cl of about −0.18, effectively corresponding to about 0.18 e^-. This certainly does not mean that there is a fraction of an electron on the Cl atom, but that the distribution of electron probability favors the Cl atom side of the molecule by about this amount.

$$\frac{2.901 \times 10^{-20} \cancel{C}}{1.6022 \times 10^{-19} \cancel{C}} = 0.1811\ e^-$$

To form a neutral compound, the charge on the H atom must be equal but opposite. Thus the measured dipole moment of HCl indicates that the H–Cl bond has approximately 18% ionic character (0.1811 × 100), or 82% covalent character. Instead of writing HCl as

$$\overset{\delta+}{H} - \overset{\delta-}{Cl}$$

we can therefore indicate the charge separation quantitatively as

$$\overset{0.18\delta+}{H} - \overset{0.18\delta-}{Cl}$$

Our calculated results are in agreement with the electronegativity difference between hydrogen and chlorine $\chi_H = 2.20$; $\chi_{Cl} = 3.16$, $\chi_{Cl} - \chi_H = 0.96$), a value well within the range for polar covalent bonds. We indicate the dipole moment by writing an arrow above the molecule.Mathematically, dipole moments are vectors, and they possess both a magnitude and a direction. The dipole moment of a molecule is the vector sum of the dipoles of the individual bonds. In HCl, for example, the dipole moment is indicated as follows:



The arrow shows the direction of electron flow by pointing toward the more electronegative atom.

The charge on the atoms of many substances in the gas phase can be calculated using measured dipole moments and bond distances. Figure 4.7.3 shows a plot of the percent ionic character versus the difference in electronegativity of the bonded atoms for several substances. According to the graph, the bonding in species such as NaCl(g) and CsF(g) is substantially less than 100% ionic in character. As the gas condenses into a solid, however, dipole–dipole interactions between polarized species increase the charge separations. In the crystal, therefore, an electron is transferred from the metal atom to the nonmetal atom, and these substances behave like classic ionic compounds. The data in Figure 4.7.3 show that diatomic species with an electronegativity difference of less than 1.5 are less than 50% ionic in character, which is consistent with our earlier description of these species as containing polar covalent bonds. The use of dipole moments to determine the ionic character of a polar bond is illustrated in Example 11.

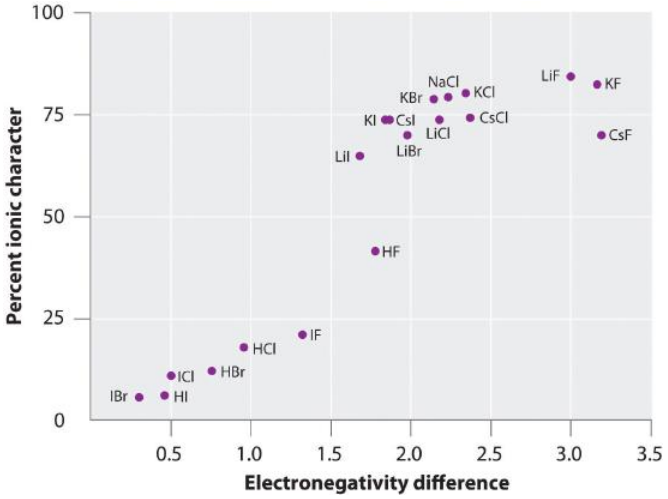


Figure 4.7.3 A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms

In the gas phase, even CsF, which has the largest possible difference in electronegativity between atoms, is not 100% ionic. Solid CsF, however, is best viewed as 100% ionic because of the additional electrostatic interactions in the lattice.

Example 4.7.1

In the gas phase, NaCl has a dipole moment of 9.001 D and an Na–Cl distance of 236.1 pm. Calculate the percent ionic character in NaCl.

Given: chemical species, dipole moment, and internuclear distance

Asked for: percent ionic character

Strategy:

A Compute the charge on each atom using the information given and Equation 4.7.2

B Find the percent ionic character from the ratio of the actual charge to the charge of a single electron.

Solution:

A The charge on each atom is given by

$$Q = \frac{\mu}{r} = 9.001 \cancel{D} \left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}} \right) \left(\frac{1}{236.1\ \cancel{pm}} \right) \left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}} \right) = 1.272 \times 10^{-19}\ C$$

Thus NaCl behaves as if it had charges of 1.272×10^{-19} C on each atom separated by 236.1 pm.

B The percent ionic character is given by the ratio of the actual charge to the charge of a single electron (the charge expected for the complete transfer of one electron):

$$\%\ ionic\ character = \left(\frac{1.272 \times 10^{-19}\ \cancel{C}}{1.6022 \times 10^{-19}\ \cancel{C}} \right) (100) = 79.39\% \simeq 79\%$$

Exercise

In the gas phase, silver chloride (AgCl) has a dipole moment of 6.08 D and an Ag–Cl distance of 228.1 pm. What is the percent ionic character in silver chloride?

Answer: 55.5%

Summary

Compounds with **polar covalent bonds** have electrons that are shared unequally between the bonded atoms. The polarity of such a bond is determined largely by the relative electronegativites of the bonded atoms. The asymmetrical charge distribution in a polar substance produces a **dipole moment**, which is the product of the partial charges on the bonded atoms and the distance between them.

Key Takeaway

- Bond polarity and ionic character increase with an increasing difference in electronegativity.

Key Equation

Dipole moment

Equation 4.7.2 $\mu = Qr$

Conceptual Problems

1. Why do ionic compounds such as KI exhibit substantially less than 100% ionic character in the gas phase?
2. Of the compounds LiI and LiF, which would you expect to behave more like a classical ionic compound? Which would have the greater dipole moment in the gas phase? Explain your answers.

Numerical Problems

1. Predict whether each compound is purely covalent, purely ionic, or polar covalent.
    1. RbCl
    2. S_8
    3. $TiCl_2$

4. $SbCl_3$
5. LiI
6. Br_2

2. Based on relative electronegativities, classify the bonding in each compound as ionic, covalent, or polar covalent. Indicate the direction of the bond dipole for each polar covalent bond.

    1. NO
    2. HF
    3. MgO
    4. $AlCl_3$
    5. SiO_2
    6. the C=O bond in acetone
    7. O_3

3. Based on relative electronegativities, classify the bonding in each compound as ionic, covalent, or polar covalent. Indicate the direction of the bond dipole for each polar covalent bond.

    1. NaBr
    2. OF_2
    3. BCl_3
    4. the S–S bond in $CH_3CH_2SSCH_2CH_3$
    5. the C–Cl bond in CH_2Cl_2
    6. the O–H bond in CH_3OH
    7. $PtCl_4^{2-}$

4. Classify each species as having 0%–40% ionic character, 40%–60% ionic character, or 60%–100% ionic character based on the type of bonding you would expect. Justify your reasoning.

    1. CaO
    2. S_8
    3. $AlBr_3$
    4. ICl
    5. Na_2S
    6. SiO_2
    7. LiBr

5. If the bond distance in HCl (dipole moment = 1.109 D) were double the actual value of 127.46 pm, what would be the effect on the charge localized on each atom? What would be the percent negative charge on Cl? At the actual bond distance, how would doubling the charge on each atom affect the dipole moment? Would this represent more ionic or covalent character?

6. Calculate the percent ionic character of HF (dipole moment = 1.826 D) if the H–F bond distance is 92 pm.

7. Calculate the percent ionic character of CO (dipole moment = 0.110 D) if the C–O distance is 113 pm.

8. Calculate the percent ionic character of PbS and PbO in the gas phase, given the following information: for PbS, r = 228.69 pm and μ = 3.59 D; for PbO, r = 192.18 pm and μ = 4.64 D. Would you classify these compounds as having covalent or polar covalent bonds in the solid state?

Contributors

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Chapter 4.8: Metallic Bonding

Learning Objectives

- To learn about metallic bonding.

Metals have several qualities that are unique, such as the ability to conduct electricity, a low ionization energy, and a low electronegativity (so they will give up electrons easily, i.e., they are cations). Their physical properties include a lustrous (shiny) appearance, and they are malleable and ductile. Metals have a crystal structure.

- Metals that are malleable can be beaten into thin sheets, for example: aluminum foil.
- Metals that are ductile can be drawn into wires, for example: copper wire.

In the 1900's, Paul Drüde came up with the sea of electrons theory by modeling metals as a mixture of atomic cores (atomic cores = positive nuclei + inner shell of electrons) and valence electrons. In this model, the valence electrons are free, delocalized, mobile, and not associated with any particular atom. For example: metallic cations surrounded by a "sea" of electrons. This model assumes that the valence electrons do not interact with each other. This model may account for:

- Malleability and Ductility: The sea of electrons surrounding the protons act like a cushion, and so when the metal is hammered on, for instance, the over all composition of the structure of the metal is not harmed or changed. The protons may be rearranged but the sea of electrons with adjust to the new formation of protons and keep the metal intact.
- Heat capacity: This is explained by the ability of free electrons to move about the solid conducting heat
- Luster: The free electrons can absorb photons in the "sea," so metals are opaque-looking. Electrons on the surface can bounce back light at the same frequency that the light hits the surface, therefore the metal appears to be shiny.
- Conductivity: Since the electrons are free, if electrons from an outside source were pushed into a metal wire at one end, the electrons would be pushed into the the wire and come out at the other end at the same rate (conductivity is the movement of charge).

Amazingly, Drude's electron sea model predates Rutherford's nuclear model of the atom and Lewis' octet rule. It is, however, a useful qualitative model of metallic bonding even to this day. As it did for Lewis' octet rule, the quantum revolution of the 1930s told us about the underlying chemistry. Drude's electron sea model assumed that valence electrons were free to move in metals, quantum mechanical calculations told us why this happened.

Metallic bonding in sodium

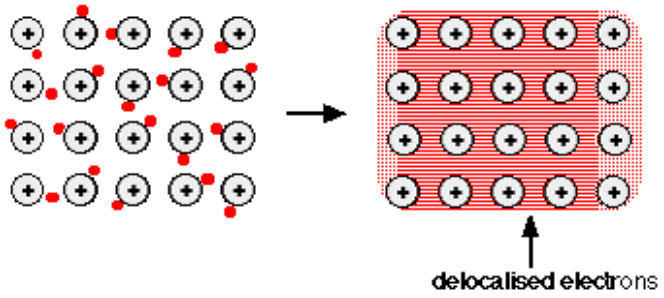
Metals tend to have high melting points and boiling points suggesting strong bonds between the atoms. Even a metal like sodium (melting point 97.8°C) melts at a considerably higher temperature than the element (neon) which precedes it in the Periodic Table.

Sodium has the electronic structure $1s^2 2s^2 2p^6 3s^1$. When sodium atoms come together, the electron in the 3s atomic orbital of one sodium atom shares space with the corresponding electron on a neighboring atom to form a molecular orbital - in much the same sort of way that a covalent bond is formed.

The difference, however, is that each sodium atom is being touched by eight other sodium atoms - and the sharing occurs between the central atom and the 3s orbitals on all of the eight other atoms. And each of these eight is in turn being touched by eight sodium atoms, which in turn are touched by eight atoms - and so on and so on, until you have taken in all the atoms in that lump of sodium.

All of the 3s orbitals on all of the atoms overlap to give a vast number of molecular orbitals which extend over the whole piece of metal. There have to be huge numbers of molecular orbitals, of course, because any orbital can only hold two electrons.

The electrons can move freely within these molecular orbitals, and so each electron becomes detached from its parent atom. The electrons are said to be delocalized. The metal is held together by the strong forces of attraction between the positive nuclei and the delocalized electrons.



This is sometimes described as "an array of positive ions in a sea of electrons".

Each positive center in the diagram represents all the rest of the atom apart from the outer electron, but that electron hasn't been lost - it may no longer have an attachment to a particular atom, but those electrons are still there in the structure. Sodium metal is therefore written as Na - not Na^+.

Metallic bonding in magnesium

If you work through the same argument with magnesium, you end up with stronger bonds and so a higher melting point./p>

Magnesium has the outer electronic structure $3s^2$. Both of these electrons become delocalised, so the "sea" has twice the electron density as it does in sodium. The remaining "ions" also have twice the charge (if you are going to use this particular view of the metal bond) and so there will be more attraction between "ions" and "sea".

More realistically, each magnesium atom has 12 protons in the nucleus compared with sodium's 11. In both cases, the nucleus is screened from the delocalised electrons by the same number of inner electrons - the 10 electrons in the $1s^2$ $2s^2$ $2p^6$ orbitals.

That means that there will be a net pull from the magnesium nucleus of 2+, but only 1+ from the sodium nucleus.

So not only will there be a greater number of delocalized electrons in magnesium, but there will also be a greater attraction for them from the magnesium nuclei. Magnesium atoms also have a slightly smaller radius than sodium atoms, and so the delocalised electrons are closer to the nuclei. Each magnesium atom also has twelve near neighbors rather than sodium's eight. Both of these factors increase the strength of the bond still further.

Metallic bonding in transition elements

Transition metals tend to have particularly high melting points and boiling points. The reason is that they can involve the 3d electrons in the delocalization as well as the 4s. The more electrons you can involve, the stronger the attractions tend to be.

The strength of a metallic bond depends on three things:

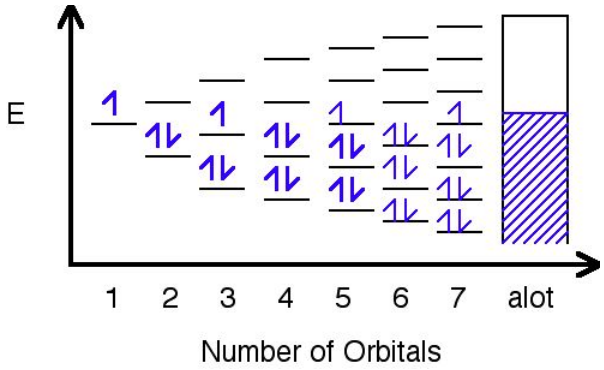
1. The number of electrons that become delocalized from the metal ions
2. The charge of the cation (metal).
3. The size of the cation.

A **strong** metallic bond will be the result of more delocalized electrons, which causes the effective nuclear charge on electrons on the cation to increase, in effect making the size of the cation smaller. Metallic bonds are strong and require a great deal of energy to break, and therefore **metals have high melting and boiling points.**

A metallic bonding theory must explain how so much bonding can occur with such few electrons (since metals are located on the left side of the periodic table and do not have many electrons in their valence shells). The theory must also account for all of a metal's unique chemical and physical properties.

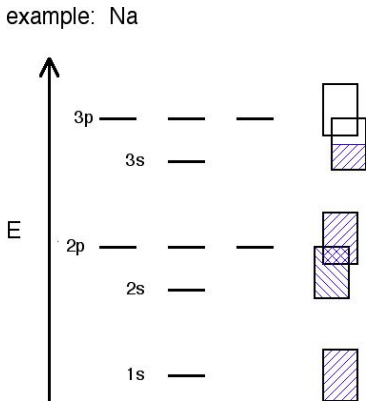
Band Theory

Band Theory was developed with some help from the knowledge gained during the quantum revolution in science. In 1928, Felix Bloch had the idea to take the quantum theory and apply it to solids. In 1927, Walter Heitler and Fritz London explained how these many levels can combine together to form bands- orbitals so close together in energy that they are continuous



In this image, orbitals are represented by the black horizontal lines, and they are being filled with an increasing number of electrons as their amount increases. Eventually, as more orbitals are added, the space in between them decreases to hardly anything, and as a result, a band is formed where the orbitals have been filled.

Different metals will produce different combinations of filled and half filled bands.



Sodium's bands are shown with the rectangles. Filled bands are colored in blue. As you can see, bands may overlap each other (the bands are shown askew to be able to tell the difference between different bands). The lowest unoccupied band is called the conduction band, and the highest occupied band is called the valence band.

The probability of finding an electron in the conduction band is shown by the equation:

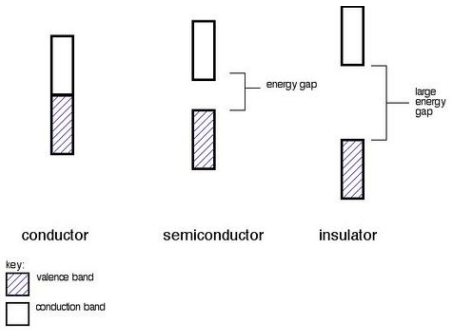
$$P = \frac{1}{e^{\Delta E/RT} + 1} \qquad \text{(Chapter 4.8.1)}$$

The ΔE in the equation stands for the change in energy or energy gap. t stands for the temperature, and R is a bonding constant. That equation and this table below show how the bigger difference in energy is, or gap, between the valence band and the

conduction band, the less likely electrons are to be found in the conduction band. This is because they cannot be excited enough to make the jump up to the conduction band.

ELEMENT	ΔE(kJ/mol) of energy gap	# of electrons/cm^3 in conduction band @ 300K	insulator, or conductor?
C (diamond)	524 (big band gap)	10^{-27}	insulator
Si	117 (smaller band gap, but not a full conductor)	10^{9}	semiconductor
Ge	66 (smaller band gap, but still not a full conductor)	10^{13}	semiconductor

Conductors, Insulators and Semiconductors



A. Conductors

Metals are conductors. There is no band gap between their valence and conduction bands, since they overlap. There is a continuous availability of electrons in these closely spaced orbitals.

B. Insulators

In insulators, the band gap between the valence band the the conduction band is so large that electrons cannot make the energy jump from the valence band to the conduction band.

C. Semiconductors

Semiconductors have a small energy gap between the valence band and the conduction band. Electrons can make the jump up to the conduction band, but not with the same ease as they do in conductors.

Outside Links

- http://www.youtube.com/watch?v=HWRHT...87AF6948F5E8F9 (start at 9 minutes)
- http://www.youtube.com/watch?v=qK6DgAM-q7U (start at 13 minutes)
- http://en.wikipedia.org/wiki/Metallic_bonding
- Metallic Bonding: http://www.youtube.com/watch?v=CGA8sRwqIFg&feature=youtube_gdata

Problems

1. How do you distinguish between a valence band and a conduction band?
2. Is the energy gap between an insulator smaller or larger than the energy gap between a semiconductor?
3. What two methods bring conductivity to semiconductors?
4. You are more likely to find electrons in a conduction band if the energy gap is smaller/larger? 5. The property of being able to be drawn into a wire is called...

Answers

1. The valence band is the highest band with electrons in it, and the conduction band is the highest band with no electrons in it.
2. Larger
3. Electron transport and hole transport
4. Smaller

5. Ductility

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1. Petrucci, Harwood, Herring, Madura. GENERAL CHEMISTRY Principles and Modern Applications 9th Edition. Macmillan Publishing Co: New Jersey. 1989.
2. Moore, John T. Chemistry Made Simple. Random House Inc: New York. 2004.

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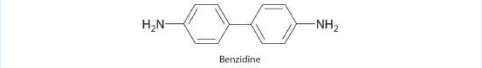
Chapter 4.9: End of Chapter Material

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APPLICATION PROBLEMS

Problems marked with a ♦ involve multiple concepts.

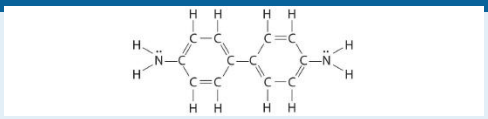
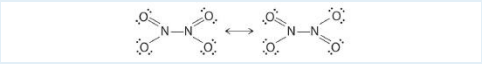
1. Until recently, benzidine was used in forensic medicine to detect the presence of human blood: when mixed with human blood, benzidine turns a characteristic blue color. Because benzidine has recently been identified as a carcinogen, other indicators have replaced it. Draw the complete Lewis dot structure for benzidine.

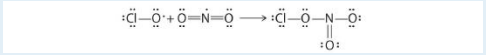


Benzidine

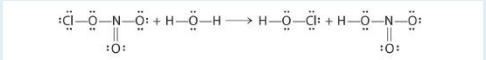
2. There are three possible ways to connect carbon, nitrogen, and oxygen to form a monoanion: CNO^-, CON^-, and OCN^-. One is the cyanate ion, a common and stable species; one is the fulminate ion, salts of which are used as explosive detonators; and one is so unstable that it has never been isolated. Use Lewis electron structures and the concept of formal charge to determine which isomer is cyanate, which is the fulminate, and which is the least stable.
3. The colorless gas N_2O_4 is a deadly poison that has been used as an oxidizing agent in rocket fuel. The compound has a single N–N bond, with a formal charge of +1 on each nitrogen atom. Draw resonance structures for this molecule.
4. ♦ An atmospheric reservoir species is a molecule that is rather unreactive, but it contains elements that can be converted to reactive forms. For example, chlorine nitrate ($ClONO_2$) is a reservoir species for both chlorine and nitrogen dioxide. In fact, most of the chlorine in the atmosphere is usually bound up in chlorine nitrate as a result of the reaction of ClO with NO_2.
   a. Draw Lewis electron structures for each species in this reaction. What difficulty is associated with the structure of the reactants? How does this affect the reactivity of the compounds?
   Chlorine nitrate can react in a surface reaction with water to form HClO and nitric acid.

ANSWERS

1. 
2.
3. 
4.
5.
6.
7. a. $ClO + NO_2 \rightarrow ClONO_2$



   b. Both reactants have one unpaired electron, which makes them more reactive than might otherwise be expected.
   c. $ClONO_2 + H_2O \rightarrow HClO + HONO_2$



8.

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CHAPTER OVERVIEW

Chapter 5: Molecular Geometry

- Chapter 5.0: Molecular Geometry
- Chapter 5.1: Predicting the Geometry of Molecules
- Chapter 5.2: Localized Bonding and Hybrid Orbitals
- Chapter 5.3 Delocalized Bonding and Molecular Orbitals
- Chapter 5.4: Polyatomic Systems, Multiple Bonds, Resonance
- Chapter 5.5: Naming Organic Molecules
- Chapter 5.6: End of Chapter Material

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Chapter 5.0: Molecular Geometry

Learning Objectives

- To extend our models of molecular bonding to determining the shape of molecules.

The Lewis electron-pair approach can be used to predict the number and types of bonds between the atoms in a substance, and it indicates which atoms have lone pairs of electrons. This approach gives no information about the actual arrangement of atoms in space, however. Moreover, the exceptions to the Leiws octet model are intellectually troublesome as they are *ad hoc* band aids applied to cases where the simple model does not work. We use our understanding of atomic orbitals to extend our discussion of structure and bonding to determining the shapes of molecules and orbitals that involve more that two atoms.

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Chapter 5.1: Predicting the Geometry of Molecules

Learning Objectives

- To use the VSEPR model to predict molecular geometries.
- To predict whether a molecule has a dipole moment.

We continue our discussion of structure and bonding by introducing the valence-shell electron-pair repulsion (VSEPR) model A model used to predict the shapes of many molecules and polyatomic ions, based on the idea that the lowest-energy arrangement for a compound is the one in which its electron pairs (bonding and nonbonding) are as far apart as possible. (pronounced “vesper”), which can be used to predict the shapes of many molecules and polyatomic ions. Keep in mind, however, that the VSEPR model, like any model, is a limited representation of reality; the model provides no information about bond lengths or the presence of multiple bonds. Following sections of this chapter will connect the VSEPR model to atomic and molecular orbitals.

The VSEPR Model

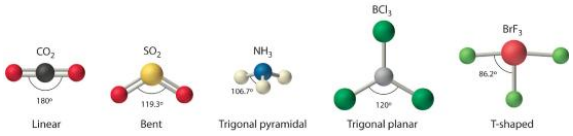
The VSEPR model can predict the structure of nearly any molecule or polyatomic ion in which the central atom is a nonmetal, as well as the structures of many molecules and polyatomic ions with a central metal atom. The VSEPR model is *not* a theory; it does not attempt to explain observations. Instead, it is a counting procedure that accurately predicts the three-dimensional structures of a large number of compounds, which cannot be predicted using the Lewis electron-pair approach.

Note the Pattern

Lewis electron structures predict the number and types of bonds, whereas VSEPR can predict the shapes of many molecules and polyatomic ions.

We can use the VSEPR model to predict the geometry of most polyatomic molecules and ions by focusing on only the number of electron pairs around the *central atom*, ignoring all other valence electrons present. According to this model, valence electrons in the Lewis structure form *groups*, which may consist of a single bond, a double bond, a triple bond, a lone pair of electrons, or even a single unpaired electron, which in the VSEPR model is counted as a lone pair. Because electrons repel each other electrostatically, the most stable arrangement of electron groups (i.e., the one with the lowest energy) is the one that minimizes repulsions. Groups are positioned around the central atom in a way that produces the molecular structure with the lowest energy, as illustrated in Figure 5.1.1 and Figure 5.1.2

Figure 5.1.1 Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms



The VSEPR model explains these differences in molecular geometry.

Figure 5.1.2 Geometries for Species with Two to Six Electron Groups

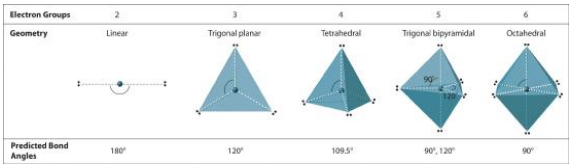


Figure 5.1.1 Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms *Groups are placed around the central atom in a way that produces a molecular structure with the lowest energy. That is, the one that minimizes repulsions.*

In the VSEPR model, the molecule or polyatomic ion is given an AX_mE_n designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and m and n are integers. Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the bond angles The angle between bonds.. Using this information, we can describe the molecular geometry The arrangement of the bonded atoms in a molecule or a polyatomic ion in space., the arrangement of the *bonded atoms* in a molecule or polyatomic ion. This procedure is summarized as follows:

1. Draw the Lewis electron structure of the molecule or polyatomic ion.
2. Determine the electron group arrangement around the central atom that minimizes repulsions.
3. Assign an AX_mE_n designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations from ideal bond angles.
4. Describe the molecular geometry.

We will illustrate the use of this procedure with several examples, beginning with atoms with two electron groups. In our discussion we will refer to Figure 5.1.2 and Figure 5.1.3 , which summarize the common molecular geometries and idealized bond angles of molecules and ions with two to six electron groups.

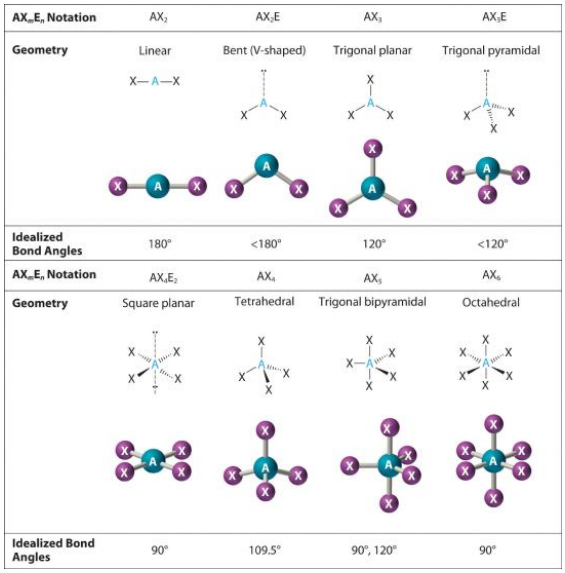


Figure 5.1.3 Common Molecular Geometries for Species with Two to Six Electron Groups*

Two Electron Groups

Our first example is a molecule with two bonded atoms and no lone pairs of electrons, BeH_2.

AX_2: BeH_2

1. The central atom, beryllium, contributes two valence electrons, and each hydrogen atom contributes one. The Lewis electron structure is

H:Be:H or H—Be—H

Lewis structure

In this case Be and H each see two electrons which, for those atoms fills the $1s^2$orbitals. This, of course, is an exception to the octet rule, but easy to understand using the aufbau principle

2. There are two electron groups around the central atom. We see from Figure 5.1.2 that the arrangement that minimizes repulsions places the groups 180° apart.

3. Both groups around the central atom are bonding pairs (BP). Thus BeH_2 is designated as AX_2.

4. From Figure 5.1.3 we see that with two bonding pairs, the molecular geometry that minimizes repulsions in BeH_2 is *linear*.

AX_2: CO_2

1. The central atom, carbon, contributes four valence electrons, and each oxygen atom contributes six. The Lewis electron structure is

:O≡C≡O:

2. The carbon atom forms two double bonds. Each double bond is a group, so there are two electron groups around the central atom. Like BeH_2, the arrangement that minimizes repulsions places the groups 180° apart.

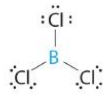
3. Once again, both groups around the central atom are bonding pairs (BP), so CO_2 is designated as AX_2.

4. VSEPR only recognizes groups around the *central* atom. Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. With two bonding pairs on the central atom and no lone pairs, the molecular geometry of CO_2 is linear (Figure 5.1.3). The structure of CO_2 is shown in Figure 5.1.1 .

Three Electron Groups

AX_3: BCl_3

1. The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven valence electrons. The Lewis electron structure is



Lewis structure

Again, we recognize this as an exception to the octet rule, but again, easy to understand based on what we have studied. The three electrons on the boron atom are shared, one each with each chlorine atom. The chlorine atoms each have a complete octet.

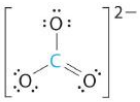
2. There are three electron groups around the central atom. To minimize repulsions, the groups are placed 120° apart (Figure 5.1.2).

3. All electron groups are bonding pairs (BP), so the structure is designated as AX_3.

4. From Figure 5.1.3 we see that with three bonding pairs around the central atom, the molecular geometry of BCl_3 is *trigonal planar*, as shown in Figure 5.1.1

AX_3: CO_3^{2-}

1. The central atom, carbon, has four valence electrons, and each oxygen atom has six valence electrons. As you learned in Chapter 4, the Lewis electron structure of one of three resonance forms is represented as



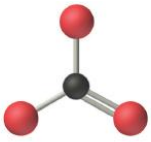
Lewis structure

We have already discussed how the electrons in the double bond are smeared over the top and bottom of the ion in a molecular bond and that the bonds linking the carbon and oxygen atoms are identical

2. The structure of CO_3^{2-} is a resonance hybrid. It has three identical bonds, each with a bond order of 1 1/3. We minimize repulsions by placing the three groups 120° apart (Figure 5.1.2).

3. All electron groups are bonding pairs (BP). With three bonding groups around the central atom, the structure is designated as AX_3.

4. We see from Figure 5.1.3 that the molecular geometry of CO_3^{2-} is trigonal planar.


Molecular geometry
(trigonal planar)

In our next example we encounter the effects of lone pairs and multiple bonds on molecular geometry for the first time.

AX_2E: SO_2

1. The central atom, sulfur, has 6 valence electrons, as does each oxygen atom. With 18 valence electrons, the Lewis electron structure is shown below.



2. There are three electron groups around the central atom, two double bonds and one lone pair. We initially place the groups in a trigonal planar arrangement to minimize repulsions (Figure 5.1.2).

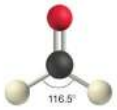
3. There are two bonding pairs and one lone pair, so the structure is designated as AX_2E. This designation has a total of three electron pairs, two X and one E. Because a lone pair is not shared by two nuclei, it occupies more space near the central atom than a bonding pair (Figure 5.1.4). Thus bonding pairs and lone pairs repel each other electrostatically in the order BP–BP < LP–BP < LP–LP. In SO_2, we have one BP–BP interaction and two LP–BP interactions.

4. The molecular geometry is described only by the positions of the nuclei, *not* by the positions of the lone pairs. Thus with two nuclei and one lone pair the shape is *bent*, or *V shaped*, which can be viewed as a trigonal planar arrangement with a missing vertex (Figure 5.1.1 and Figure 5.1.3).



Figure 5.1.4 The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair *As with SO_2, this composite model of electron distribution and negative electrostatic potential in ammonia shows that a lone pair of electrons occupies a larger region of space around the nitrogen atom than does a bonding pair of electrons that is shared with a hydrogen atom.*

Like lone pairs of electrons, multiple bonds occupy more space around the central atom than a single bond, which can cause other bond angles to be somewhat smaller than expected. This is because a multiple bond has a higher electron density than a single bond, so its electrons occupy more space than those of a single bond. For example, in a molecule such as CH_2O (AX_3), whose structure is shown below, the double bond repels the single bonds more strongly than the single bonds repel each other. This causes a deviation from ideal geometry (an H–C–H bond angle of 116.5° rather than 120°).



Four Electron Groups

One of the limitations of Lewis structures is that they depict molecules and ions in only two dimensions. With four electron groups, we must learn to show molecules and ions in three dimensions.

AX_4: CH_4

1. The central atom, carbon, contributes four valence electrons, and each hydrogen atom has one valence electron, so the full Lewis electron structure is



Lewis structure

2. There are four electron groups around the central atom. As shown in Figure 5.1.2 repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5°.

3. All electron groups are bonding pairs, so the structure is designated as AX_4.

4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Figure 5.1.3).



Molecular geometry
(tetrahedral)

AX_3E: NH_3

1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure



Lewis structure

2. There are four electron groups around nitrogen, three bonding pairs and one lone pair. Repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

3. With three bonding pairs and one lone pair, the structure is designated as AX_3E. This designation has a total of four electron pairs, three X and one E. We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

4. There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*. In essence, this is a tetrahedron with a vertex missing (Figure 5.1.3). However, the H–N–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions (Figure 5.1.3 and Figure 5.1.4).

AX_2E_2: H_2O

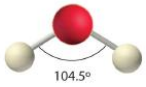
1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure



2. There are four groups around the central oxygen atom, two bonding pairs and two lone pairs. Repulsions are minimized by directing the bonding pairs and the lone pairs to the corners of a tetrahedron Figure 5.1.2

3. With two bonding pairs and two lone pairs, the structure is designated as AX_2E_2 with a total of four electron pairs. Due to LP–LP, LP–BP, and BP–BP interactions, we expect a significant deviation from idealized tetrahedral angles.

4. With two hydrogen atoms and two lone pairs of electrons, the structure has significant lone pair interactions. There are two nuclei about the central atom, so the molecular shape is *bent*, or *V shaped*, with an H–O–H angle that is even less than the H–N–H angles in NH_3, as we would expect because of the presence of two lone pairs of electrons on the central atom rather than one.. This molecular shape is essentially a tetrahedron with two missing vertices.



Five Electron Groups

In previous examples it did not matter where we placed the electron groups because all positions were equivalent. In some cases, however, the positions are not equivalent. We encounter this situation for the first time with five electron groups.

AX_5: PCl_5

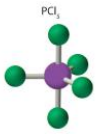
1. Phosphorus has five valence electrons and each chlorine has seven valence electrons, so the Lewis electron structure of PCl_5 involves an expanded octet. In the following section we will describe how this expanded octet is formed by the combination of a d orbital with an s and three p orbitals.



2. There are five bonding groups around phosphorus, the central atom. The structure that minimizes repulsions is a *trigonal bipyramid*, which consists of two trigonal pyramids that share a base (Figure 5.1.2):

3. All electron groups are bonding pairs, so the structure is designated as AX_5. There are no lone pair interactions.

4. The molecular geometry of PCl_5 is *trigonal bipyramidal*, as shown in Figure 5.1.3 . The molecule has three atoms in a plane in *equatorial* positions and two atoms above and below the plane in *axial* positions. The three equatorial positions are separated by 120° from one another, and the two axial positions are at 90° to the equatorial plane. The axial and equatorial positions are not chemically equivalent, as we will see in our next example.



AX_4E: SF_4

1. The sulfur atom has six valence electrons and each fluorine has seven valence electrons, so the Lewis electron structure is



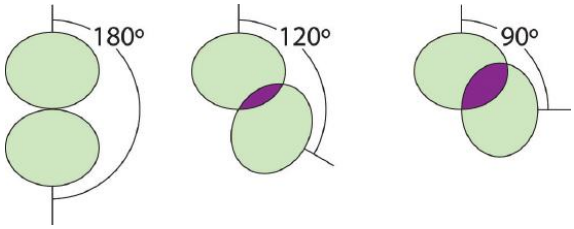
Lewis structure

With an expanded valence, this species is an exception to the octet rule.

2. There are five groups around sulfur, four bonding pairs and one lone pair. With five electron groups, the lowest energy arrangement is a trigonal bipyramid, as shown in Figure 5.1.2

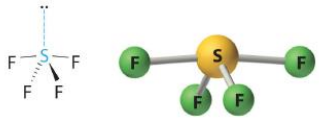
3. We designate SF_4 as AX_4E; it has a total of five electron pairs. However, because the axial and equatorial positions are not chemically equivalent, where do we place the lone pair? If we place the lone pair in the equatorial position, we have three LP–BP repulsions at 90°. If we place it in the axial position, we have two 90° LP–BP repulsions at 90°. With fewer 90° LP–BP repulsions, we can predict that the structure with the lone pair of electrons in the equatorial position is more stable than the one with the lone pair in the axial position. We also expect a deviation from ideal geometry because a lone pair of electrons occupies more space than a bonding pair.

Figure 5.1.5 Illustration of the Area Shared by Two Electron Pairs versus the Angle between Them



At 90°, the two electron pairs share a relatively large region of space, which leads to strong repulsive electron–electron interactions.

4. With four nuclei and one lone pair of electrons, the molecular structure is based on a trigonal bipyramid with a missing equatorial vertex; it is described as a *seesaw*. The F_{axial}–S–F_{axial} angle is 173° rather than 180° because of the lone pair of electrons in the equatorial plane.



Molecular geometry (seesaw)

AX_3E_2: BrF_3

1. The bromine atom has seven valence electrons, and each fluorine has seven valence electrons, so the Lewis electron structure is

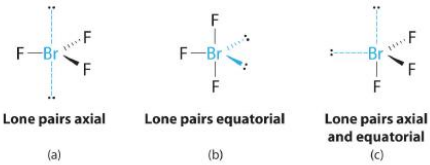


Lewis structure

Once again, we have a compound that is an exception to the octet rule.

2. There are five groups around the central atom, three bonding pairs and two lone pairs. We again direct the groups toward the vertices of a trigonal bipyramid.

3. With three bonding pairs and two lone pairs, the structural designation is AX_3E_2 with a total of five electron pairs. Because the axial and equatorial positions are not equivalent, we must decide how to arrange the groups to minimize repulsions. If we place both lone pairs in the axial positions, we have six LP–BP repulsions at 90°. If both are in the equatorial positions, we have four LP–BP repulsions at 90°. If one lone pair is axial and the other equatorial, we have one LP–LP repulsion at 90° and three LP–BP repulsions at 90°:



	Lone pairs axial (a)	Lone pairs equatorial (b)	Lone pairs axial and equatorial (c)
Interactions			
90° LP–LP	0	0	1
90° LP–BP	6	4	3

Structure (c) can be eliminated because it has a LP–LP interaction at 90°. Structure (b), with fewer LP–BP repulsions at 90° than (a), is lower in energy. However, we predict a deviation in bond angles because of the presence of the two lone pairs of electrons.

4. The three nuclei in BrF_3 determine its molecular structure, which is described as *T shaped*. This is essentially a trigonal bipyramid that is missing two equatorial vertices. The F_{axial}–Br–F_{axial} angle is 172°, less than 180° because of LP–BP repulsions (Figure 5.1.1).

Note the Pattern

Because lone pairs occupy more space around the central atom than bonding pairs, electrostatic repulsions are more important for lone pairs than for bonding pairs.

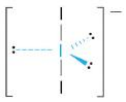
AX_2E_3: I_3^-

1. Each iodine atom contributes seven electrons and the negative charge one, so the Lewis electron structure is



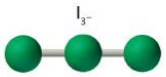
2. There are five electron groups about the central atom in I_3^-, two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

3. With two bonding pairs and three lone pairs, I_3^- has a total of five electron pairs and is designated as AX_2E_3. We must now decide how to arrange the lone pairs of electrons in a trigonal bipyramid in a way that minimizes repulsions. Placing them in the axial positions eliminates 90° LP–LP repulsions and minimizes the number of 90° LP–BP repulsions.



The three lone pairs of electrons have equivalent interactions with the three iodine atoms, so we do not expect any deviations in bonding angles.

4. With three nuclei and three lone pairs of electrons, the molecular geometry of I_3^- is linear. This can be described as a trigonal bipyramid with three equatorial vertices missing. The ion has an I–I–I angle of 180°, as expected.

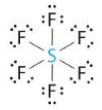


Six Electron Groups

Six electron groups form an *octahedron*, a polyhedron made of identical equilateral triangles and six identical vertices (Figure 5.1.2).

AX_6: SF_6

1. The central atom, sulfur, contributes six valence electrons, and each fluorine atom has seven valence electrons, so the Lewis electron structure is



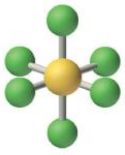
Lewis structure

With an expanded valence, we know from Chapter 4 Section 4.6 that this species is an exception to the octet rule.

2. There are six electron groups around the central atom, each a bonding pair. We see from Figure 5.1.2 that the geometry that minimizes repulsions is *octahedral*.

3. With only bonding pairs, SF_6 is designated as AX_6. All positions are chemically equivalent, so all electronic interactions are equivalent.

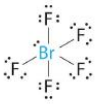
4. There are six nuclei, so the molecular geometry of SF_6 is octahedral.



Molecular geometry
(octahedral)

AX_5E: BrF_5

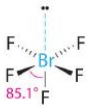
1. The central atom, bromine, has seven valence electrons, as does each fluorine, so the Lewis electron structure is



Lewis structure

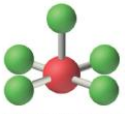
With its expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the Br, five bonding pairs and one lone pair. Placing five F atoms around Br while minimizing BP–BP and LP–BP repulsions gives the following structure:



3. With five bonding pairs and one lone pair, BrF_5 is designated as AX_5E; it has a total of six electron pairs. The BrF_5 structure has four fluorine atoms in a plane in an equatorial position and one fluorine atom and the lone pair of electrons in the axial positions. We expect all F_{axial}–Br–$F_{equatorial}$ angles to be less than 90° because of the lone pair of electrons, which occupies more space than the bonding electron pairs.

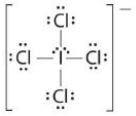
4. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. This molecular structure is *square pyramidal*. The F_{axial}–B–$F_{equatorial}$ angles are 85.1°, less than 90° because of LP–BP repulsions.



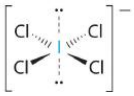
Molecular geometry
(square pyramidal)

AX_4E_2: ICl_4^-

1. The central atom, iodine, contributes seven electrons. Each chlorine contributes seven, and there is a single negative charge. The Lewis electron structure is

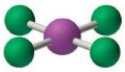


2. There are six electron groups around the central atom, four bonding pairs and two lone pairs. The structure that minimizes LP–LP, LP–BP, and BP–BP repulsions is



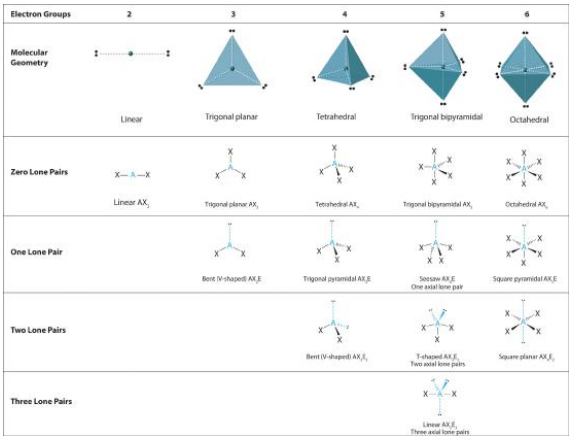
3. ICl_4^- is designated as AX_4E_2 and has a total of six electron pairs. Although there are lone pairs of electrons, with four bonding electron pairs in the equatorial plane and the lone pairs of electrons in the axial positions, all LP–BP repulsions are the same. Therefore, we do not expect any deviation in the Cl–I–Cl bond angles.

4. With five nuclei, the ICl_4^- ion forms a molecular structure that is *square planar*, an octahedron with two opposite vertices missing.

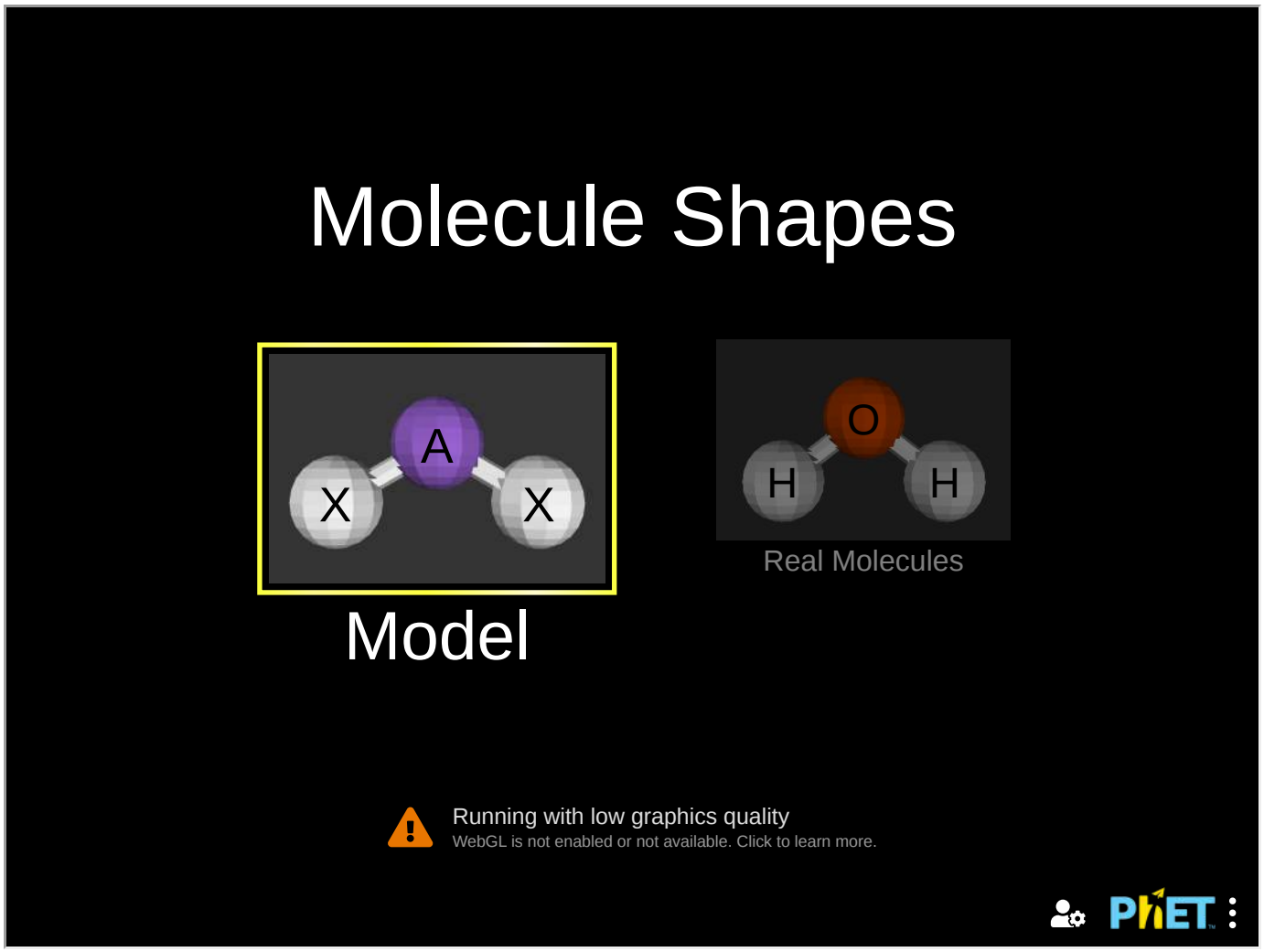


The relationship between the number of electron groups around a central atom, the number of lone pairs of electrons, and the molecular geometry is summarized in Figure 5.1.6 .

Figure 5.1.6 Overview of Molecular Geometries



This PheT applet will allow you to create all of the molecular shapes discussed above with and without lone pairs. You can investigate the structure of molecules, or of model shapes using VSEPR. By placing the cursor on any of the non central atoms or lone pairs you can rotate the molecules.



Example 5.1.1

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

1. PF_5 (phosphorus pentafluoride, a catalyst used in certain organic reactions)
2. H_30^+ (hydronium ion)

Given: two chemical species

Asked for: molecular geometry

Strategy:

A Draw the Lewis electron structure of the molecule or polyatomic ion.

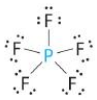
B Determine the electron group arrangement around the central atom that minimizes repulsions.

C Assign an AX_mE_n designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations in bond angles.

D Describe the molecular geometry.

Solution:

1. **A** The central atom, P, has five valence electrons and each fluorine has seven valence electrons, so the Lewis structure of PF_5 is



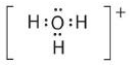
B There are five bonding groups about phosphorus. The structure that minimizes repulsions is a trigonal bipyramid (Figure 5.1.6).

C All electron groups are bonding pairs, so PF_5 is designated as AX_5. Notice that this gives a total of five electron pairs. With no lone pair repulsions, we do not expect any bond angles to deviate from the ideal.

D The PF_5 molecule has five nuclei and no lone pairs of electrons, so its molecular geometry is trigonal bipyramidal.



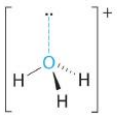
2. **A** The central atom, O, has six valence electrons, and each H atom contributes one valence electron. Subtracting one electron for the positive charge gives a total of eight valence electrons, so the Lewis electron structure is



B There are four electron groups around oxygen, three bonding pairs and one lone pair. Like NH_3, repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

C With three bonding pairs and one lone pair, the structure is designated as AX_3E and has a total of four electron pairs (three X and one E). We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

D There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*, in essence a tetrahedron missing a vertex. However, the H–O–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions:



Exercise

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

1. XeO_3
2. PF_6^-
3. NO_2^+

Answer:

1. trigonal pyramidal
2. octahedral
3. linear

Example 5.1.2

Predict the molecular geometry of each molecule.

1. XeF_2
2. $SnCl_2$

Given: two chemical compounds

Asked for: molecular geometry

Strategy:

Use the strategy given in Example 1.

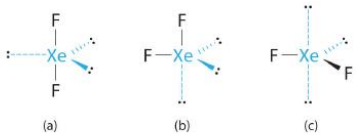
Solution:

1. **A** Xenon contributes eight electrons and each fluorine seven valence electrons, so the Lewis electron structure is



B There are five electron groups around the central atom, two bonding pairs and three lone pairs. Repulsions are minimized by placing the groups in the corners of a trigonal bipyramid.

C From B, XeF_2 is designated as AX_2E_3 and has a total of five electron pairs (two X and three E). With three lone pairs about the central atom, we can arrange the two F atoms in three possible ways: both F atoms can be axial, one can be axial and one equatorial, or both can be equatorial:



Interactions			
90 LP–LP	0	2	2

The structure with the lowest energy is the one that minimizes LP–LP repulsions. Both (b) and (c) have two 90° LP–LP interactions, whereas structure (a) has none. Thus both F atoms are in the axial positions, like the two iodine atoms around the central iodine in I_3^-. All LP–BP interactions are equivalent, so we do not expect a deviation from an ideal 180° in the F–Xe–F bond angle.

D With two nuclei about the central atom, the molecular geometry of XeF_2 is linear. It is a trigonal bipyramid with three missing equatorial vertices.

2. **A** The tin atom donates 4 valence electrons and each chlorine atom donates 7 valence electrons. With 18 valence electrons, the Lewis electron structure is



B There are three electron groups around the central atom, two bonding groups and one lone pair of electrons. To minimize repulsions the three groups are initially placed at 120° angles from each other.

C From B we designate $SnCl_2$ as AX_2E. It has a total of three electron pairs, two X and one E. Because the lone pair of electrons occupies more space than the bonding pairs, we expect a decrease in the Cl–Sn–Cl bond angle due to increased LP–BP repulsions.

D With two nuclei around the central atom and one lone pair of electrons, the molecular geometry of $SnCl_2$ is bent, like SO_2, but with a Cl–Sn–Cl bond angle of 95°. The molecular geometry can be described as a trigonal planar arrangement with one vertex missing.

Exercise

Predict the molecular geometry of each molecule.

1. SO_3
2. XeF_4

Answers:

1. trigonal planar
2. square planar

Molecules with No Single Central Atom

The VSEPR model can be used to predict the structure of somewhat more complex molecules with no single central atom by treating them as linked AX_mE_n fragments. We will demonstrate with methyl isocyanate (CH_3–N=C=O), a volatile and highly toxic molecule that is used to produce the pesticide Sevin. In 1984, large quantities of Sevin were accidentally released in Bhopal, India, when water leaked into storage tanks. The resulting highly exothermic reaction caused a rapid increase in pressure that ruptured the tanks, releasing large amounts of methyl isocyanate that killed approximately 3800 people and wholly or partially disabled about 50,000 others. In addition, there was significant damage to livestock and crops.

We can treat methyl isocyanate as linked AX_mE_n fragments beginning with the carbon atom at the left, which is connected to three H atoms and one N atom by single bonds. The four bonds around carbon mean that it must be surrounded by four bonding electron pairs in a configuration similar to AX_4. We can therefore predict the CH_3–N portion of the molecule to be roughly tetrahedral, similar to methane:

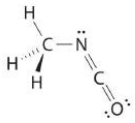


The nitrogen atom is connected to one carbon by a single bond and to the other carbon by a double bond, producing a total of three bonds, C–N=C. For nitrogen to have an octet of electrons, it must also have a lone pair:



Because multiple bonds are not shown in the VSEPR model, the nitrogen is effectively surrounded by three electron pairs. Thus according to the VSEPR model, the C–N=C fragment should be bent with an angle less than 120°.

The carbon in the –N=C=O fragment is doubly bonded to both nitrogen and oxygen, which in the VSEPR model gives carbon a total of two electron pairs. The N=C=O angle should therefore be 180°, or linear. The three fragments combine to give the following structure:



We predict that all four nonhydrogen atoms lie in a single plane, with a C–N–C angle of approximately 120°. The experimentally determined structure of methyl isocyanate confirms our prediction (Figure 5.1.7).

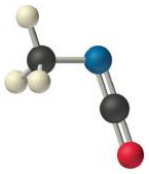


Figure 5.1.7 The Experimentally Determined Structure of Methyl Isocyanate

Certain patterns are seen in the structures of moderately complex molecules. For example, carbon atoms with four bonds (such as the carbon on the left in methyl isocyanate) are generally tetrahedral. Similarly, the carbon atom on the right has two double bonds that are similar to those in CO_2, so its geometry, like that of CO_2, is linear. Recognizing similarities to simpler molecules will help you predict the molecular geometries of more complex molecules.

Example 5.1.3

Use the VSEPR model to predict the molecular geometry of propyne ($H_3C–C≡CH$), a gas with some anesthetic properties.

Given: chemical compound

Asked for: molecular geometry

Strategy:

Count the number of electron groups around each carbon, recognizing that in the VSEPR model, a multiple bond counts as a single group. Use Figure 5.1.3 to determine the molecular geometry around each carbon atom and then deduce the structure of the molecule as a whole.

Solution:

Because the carbon atom on the left is bonded to four other atoms, we know that it is approximately tetrahedral. The next two carbon atoms share a triple bond, and each has an additional single bond. Because a multiple bond is counted as a single bond in the VSEPR model, each carbon atom behaves as if it had two electron groups. This means that both of these carbons are linear, with C–C≡C and C≡C–H angles of 180°.

Exercise

Predict the geometry of allene ($H_2C=C=CH_2$), a compound with narcotic properties that is used to make more complex organic molecules.

Answer: The terminal carbon atoms are trigonal planar, the central carbon is linear, and the C–C–C angle is 180°.

Molecular Dipole Moments

In Chapter 4 , you learned how to calculate the **dipole moments** of simple diatomic molecules. In more complex molecules with polar covalent bonds, the three-dimensional geometry and the compound's symmetry determine whether there is a net dipole moment. Mathematically, dipole moments are *vectors*; they possess both a *magnitude* and a *direction*. The dipole moment of a molecule is therefore the *vector sum* of the dipole moments of the individual bonds in the molecule. If the individual bond dipole moments cancel one another, there is no net dipole moment. Such is the case for CO_2, a linear molecule (part (a) in Figure 5.1.8). Each C–O bond in CO_2 is polar, yet experiments show that the CO_2 molecule has no dipole moment. Because the two C–O bond dipoles in CO_2 are equal in magnitude and oriented at 180° to each other, they cancel. As a result, the CO_2 molecule has no *net* dipole moment even though it has a substantial separation of charge. In contrast, the H_2O molecule is not linear (part (b) in Figure 5.1.8); it is bent in three-dimensional space, so the dipole moments do not cancel each other. Thus a molecule such as H_2O has a net dipole moment. We expect the concentration of negative charge to be on the oxygen, the more electronegative atom, and positive charge on the two hydrogens. This charge polarization allows H_2O to hydrogen-bond to other polarized or charged species, including other water molecules.

Figure 5.1.8 How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures

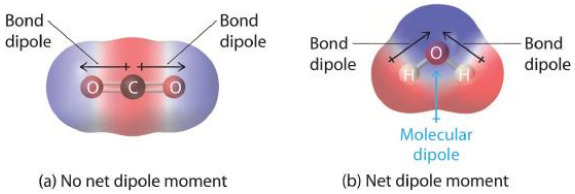


Figure 5.1.8 How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures *(a) In CO_2, the C–O bond dipoles are equal in magnitude but oriented in opposite directions (at 180°). Their vector sum is zero, so CO_2 therefore has no net dipole. (b) In H_2O, the O–H bond dipoles are also equal in magnitude, but they are oriented at 104.5° to each other. Hence the vector sum is not zero, and H_2O has a net dipole moment.*

Other examples of molecules with polar bonds are shown in Figure 5.1.9 "Molecules with Polar Bonds". In molecular geometries that are highly symmetrical (most notably tetrahedral and square planar, trigonal bipyramidal, and octahedral), individual bond dipole moments completely cancel, and there is no net dipole moment. Although a molecule like $CHCl_3$ is best described as tetrahedral, the atoms bonded to carbon are not identical. Consequently, the bond dipole moments cannot cancel one another, and the molecule has a dipole moment. Due to the arrangement of the bonds in molecules that have V-shaped, trigonal pyramidal, seesaw, T-shaped, and square pyramidal geometries, the bond dipole moments cannot cancel one another. Consequently, molecules with these geometries always have a nonzero dipole moment.

Figure 5.1.9 Molecules with Polar Bonds

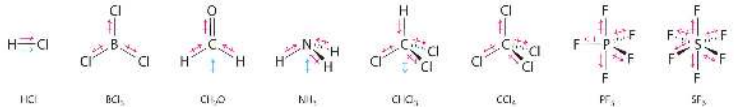


Figure 5.1.9 Molecules with Polar Bonds

Individual bond dipole moments are indicated in red. Due to their different three-dimensional structures, some molecules with polar bonds have a net dipole moment (HCl, CH_2O, NH_3, and $CHCl_3$), indicated in blue, whereas others do not because the bond dipole moments cancel (BCl_3, CCl_4, PF_5, and SF_6).

Note the Pattern

Molecules with asymmetrical charge distributions have a net dipole moment.

Example 5.1.4

Which molecule(s) has a net dipole moment?

1. H_2S
2. NHF_2
3. BF_3

Given: three chemical compounds

Asked for: net dipole moment

Strategy:

For each three-dimensional molecular geometry, predict whether the bond dipoles cancel. If they do not, then the molecule has a net dipole moment.

Solution:

1. The total number of electrons around the central atom, S, is eight, which gives four electron pairs. Two of these electron pairs are bonding pairs and two are lone pairs, so the molecular geometry of H_2S is bent (Figure 5.1.6). The bond dipoles cannot cancel one another, so the molecule has a net dipole moment.



2. *Difluoroamine has a trigonal pyramidal molecular geometry. Because there is one hydrogen and two fluorines, and because of the lone pair of electrons on nitrogen, the molecule is not symmetrical, and the bond dipoles of NHF_2 cannot cancel one another. This means that NHF_2 has a net dipole moment. We expect polarization from the two fluorine atoms, the most electronegative atoms in the periodic table, to have a greater affect on the net dipole moment than polarization from the lone pair of electrons on nitrogen.*



3. *The molecular geometry of BF_3 is trigonal planar. Because all the B–F bonds are equal and the molecule is highly symmetrical, the dipoles cancel one another in three-dimensional space. Thus BF_3 has a net dipole moment of zero:*



Exercise

Which molecule(s) has a net dipole moment?

1. CH_3Cl
2. SO_3
3. XeO_3

Answer: CH_3Cl; XeO_3

Summary

Lewis electron structures give no information about **molecular geometry**, the arrangement of bonded atoms in a molecule or polyatomic ion, which is crucial to understanding the chemistry of a molecule. The **valence-shell electron-pair repulsion (VSEPR) model** allows us to predict which of the possible structures is actually observed in most cases. It is based on the assumption that pairs of electrons occupy space, and the lowest-energy structure is the one that minimizes electron pair–electron pair repulsions. In the VSEPR model, the molecule or polyatomic ion is given an AX_mE_n designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and m and n are integers. Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the **bond angles**. From this we can describe the **molecular geometry**. A combination of VSEPR and a bonding model, such as Lewis electron structures, however, is necessary to understand the presence of multiple bonds.

Molecules with polar covalent bonds can have a *dipole moment*, an asymmetrical distribution of charge that results in a tendency for molecules to align themselves in an applied electric field. Any diatomic molecule with a polar covalent bond has a dipole moment, but in polyatomic molecules, the presence or absence of a net dipole moment depends on the structure. For some highly symmetrical structures, the individual bond dipole moments cancel one another, giving a dipole moment of zero.

Key Takeaway

- The VSEPR model can be used to predict the shapes of many molecules and polyatomic ions, but it gives no information about bond lengths and the presence of multiple bonds.

Conceptual Problems

1. What is the main difference between the VSEPR model and Lewis electron structures?
2. What are the differences between molecular geometry and Lewis electron structures? Can two molecules with the same Lewis electron structures have different molecular geometries? Can two molecules with the same molecular geometry have different Lewis electron structures? In each case, support your answer with an example.
3. How does the VSEPR model deal with the presence of multiple bonds?
4. Three molecules have the following generic formulas: AX_2, AX_2E, and AX_2E_2. Predict the molecular geometry of each, and arrange them in order of increasing X–A–X angle.
5. Which has the smaller angles around the central atom—H_2S or SiH_4? Why? Do the Lewis electron structures of these molecules predict which has the smaller angle?
6. Discuss in your own words why lone pairs of electrons occupy more space than bonding pairs. How does the presence of lone pairs affect molecular geometry?
7. When using VSEPR to predict molecular geometry, the importance of repulsions between electron pairs decreases in the following order: LP–LP, LP–BP, BP–BP. Explain this order. Draw structures of real molecules that separately show each of these interactions.
8. How do multiple bonds affect molecular geometry? Does a multiple bond take up more or less space around an atom than a single bond? a lone pair?
9. Straight-chain alkanes do not have linear structures but are “kinked.” Using *n*-hexane as an example, explain why this is so. Compare the geometry of 1-hexene to that of *n*-hexane.
10. How is molecular geometry related to the presence or absence of a molecular dipole moment?
11. How are molecular geometry and dipole moments related to physical properties such as melting point and boiling point?
12. What two features of a molecule’s structure and bonding are required for a molecule to be considered polar? Is COF_2 likely to have a significant dipole moment? Explain your answer.
13. When a chemist says that a molecule is *polar*, what does this mean? What are the general physical properties of polar molecules?
14. Use the VSPER model and your knowledge of bonding and dipole moments to predict which molecules will be liquids or solids at room temperature and which will be gases. Explain your rationale for each choice. Justify your answers.
    1. CH_3Cl
    2. PCl_3
    3. CO

4. SF_6
5. IF_5
6. CH_3OCH_3
7. CCl_3H
8. H_3COH

15. The idealized molecular geometry of BrF_5 is square pyramidal, with one lone pair. What effect does the lone pair have on the actual molecular geometry of BrF_5? If LP–BP repulsions were *weaker* than BP–BP repulsions, what would be the effect on the molecular geometry of BrF_5?
16. Which has the smallest bond angle around the central atom—H_2S, H_2Se, or H_2Te? the largest? Justify your answers.
17. Which of these molecular geometries *always* results in a molecule with a net dipole moment: linear, bent, trigonal planar, tetrahedral, seesaw, trigonal pyramidal, square pyramidal, and octahedral? For the geometries that do not always produce a net dipole moment, what factor(s) will result in a net dipole moment?

Answers

1.
2.
3. To a first approximation, the VSEPR model assumes that multiple bonds and single bonds have the same effect on electron pair geometry and molecular geometry; in other words, VSEPR treats multiple bonds like single bonds. Only when considering fine points of molecular structure does VSEPR recognize that multiple bonds occupy more space around the central atom than single bonds.
4.
5.
6.
7.
8.
9.
10.
11. Physical properties like boiling point and melting point depend upon the existence and magnitude of the dipole moment of a molecule. In general, molecules that have substantial dipole moments are likely to exhibit greater intermolecular interactions, resulting in higher melting points and boiling points.
12.
13. The term “polar” is generally used to mean that a molecule has an asymmetrical structure and contains polar bonds. The resulting dipole moment causes the substance to have a higher boiling or melting point than a nonpolar substance.
14.
15.
16.
17.

Numerical Problems

1. Give the number of electron groups around the central atom and the molecular geometry for each molecule. Classify the electron groups in each species as bonding pairs or lone pairs.
    1. BF_3
    2. PCl_3
    3. XeF_2
    4. $AlCl_4^-$
    5. CH_2Cl_2
2. Give the number of electron groups around the central atom and the molecular geometry for each species. Classify the electron groups in each species as bonding pairs or lone pairs.
    1. ICl_3
    2. CCl_3^+
    3. H_2Te
    4. XeF_4
    5. NH_4^+
3. Give the number of electron groups around the central atom and the molecular geometry for each molecule. For structures that are not linear, draw three-dimensional representations, clearly showing the positions of the lone pairs of electrons.
    1. HCl

2. NF_3
3. ICl_2^+
4. N_3^-
5. H_3O^+

4. Give the number of electron groups around the central atom and the molecular geometry for each molecule. For structures that are not linear, draw three-dimensional representations, clearly showing the positions of the lone pairs of electrons.

1. SO_3
2. NH_2^-
3. NO_3^-
4. I_3^-
5. OF_2

5. What is the molecular geometry of ClF_3? Draw a three-dimensional representation of its structure and explain the effect of any lone pairs on the idealized geometry.

6. Predict the molecular geometry of each of the following.

1. ICl_3
2. AsF_5
3. NO_2^-
4. $TeCl_4$

7. Predict whether each molecule has a net dipole moment. Justify your answers and indicate the direction of any bond dipoles.

1. NO
2. HF
3. PCl_3
4. CO_2
5. SO_2
6. SF_4

8. Predict whether each molecule has a net dipole moment. Justify your answers and indicate the direction of any bond dipoles.

1. OF_2
2. BCl_3
3. CH_2Cl_2
4. TeF_4
5. CH_3OH
6. XeO_4

9. Of the molecules $Cl_2C{=}Cl_2$, IF_3, and SF_6, which has a net dipole moment? Explain your reasoning.

10. Of the molecules SO_3, XeF_4, and $H_2C{=}Cl_2$, which has a net dipole moment? Explain your reasoning.

Answers

1.

1. trigonal planar (all electron groups are bonding pairs)
2. tetrahedral (one lone pair on P)
3. trigonal bipyramidal (three lone pairs on Xe)
4. tetrahedral (all electron groups on Al are bonding pairs)
5. tetrahedral (all electron groups on C are bonding pairs)

2.

3.

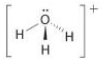
1. four electron groups, linear molecular geometry
2. four electron groups, pyramidal molecular geometry



3. four electron groups, bent molecular geometry



4. two electron groups, linear molecular geometry
5. four electron groups, pyramidal molecular geometry



4.
5.



The idealized geometry is T shaped, but the two lone pairs of electrons on Cl will distort the structure, making the F–Cl–F angle *less* than 180°.

6.
7.
8.
9. $Cl_2C=CCl_2$: Although the C–Cl bonds are rather polar, the individual bond dipoles cancel one another in this symmetrical structure, and $Cl_2C=CCl_2$ does not have a net dipole moment.



IF_3: In this structure, the individual I–F bond dipoles cannot cancel one another, giving IF_3 a net dipole moment.



SF_6: The S–F bonds are quite polar, but the individual bond dipoles cancel one another in an octahedral structure. Thus, SF_6 has no net dipole moment.



10.

Contributors

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Chapter 5.2: Localized Bonding and Hybrid Orbitals

Learning Objectives

- To describe the bonding in simple compounds using valence bond theory.

Although the VSEPR model is a simple and useful method for qualitatively predicting the structures of a wide range of compounds, it is *not* infallible. It predicts, for example, that H_2S and PH_3 should have structures similar to those of H_2O and NH_3, respectively. In fact, structural studies have shown that the H–S–H and H–P–H angles are more than 12° smaller than the corresponding bond angles in H_2O and NH_3. More disturbing, the VSEPR model predicts that the simple group 2 halides (MX_2), which have four valence electrons, should all have linear X–M–X geometries. Instead, many of these species, including SrF_2 and BaF_2, are significantly bent. A more sophisticated treatment of bonding is needed for systems such as these. In this section, we present a quantum mechanical description of bonding, in which bonding electrons are viewed as being localized between the nuclei of the bonded atoms. The overlap of bonding orbitals is substantially increased through a process called *hybridization*, which results in the formation of stronger bonds.

Valence Bond Theory: A Localized Bonding Approach

In Chapter 4, you learned that as two hydrogen atoms approach each other from an infinite distance, the energy of the system reaches a minimum. This region of minimum energy in the energy diagram corresponds to the formation of a covalent bond between the two atoms at an H–H distance of 74 pm (Figure 4.4.2). According to quantum mechanics, bonds form between atoms because their atomic orbitals overlap, with each region of overlap accommodating a maximum of two electrons with opposite spin, in accordance with the Pauli principle. In this case, a bond forms between the two hydrogen atoms when the singly occupied 1*s* atomic orbital of one hydrogen atom overlaps with the singly occupied 1*s* atomic orbital of a second hydrogen atom. Electron density between the nuclei is increased because of this orbital overlap and results in a *localized electron-pair bond* (Figure 5.2.1).

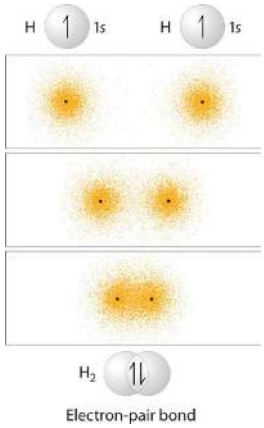


Figure 5.2.1 Overlap of Two Singly Occupied Hydrogen 1*s* Atomic Orbitals Produces an H–H Bond in H_2 *The formation of H_2 from two hydrogen atoms, each with a single electron in a 1s orbital, occurs as the electrons are shared to form an electron-pair bond, as indicated schematically by the gray spheres and black arrows. The orange electron density distributions show that the formation of an H_2 molecule increases the electron density in the region between the two positively charged nuclei.*

Although Lewis and VSEPR structures also contain localized electron-pair bonds, neither description uses an atomic orbital approach to predict the stability of the bond. Doing so forms the basis for a description of chemical bonding known as valence bond theory (A localized bonding model that assumes that the strength of a covalent bond is proportional to the amount of overlap between atomic orbitals and that an atom can use different combinations of atomic orbitals (hybrids) to maximize the overlap between bonded atoms.), which is built on two assumptions:

1. The strength of a covalent bond is proportional to the amount of overlap between atomic orbitals; that is, the greater the overlap, the more stable the bond.
2. An atom can use different combinations of atomic orbitals to maximize the overlap of orbitals used by bonded atoms.

Figure 5.2.2 shows an electron-pair bond formed by the overlap of two *ns* atomic orbitals, two *np* atomic orbitals, and an *ns* and an *np* orbital where $n = 2$. Maximum overlap occurs between orbitals with the same spatial orientation and similar energies.

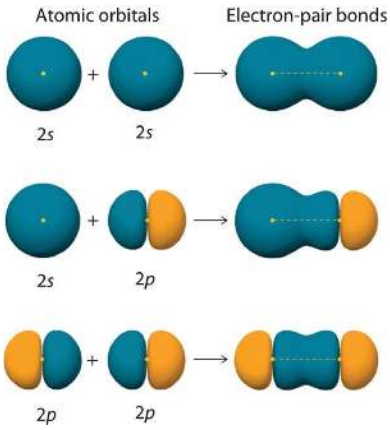


Figure 5.2.2 Three Different Ways to Form an Electron-Pair Bond *An electron-pair bond can be formed by the overlap of any of the following combinations of two singly occupied atomic orbitals: two ns atomic orbitals (a), an ns and an np atomic orbital (b), and two np atomic orbitals (c) where n = 2. The positive lobe is indicated in yellow, and the negative lobe is in blue.*

Let's examine the bonds in BeH_2, for example. According to the VSEPR model, BeH_2 is a linear compound with four valence electrons and two Be–H bonds. Its bonding can also be described using an atomic orbital approach. Beryllium has a $1s^2 2s^2$ electron configuration, and each H atom has a $1s^1$ electron configuration. Because the Be atom has a filled 2*s* subshell, however, it has no singly occupied orbitals available to overlap with the singly occupied 1*s* orbitals on the H atoms. If a singly occupied 1*s* orbital on hydrogen were to overlap with a filled 2*s* orbital on beryllium, the resulting bonding orbital would contain *three* electrons, but the maximum allowed by quantum mechanics is *two*. How then is beryllium able to bond to two hydrogen atoms? One way would be to add enough energy to excite one of its 2*s* electrons into an empty 2*p* orbital and reverse its spin, in a process called promotion (The excitation of an electron from a filled ns^2 to an *nsnp* valence orbital)



In this excited state, the Be atom would have two singly occupied atomic orbitals (the 2*s* and one of the 2*p* orbitals), each of which could overlap with a singly occupied 1*s* orbital of an H atom to form an electron-pair bond. Although this would produce BeH_2, the two Be–H bonds would not be equivalent: the 1*s* orbital of one hydrogen atom would overlap with a Be 2*s* orbital, and the 1*s* orbital of the other hydrogen atom would overlap with an orbital of a different energy, a Be 2*p* orbital. Experimental evidence indicates, however, that the two Be–H bonds have identical energies. To resolve this discrepancy and explain how molecules such as BeH_2 form, scientists developed the concept of hybridization.

Hybridization of *s* and *p* Orbitals

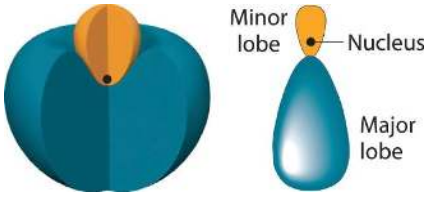
The localized bonding approach uses a process called hybridization (A process in which two or more atomic orbitals that are similar in energy but not equivalent are combined mathematically to produce sets of equivalent orbitals that are properly oriented to form bonds), in which atomic orbitals that are similar in energy but not equivalent are combined mathematically to produce sets of equivalent orbitals that are properly oriented to form bonds. These new combinations are called hybrid atomic orbitalsNew atomic orbitals formed from the process of hybridization. because they are produced by combining (*hybridizing*) two or more atomic orbitals from the same atom.

In BeH_2, we can generate two equivalent orbitals by combining the 2*s* orbital of beryllium and any one of the three degenerate 2*p* orbitals. By taking the sum and the difference of Be 2*s* and $2p_z$ atomic orbitals, for example, we produce two new orbitals with major and minor lobes oriented along the *z*-axes, as shown in Figure 5.2.3. Because the difference A − B can also be written as A + (−B), in Figure 5.2.3 and subsequent figures we have reversed the phase(s) of the orbital being subtracted, which is the same as

multiplying it by −1 and adding. This gives us Equation 5.2.1, where the value $1/\sqrt{2}$ is needed mathematically to indicate that the 2*s* and 2*p* orbitals contribute equally to each hybrid orbital.

$$sp_1 = \frac{1}{\sqrt{2}}(2s + 2p_z) \quad and \quad sp_2 = \frac{1}{\sqrt{2}}(2s - 2p_z)$$

Generally we do not use the subsript labels on the two *sp* orbitals, but we have done so here to emphasize that there are two different orbitals. It is also important to remember that the two *sp* orbitals are built from orbitals of the same atom and centered on the nucleus of that atom. Later in this chapter we will meet molecular orbitals which are linear combinations of atomic orbitals (LCAO in theoretical chemistry speak) centered on *different* atoms. It is often difficult for students to figure out the difference



The position of the atomic nucleus with respect to an sp hybrid orbital. *The nucleus is actually located slightly inside the minor lobe, not at the node separating the major and minor lobes.*

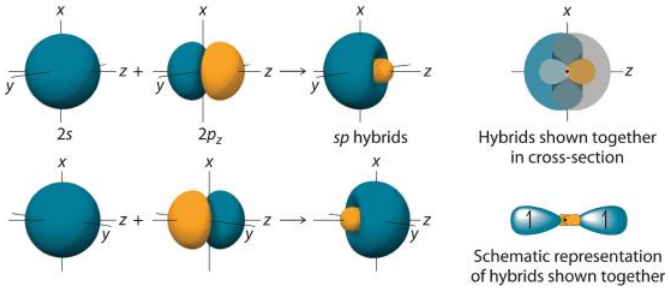
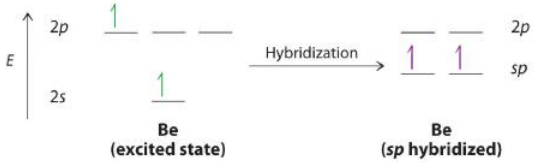


Figure 5.2.3 The Formation of *sp* Hybrid Orbitals *Taking the mathematical sum and difference of an ns and an np atomic orbital where n = 2 gives two equivalent sp hybrid orbitals oriented at 180° to each other.*

The nucleus resides just inside the minor lobe of each orbital. In this case, the new orbitals are called *sp hybrids* because they are formed from one *s* and one *p* orbital. The two new orbitals are equivalent in energy, and their energy is between the energy values associated with pure *s* and *p* orbitals, as illustrated in this diagram:



This yield two singly occupied *sp* hybrid orbitals (The two equivalent hybrid orbitals that result when one *ns* orbital and one *np* orbital are combined (hybridized)). The two *sp* hybrid orbitals are oriented at 180° from each other. They are equivalent in energy, and their energy is between the energy values associated with pure *sp* orbitals. can now form an electron-pair bond with the singly occupied 1*s* atomic orbital of one of the H atoms. As shown in Figure 5.2.4, each *sp* orbital on Be has the correct orientation for the major lobes to overlap with the 1*s* atomic orbital of an H atom. The formation of two energetically equivalent Be–H bonds produces a linear BeH_2 molecule. Thus valence bond theory does what neither the Lewis electron structure nor the VSEPR model is able to do; it explains why the bonds in BeH_2 are equivalent in energy and why BeH_2 has a linear geometry.

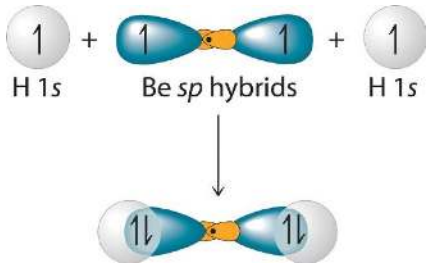


Figure 5.2.4 Explanation of the Bonding in BeH_2 Using *sp* Hybrid Orbitals *Each singly occupied sp hybrid orbital on beryllium can form an electron-pair bond with the singly occupied 1s orbital of a hydrogen atom. Because the two sp hybrid orbitals are oriented at a 180° angle, the BeH_2 molecule is linear.*

Because both promotion and hybridization require an input of energy, the formation of a set of singly occupied hybrid atomic orbitals is energetically uphill. The overall process of forming a compound with hybrid orbitals will be energetically favorable *only* if the amount of energy released by the formation of covalent bonds is greater than the amount of energy used to form the hybrid orbitals (Figure 5.2.5). As we will see, some compounds are highly unstable or do not exist because the amount of energy required to form hybrid orbitals is greater than the amount of energy that would be released by the formation of additional bonds.

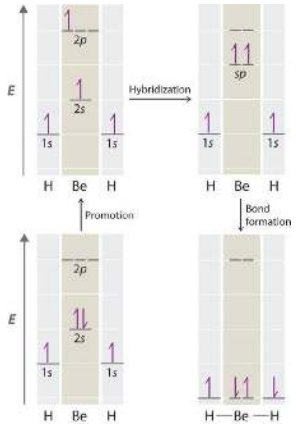
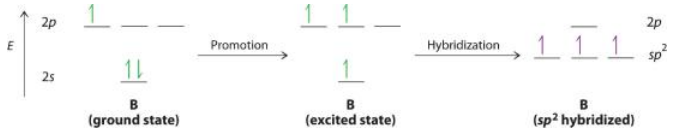


Figure 5.2.5 A Hypothetical Stepwise Process for the Formation of BeH_2 from a Gaseous Be Atom and Two Gaseous H Atoms *The promotion of an electron from the 2s orbital of beryllium to one of the 2p orbitals is energetically uphill. The overall process of forming a BeH_2 molecule from a Be atom and two H atoms will therefore be energetically favorable only if the amount of energy released by the formation of the two Be–H bonds is greater than the amount of energy required for promotion and hybridization.*

The concept of hybridization also explains why boron, with a $2s^2 2p^1$ valence electron configuration, forms three bonds with fluorine to produce BF_3, as predicted by the Lewis and VSEPR approaches. With only a single unpaired electron in its ground state, boron should form only a single covalent bond. By the promotion of one of its 2*s* electrons to an unoccupied 2*p* orbital, however, followed by the hybridization of the three singly occupied orbitals (the 2*s* and two 2*p* orbitals), boron acquires a set of three equivalent hybrid orbitals with one electron each, as shown here:



The hybrid orbitals are degenerate and are oriented at 120° angles to each other (Figure 5.2.6). Because the hybrid atomic orbitals are formed from one *s* and two *p* orbitals, boron is said to be sp^2 *hybridized* (pronounced “s-p-two” or “s-p-squared”). The singly occupied sp^2 hybrid atomic orbitalsThe three equivalent hybrid orbitals that result when one *ns* orbital and two np orbitals are combined (hybridized). The three sp^2 hybrid orbitals are oriented in a plane at 120° from each other. They are equivalent in energy, and their energy is between the energy values associated with pure s and pure p orbitals. can overlap with the singly occupied orbitals on each of the three F atoms to form a trigonal planar structure with three energetically equivalent B–F bonds.

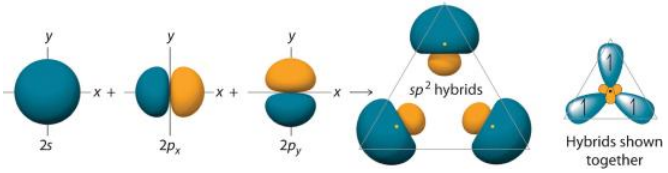
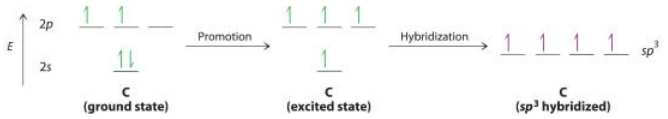


Figure 5.2.6 Formation of sp^2 Hybrid Orbitals *Combining one ns and two np atomic orbitals gives three equivalent sp^2 hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.*

Looking at the $2s^22p^2$ valence electron configuration of carbon, we might expect carbon to use its two unpaired 2*p* electrons to form compounds with only two covalent bonds. We know, however, that carbon typically forms compounds with four covalent bonds. We can explain this apparent discrepancy by the hybridization of the 2*s* orbital and the three 2*p* orbitals on carbon to give a set of four degenerate sp^3 ("s-p-three" or "s-p-cubed") hybrid orbitals, each with a single electron:



The large lobes of the hybridized orbitals are oriented toward the vertices of a tetrahedron, with 109.5° angles between them (Figure 5.2.7). Like all the hybridized orbitals discussed earlier, the sp^3 hybrid atomic orbitals (The four equivalent hybrid orbitals that result when one *ns* orbital and three *np* orbitals are combined (hybridized). The four sp^3 hybrid orbitals point at the vertices of a tetrahedron, so they are oriented at 109.5° from each other. They are equivalent in energy, and their energy is between the energy values associated with pure *s* and pure *p* orbitals. are predicted to be equal in energy.

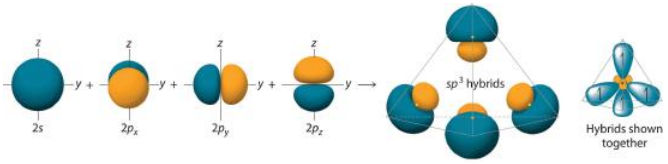


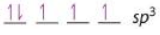
Figure 5.2.7 Formation of sp^3 Hybrid Orbitals *Combining one ns and three np atomic orbitals results in four sp^3 hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.*

In addition to explaining why some elements form more bonds than would be expected based on their valence electron configurations, and why the bonds formed are equal in energy, valence bond theory explains why these compounds are so stable: the amount of energy released increases with the number of bonds formed. In the case of carbon, for example, much more energy is released in the formation of four bonds than two, so compounds of carbon with four bonds tend to be more stable than those with only two. Carbon does form compounds with only two covalent bonds (such as CH_2 or CF_2), but these species are highly reactive, unstable intermediates that form in only certain chemical reactions.

Note the Pattern

Valence bond theory explains the number of bonds formed in a compound and the relative bond strengths.

The bonding in molecules such as NH_3 or H_2O, which have lone pairs on the central atom, can also be described in terms of hybrid atomic orbitals. In NH_3, for example, N, with a $2s^22p^3$ valence electron configuration, can hybridize its 2*s* and 2*p* orbitals to produce four sp^3 hybrid orbitals. Placing five valence electrons in the four hybrid orbitals, we obtain three that are singly occupied and one with a pair of electrons:



The three singly occupied sp^3 lobes can form bonds with three H atoms, while the fourth orbital accommodates the lone pair of electrons. Similarly, H_2O has an sp^3 hybridized oxygen atom that uses two singly occupied sp^3 lobes to bond to two H atoms, and two to accommodate the two lone pairs predicted by the VSEPR model. Such descriptions explain the approximately tetrahedral distribution of electron pairs on the central atom in NH_3 and H_2O. Unfortunately, however, recent experimental evidence indicates that in CH_4 and NH_3, the hybridized orbitals are *not* entirely equivalent in energy, making this bonding model an active area of research.

Example 5.2.1

Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

1. H_2S
2. $CHCl_3$

Given: two chemical compounds

Asked for: number of electron pairs and molecular geometry, hybridization, and bonding

Strategy:

A Using the approach from Example 1, determine the number of electron pairs and the molecular geometry of the molecule.

B From the valence electron configuration of the central atom, predict the number and type of hybrid orbitals that can be produced. Fill these hybrid orbitals with the total number of valence electrons around the central atom and describe the hybridization.

Solution:

1. **A** H_2S has four electron pairs around the sulfur atom with two bonded atoms, so the VSEPR model predicts a molecular geometry that is bent, or V shaped. **B** Sulfur has a $3s^2 3p^4$ valence electron configuration with six electrons, but by hybridizing its 3*s* and 3*p* orbitals, it can produce four sp^3 hybrids. If the six valence electrons are placed in these orbitals, two have electron pairs and two are singly occupied. The two sp^3 hybrid orbitals that are singly occupied are used to form S–H bonds, whereas the other two have lone pairs of electrons. Together, the four sp^3 hybrid orbitals produce an approximately tetrahedral arrangement of electron pairs, which agrees with the molecular geometry predicted by the VSEPR model.
2. **A** The $CHCl_3$ molecule has four valence electrons around the central atom. In the VSEPR model, the carbon atom has four electron pairs, and the molecular geometry is tetrahedral. **B** Carbon has a $2s^2 2p^2$ valence electron configuration. By hybridizing its 2*s* and 2*p* orbitals, it can form four sp^3 hybridized orbitals that are equal in energy. Eight electrons around the central atom (four from C, one from H, and one from each of the three Cl atoms) fill three sp^3 hybrid orbitals to form C–Cl bonds, and one forms a C–H bond. Similarly, the Cl atoms, with seven electrons each in their 3*s* and 3*p* valence subshells, can be viewed as sp^3 hybridized. Each Cl atom uses a singly occupied sp^3 hybrid orbital to form a C–Cl bond and three hybrid orbitals to accommodate lone pairs.

Exercise

Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

1. the BF_4^- ion
2. hydrazine ($H_2N–NH_2$)

Answer:

1. B is sp^3 hybridized; F is also sp^3 hybridized so it can accommodate one B–F bond and three lone pairs. The molecular geometry is tetrahedral.
2. Each N atom is sp^3 hybridized and uses one sp^3 hybrid orbital to form the N–N bond, two to form N–H bonds, and one to accommodate a lone pair. The molecular geometry about each N is trigonal pyramidal.

Note the Pattern

The number of hybrid orbitals used by the central atom is the same as the number of electron pairs around the central atom.

Hybridization Using *d* Orbitals

Hybridization is not restricted to the *ns* and *np* atomic orbitals. The bonding in compounds with central atoms in the period 3 and below can also be described using hybrid atomic orbitals. In these cases, the central atom can use its valence $(n - 1)d$ orbitals as well as its *ns* and *np* orbitals to form hybrid atomic orbitals, which allows it to accommodate five or more bonded atoms (as in PF_5 and SF_6). Using the *ns* orbital, all three *np* orbitals, and one $(n - 1)d$ orbital gives a set of five sp^3d hybrid orbitals (The five hybrid orbitals that result when one *s* three *p* and one *d* orbitals are combined (hybridized)). that point toward the vertices of a trigonal

bipyramid (part (a) in Figure 5.2.8). In this case, the five hybrid orbitals are *not* all equivalent: three form a triangular array oriented at 120° angles, and the other two are oriented at 90° to the first three and at 180° to each other.

Similarly, the combination of the *ns* orbital, all three *np* orbitals, and *two nd* orbitals gives a set of six equivalent sp^3d^2 hybrid orbitals (The six equivalent hybrid orbitals that result when one *s*, three p, and two d orbitals are combined (hybridized). oriented toward the vertices of an octahedron (part (b) in Figure 5.2.8). In the VSEPR model, PF_5 and SF_6 are predicted to be trigonal bipyramidal and octahedral, respectively, which agrees with a valence bond description in which sp^3d or sp^3d^2 hybrid orbitals are used for bonding.

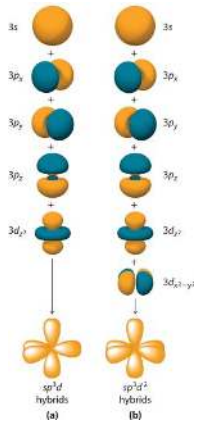


Figure 5.2.8 Hybrid Orbitals Involving *d* Orbitals *The formation of a set of (a) five sp^3d hybrid orbitals and (b) six sp^3d^2 hybrid orbitals from ns, np, and nd atomic orbitals where n = 4.*

Example 5.2.2

What is the hybridization of the central atom in each species? Describe the bonding in each species.

1. XeF_4
2. SO_4^{2-}
3. SF_4

Given: three chemical species

Asked for: hybridization of the central atom

Strategy:

A Determine the geometry of the molecule using the strategy in Example 1. From the valence electron configuration of the central atom and the number of electron pairs, determine the hybridization.

B Place the total number of electrons around the central atom in the hybrid orbitals and describe the bonding.

Solution:

1. **A** Using the VSEPR model, we find that Xe in XeF_4 forms four bonds and has two lone pairs, so its structure is square planar and it has six electron pairs. The six electron pairs form an octahedral arrangement, so the Xe must be sp^3d^2 hybridized. **B** With 12 electrons around Xe, four of the six sp^3d^2 hybrid orbitals form Xe–F bonds, and two are occupied by lone pairs of electrons.
2. **A** The S in the SO_4^{2-} ion has four electron pairs and has four bonded atoms, so the structure is tetrahedral. The sulfur must be sp^3 hybridized to generate four S–O bonds. **B** Filling the sp^3 hybrid orbitals with eight electrons from four bonds produces four filled sp^3 hybrid orbitals.
3. **A** The S atom in SF_4 contains five electron pairs and four bonded atoms. The molecule has a seesaw structure with one lone pair:



To accommodate five electron pairs, the sulfur atom must be sp^3d hybridized. **B** Filling these orbitals with 10 electrons gives four sp^3d hybrid orbitals forming S–F bonds and one with a lone pair of electrons.

Exercise

What is the hybridization of the central atom in each species? Describe the bonding.

1. PCl_4^+
2. BrF_3
3. SiF_6^{2-}

Answer:

1. sp^3 with four P–Cl bonds
2. sp^3d with three Br–F bonds and two lone pairs
3. sp^3d^2 with six Si–F bonds

Hybridization using *d* orbitals allows chemists to explain the structures and properties of many molecules and ions. Like most such models, however, it is not universally accepted. Nonetheless, it does explain a fundamental difference between the chemistry of the elements in the period 2 (C, N, and O) and those in period 3 and below (such as Si, P, and S).

Period 2 elements do not form compounds in which the central atom is covalently bonded to five or more atoms, although such compounds are common for the heavier elements. Thus whereas carbon and silicon both form tetrafluorides (CF_4 and SiF_4), only SiF_4 reacts with F^- to give a stable hexafluoro dianion, SiF_6^{2-}. Because there are no 2*d* atomic orbitals, the formation of octahedral CF_6^{2-} would require hybrid orbitals created from 2*s*, 2*p*, and 3*d* atomic orbitals. The 3*d* orbitals of carbon are so high in energy that the amount of energy needed to form a set of sp^3d^2 hybrid orbitals cannot be equaled by the energy released in the formation of two additional C–F bonds. These additional bonds are expected to be weak because the carbon atom (and other atoms in period 2) is so small that it cannot accommodate five or six F atoms at normal C–F bond lengths due to repulsions between electrons on adjacent fluorine atoms. Perhaps not surprisingly, then, species such as CF_6^{2-} have never been prepared.

Example 5.2.3

What is the hybridization of the oxygen atom in OF_4? Is OF_4 likely to exist?

Given: chemical compound

Asked for: hybridization and stability

Strategy:

A Predict the geometry of OF_4 using the VSEPR model.

B From the number of electron pairs around O in OF_4, predict the hybridization of O. Compare the number of hybrid orbitals with the number of electron pairs to decide whether the molecule is likely to exist.

Solution:

A The VSEPR model predicts that OF_4 will have five electron pairs, resulting in a trigonal bipyramidal geometry with four bonding pairs and one lone pair. **B** To accommodate five electron pairs, the O atom would have to be sp^3d hybridized. The only *d* orbital available for forming a set of sp^3d hybrid orbitals is a 3*d* orbital, which is *much* higher in energy than the 2*s* and 2*p* valence orbitals of oxygen. As a result, the OF_4 molecule is unlikely to exist. In fact, it has not been detected.

Exercise

What is the hybridization of the boron atom in BF_6^{3-}? Is this ion likely to exist?

Answer: sp^3d^2 hybridization; no

Summary

The *localized bonding* model (called **valence bond theory**) assumes that covalent bonds are formed when atomic orbitals overlap and that the strength of a covalent bond is proportional to the amount of overlap. It also assumes that atoms use combinations of atomic orbitals (*hybrids*) to maximize the overlap with adjacent atoms. The formation of **hybrid atomic orbitals** can be viewed as

occurring via **promotion** of an electron from a filled ns^2 subshell to an empty np or $(n - 1)d$ valence orbital, followed by **hybridization**, the combination of the orbitals to give a new set of (usually) equivalent orbitals that are oriented properly to form bonds. The combination of an ns and an np orbital gives rise to two equivalent **sp hybrids** oriented at 180°, whereas the combination of an ns and two or three np orbitals produces three equivalent $\boldsymbol{sp^2}$ **hybrids** or four equivalent $\boldsymbol{sp^3}$ **hybrids**, respectively. The bonding in molecules with more than an octet of electrons around a central atom can be explained by invoking the participation of one or two $(n - 1)d$ orbitals to give sets of five sp^3d or six $\boldsymbol{sp^3d^2}$ **hybrid** orbitals, capable of forming five or six bonds, respectively. The spatial orientation of the hybrid atomic orbitals is consistent with the geometries predicted using the VSEPR model.

Key Takeaway

- Hybridization increases the overlap of bonding orbitals and explains the molecular geometries of many species whose geometry cannot be explained using a VSEPR approach.

Conceptual Problems

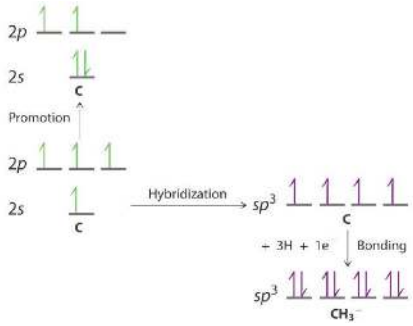
1. Arrange sp, sp^3, and sp^2 in order of increasing strength of the bond formed to a hydrogen atom. Explain your reasoning.
2. What atomic orbitals are combined to form sp^3, sp, sp^3d^2, and sp^3d? What is the maximum number of electron-pair bonds that can be formed using each set of hybrid orbitals?
3. Why is it incorrect to say that an atom with sp^2 hybridization will form only three bonds? The carbon atom in the carbonate anion is sp^2 hybridized. How many bonds to carbon are present in the carbonate ion? Which orbitals on carbon are used to form each bond?
4. If hybridization did not occur, how many bonds would N, O, C, and B form in a neutral molecule, and what would be the approximate molecular geometry?
5. How are hybridization and molecular geometry related? Which has a stronger correlation—molecular geometry and hybridization or Lewis structures and hybridization?
6. In the valence bond approach to bonding in BeF_2, which step(s) require(s) an energy input, and which release(s) energy?
7. The energies of hybrid orbitals are intermediate between the energies of the atomic orbitals from which they are formed. Why?
8. How are lone pairs on the central atom treated using hybrid orbitals?
9. Because nitrogen bonds to only three hydrogen atoms in ammonia, why doesn't the nitrogen atom use sp^2 hybrid orbitals instead of sp^3 hybrids?
10. Using arguments based on orbital hybridization, explain why the CCl_6^{2-} ion does not exist.
11. Species such as NF_5^{2-} and OF_4^{2-} are unknown. If $3d$ atomic orbitals were much lower energy, low enough to be involved in hybrid orbital formation, what effect would this have on the stability of such species? Why? What molecular geometry, electron-pair geometry, and hybridization would be expected for each molecule?

Numerical Problems

1. Draw an energy-level diagram showing promotion and hybridization to describe the bonding in CH_3^-. How does your diagram compare with that for methane? What is the molecular geometry?
2. Draw an energy-level diagram showing promotion and hybridization to describe the bonding in CH_3^+. How does your diagram compare with that for methane? What is the molecular geometry?
3. Draw the molecular structure, including any lone pairs on the central atom, state the hybridization of the central atom, and determine the molecular geometry for each molecule.
    1. BBr_3
    2. PCl_3
    3. NO_3^-

4. Draw the molecular structure, including any lone pairs on the central atom, state the hybridization of the central atom, and determine the molecular geometry for each species.
    1. $AsBr_3$
    2. CF_3^+
    3. H_2O
5. What is the hybridization of the central atom in each of the following?
    1. CF_4
    2. CCl_2^{2-}
    3. IO_3^-
    4. SiH_4
6. What is the hybridization of the central atom in each of the following?
    1. CCl_3^+
    2. CBr_2O
    3. CO_3^{2-}
    4. IBr_2^-
7. What is the hybridization of the central atom in PF_6^-? Is this ion likely to exist? Why or why not? What would be the shape of the molecule?
8. What is the hybridization of the central atom in SF_5^-? Is this ion likely to exist? Why or why not? What would be the shape of the molecule?

Answers

1. 

   The promotion and hybridization process is exactly the same as shown for CH_4 in the chapter. The only difference is that the C atom uses the four singly occupied sp^3 hybrid orbitals to form electron-pair bonds with only *three* H atoms, and an electron is added to the fourth hybrid orbital to give a charge of 1–. The electron-pair geometry is tetrahedral, but the molecular geometry is pyramidal, as in NH_3.

2.

3. 1. 

      sp^2, trigonal planar

   2. 

      sp^3, pyramidal

   3. 

sp^2, trigonal planar

4.

5. The central atoms in CF_4, CCl_2^{2-}, IO_3^-, and SiH_4 are all sp^3 hybridized.

6.

7. The phosphorus atom in the PF_6^- ion is sp^3d^2 hybridized, and the ion is octahedral. The PF_6^- ion is isoelectronic with SF_6 and has essentially the same structure. It should therefore be a stable species.

8.

Contributors

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Chapter 5.3 Delocalized Bonding and Molecular Orbitals

Learning Objective

- To predict the orbital structure of molecules.
- To use molecular orbital theory to predict bond order.

None of the approaches we have described so far can adequately explain why some compounds are colored and others are not, why some substances with unpaired electrons are stable, and why others are effective semiconductors. These approaches also cannot describe the nature of resonance. Such limitations led to the development of a new approach to bonding in which electrons are *not* viewed as being localized between the nuclei of bonded atoms but are instead delocalized throughout the entire molecule. Just as with the valence bond theory, the approach we are about to discuss is based on a quantum mechanical model.

In Chapter 2, we described the electrons in isolated atoms as having certain spatial distributions, called *orbitals*, each with a particular *orbital energy*. Just as the positions and energies of electrons in *atoms* can be described in terms of *atomic orbitals* (AOs), the positions and energies of electrons in *molecules* can be described in terms of molecular orbitals (MOs) A particular spatial distribution of electrons in a molecule that is associated with a particular orbital energy.—a spatial distribution of electrons *in a molecule* that is associated with a particular orbital energy. As the name suggests, molecular orbitals are not localized on a single atom but extend over the entire molecule. Consequently, the molecular orbital approach, called molecular orbital theory A delocalized bonding model in which molecular orbitals are created from the linear combination of atomic orbitals (LCAOs), is a *delocalized* approach to bonding.

Note the Pattern

Molecular orbital theory is a delocalized bonding approach that explains the colors of compounds, their stability, and resonance.

Molecular Orbital Theory: A Delocalized Bonding Approach

Although the molecular orbital theory is computationally demanding, the principles on which it is based are similar to those we used to determine electron configurations for atoms. The key difference is that in molecular orbitals, the electrons are allowed to interact with more than one atomic nucleus at a time. Just as with atomic orbitals, we create an energy-level diagram by listing the molecular orbitals in order of increasing energy. We then fill the orbitals with the required number of valence electrons according to the Pauli principle. This means that each molecular orbital can accommodate a maximum of two electrons with opposite spins.

Molecular Orbitals Involving Only *ns* Atomic Orbitals

We begin our discussion of molecular orbitals with the simplest molecule, H_2, formed from two isolated hydrogen atoms, each with a $1s^1$ electron configuration. As we explained in Chapter 2, electrons can behave like waves. In the molecular orbital approach, the overlapping atomic orbitals are described by mathematical equations called *wave functions*. (For more information on wave functions, see Section 2.2) The 1*s* atomic orbitals on the two hydrogen atoms interact to form two new molecular orbitals, one produced by taking the *sum* of the two H 1*s* wave functions, and the other produced by taking their *difference*:

$$MO(1) = AO(atom\ A) + AO(atom B)$$
$$MO(1) = AO(atom\ A) - AO(atom B)$$

The molecular orbitals created from Equation 5.3.1 are called linear combinations of atomic orbitals (LCAOs) Molecular orbitals created from the sum and the difference of two wave functions (atomic orbitals). A molecule must have as many molecular orbitals as there are atomic orbitals.

Adding two atomic orbitals corresponds to *constructive* interference between two waves, thus reinforcing their intensity; the internuclear electron probability density is *increased*. The molecular orbital corresponding to the sum of the two H 1*s* orbitals is called a σ_{1s} combination (pronounced “sigma one ess”) (part (a) and part (b) in Figure 5.3.1). In a sigma (σ) orbital, A bonding molecular orbital in which the electron density along the internuclear axis and between the nuclei has cylindrical symmetry, the electron density along the internuclear axis and between the nuclei has cylindrical symmetry; that is, all cross-sections perpendicular to the internuclear axis are circles. The subscript 1*s* denotes the atomic orbitals from which the molecular orbital was derived:The ≈ sign is used rather than an = sign because we are ignoring certain constants that are not important to our argument.

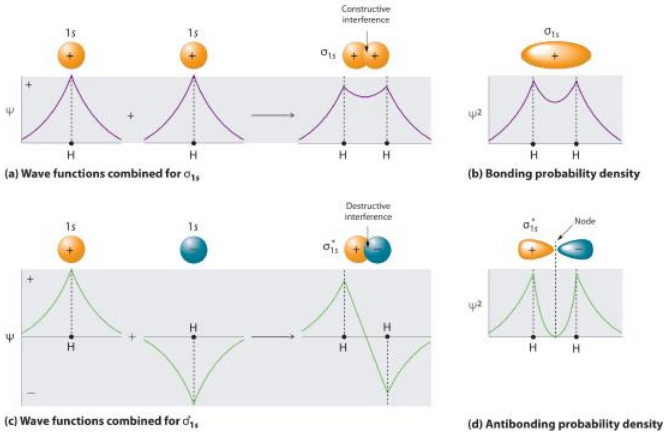


Figure 5.3.1 Molecular Orbitals for the H_2 Molecule *(a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wave functions (Ψ) of two H 1s atomic orbitals. (b) This plot of the square of the wave function (Ψ^2) for the bonding σ_{1s} molecular orbital illustrates the increased electron probability density between the two hydrogen nuclei. (Recall from Chapter 2 that the probability density is proportional to the square of the wave function.) (c) This diagram shows the formation of an antibonding σ^*_{1s} molecular orbital for H_2 as the difference of the wave functions (Ψ) of two H 1s atomic orbitals. (d) This plot of the square of the wave function (Ψ^2) for the σ^*_{1s} antibonding molecular orbital illustrates the node corresponding to zero electron probability density between the two hydrogen nuclei.*

$$\sigma_{1s} \approx 1s\,(A) + 1s\,(B)$$

Conversely, subtracting one atomic orbital from another corresponds to *destructive* interference between two waves, which reduces their intensity and causes a *decrease* in the internuclear electron probability density (part (c) and part (d) in Figure 5.3.1). The resulting pattern contains a *node* where the electron density is zero. The molecular orbital corresponding to the difference is called σ^*_{1s} ("sigma one ess star"). In a sigma star (σ*) orbital An antibonding molecular orbital in which there is a region of zero electron probability (a nodal plane) perpendicular to the internuclear axis., there is a region of zero electron probability, a nodal plane, perpendicular to the internuclear axis:

$$\sigma^*_{1s} \approx 1s\,(A) - 1s\,(B)$$

Note the Pattern

A molecule must have as many molecular orbitals as there are atomic orbitals.

The electron density in the σ_{1s} molecular orbital is greatest between the two positively charged nuclei, and the resulting electron–nucleus electrostatic attractions reduce repulsions between the nuclei. Thus the σ_{1s} orbital represents a bonding molecular orbital. A molecular orbital that forms when atomic orbitals or orbital lobes with the same sign interact to give increased electron probability between the nuclei due to constructive reinforcement of the wave functions. In contrast, electrons in the σ^*_{1s} orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the σ^*_{1s} orbital is an antibonding molecular orbital A molecular orbital that forms when atomic orbitals or orbital lobes of opposite sign interact to give decreased electron probability between the nuclei due to destructuve reinforcement of the wave functions..

Note the Pattern

Antibonding orbitals contain a node perpendicular to the internuclear axis; bonding orbitals do not.

Energy-Level Diagrams

Because electrons in the σ_{1s} orbital interact simultaneously with both nuclei, they have a lower energy than electrons that interact with only one nucleus. This means that the σ_{1s} molecular orbital has a *lower* energy than either of the hydrogen 1*s* atomic orbitals. Conversely, electrons in the σ^*_{1s} orbital interact with only one hydrogen nucleus at a time. In addition, they are farther away from the nucleus than they were in the parent hydrogen 1*s* atomic orbitals. Consequently, the σ^*_{1s} molecular orbital has a *higher* energy than either of the hydrogen 1*s* atomic orbitals. The σ_{1s} (bonding) molecular orbital is *stabilized* relative to the 1*s* atomic orbitals, and the σ^*_{1s} (antibonding) molecular orbital is *destabilized*. The relative energy levels of these orbitals are shown in the energy-level

diagram A schematic drawing that compares the energies of the molecular orbitals (bonding, antibonding, and nonbonding) with the energies of the parent atomic orbitals. in Figure 5.3.2

Note the Pattern

A bonding molecular orbital is *always* lower in energy (more stable) than the component atomic orbitals, whereas an antibonding molecular orbital is *always* higher in energy (less stable).

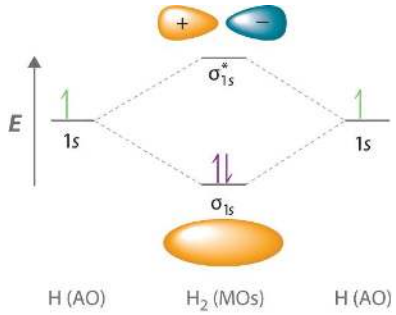


Figure 5.3.2 Molecular Orbital Energy-Level Diagram for H_2 *The two available electrons (one from each H atom) in this diagram fill the bonding σ_{1s} molecular orbital. Because the energy of the σ_{1s} molecular orbital is lower than that of the two H 1s atomic orbitals, the H_2 molecule is more stable (at a lower energy) than the two isolated H atoms.*

To describe the bonding in a homonuclear diatomic molecule A molecule that consists of two atoms of the same element. such as H_2, we use molecular orbitals; that is, for a molecule in which two identical atoms interact, we insert the total number of valence electrons into the energy-level diagram (Figure 5.3.2). We fill the orbitals according to the Pauli principle and Hund's rule: each orbital can accommodate a maximum of two electrons with opposite spins, and the orbitals are filled in order of increasing energy. Because each H atom contributes one valence electron, the resulting two electrons are exactly enough to fill the σ_{1s} bonding molecular orbital. The two electrons enter an orbital whose energy is lower than that of the parent atomic orbitals, so the H_2 molecule is more stable than the two isolated hydrogen atoms. Thus molecular orbital theory correctly predicts that H_2 is a stable molecule. Because bonds form when electrons are concentrated in the space between nuclei, this approach is also consistent with our earlier discussion of electron-pair bonds.

Bond Order in Molecular Orbital Theory

In the Lewis electron structures described in Chapter 4 , the number of electron pairs holding two atoms together was called the *bond order*. In the molecular orbital approach, bond order One-half the net number of bonding electrons in a molecule. is defined as one-half the *net* number of bonding electrons:

$$\textit{bond order} = \frac{\textit{number of bonding electrons} - \textit{number of antibonding electrons}}{2}$$

To calculate the bond order of H_2, we see from Figure 5.3.2 that the σ_{1s} (bonding) molecular orbital contains two electrons, while the σ^*_{1s} (antibonding) molecular orbital is empty. The bond order of H_2 is therefore

$$\frac{2-0}{2} = 1$$

This result corresponds to the single covalent bond predicted by Lewis dot symbols. Thus molecular orbital theory and the Lewis electron-pair approach agree that a single bond containing two electrons has a bond order of 1. Double and triple bonds contain four or six electrons, respectively, and correspond to bond orders of 2 and 3.

We can use energy-level diagrams such as the one in Figure 5.3.2 to describe the bonding in other pairs of atoms and ions where $n = 1$, such as the H_2^+ ion, the He_2^+ ion, and the He_2 molecule. Again, we fill the lowest-energy molecular orbitals first while being sure not to violate the Pauli principle or Hund's rule.

Part (a) in Figure 5.3.3 shows the energy-level diagram for the H_2^+ ion, which contains two protons and only one electron. The single electron occupies the σ_{1s} bonding molecular orbital, giving a $(\sigma_{1s})^1$ electron configuration. The number of electrons in an orbital is indicated by a superscript. In this case, the bond order is (1-0)/2=1/2 Because the bond order is greater than zero, the H_2^+ ion should be more stable than an isolated H atom and a proton. We can therefore use a molecular orbital energy-level diagram and

the calculated bond order to predict the relative stability of species such as H_2^+. With a bond order of only 1/2 the bond in H_2^+ should be weaker than in the H_2 molecule, and the H–H bond should be longer. As shown in Table 5.3.1 , these predictions agree with the experimental data.

Part (b) in Figure 5.3.3 is the molecular orbital energy-level diagram for He_2^+. This ion has a total of three valence electrons. Because the first two electrons completely fill the σ_{1s} molecular orbital, the Pauli principle states that the third electron must be in the σ_{1s}^* antibonding orbital, giving a $(\sigma_{1s})^2(\sigma_{1s}^*)^1$ electron configuration. This electron configuration gives a bond order of (2-1)/2=1/2. As with H_2^+, the He_2^+ ion should be stable, but the He–He bond should be weaker and longer than in H_2. In fact, the He_2^+ ion can be prepared, and its properties are consistent with our predictions (Table 5.1.1).

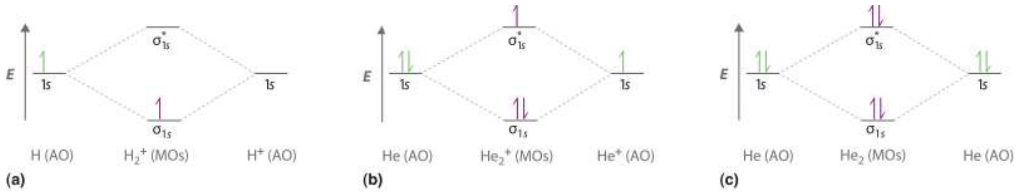


Figure 5.3.3 Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1*s* Atomic Orbitals*(a) The H_2^+ ion, (b) the He_2^+ ion, and (c) the He_2 molecule are shown here.*

Table 5.1.1 Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions

Molecule or Ion	Electron Configuration	Bond Order	Bond Length (pm)	Bond Energy (kJ/mol)
H_2^+	$(\sigma_{1s})^1$	1/2	106	269
H_2	$(\sigma_{1s})^2$	1	74	436
He_2^+	$(\sigma_{1s})^2(\sigma_{1s}^*)^1$	1/2	108	251
He_2	$(\sigma_{1s})^2(\sigma_{1s}^*)^2$	0	not observed	not observed

Finally, we examine the He_2 molecule, formed from two He atoms with $1s^2$ electron configurations. Part (c) in Figure 5.3.3 is the molecular orbital energy-level diagram for He_2. With a total of four valence electrons, both the σ_{1s} bonding and σ_{1s}^* antibonding orbitals must contain two electrons. This gives a $(\sigma_{1s})^2(\sigma_{1s}^*)^1$ electron configuration, with a predicted bond order of $(2 - 2) \div 2 = 0$, which indicates that the He_2 molecule has no net bond and is not a stable species. Experiments show that the He_2 molecule is actually *less* stable than two isolated He atoms due to unfavorable electron–electron and nucleus–nucleus interactions.

In molecular orbital theory, *electrons in antibonding orbitals effectively cancel the stabilization resulting from electrons in bonding orbitals*. Consequently, any system that has equal numbers of bonding and antibonding electrons will have a bond order of 0, and it is predicted to be unstable and therefore not to exist in nature. In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory is able to accommodate systems with an odd number of electrons, such as the H_2^+ ion.

Note the Pattern

In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory can accommodate systems with an odd number of electrons.

Example 5.3.1

Use a molecular orbital energy-level diagram, such as those in Figure 5.3.3 , to predict the bond order in the He_2^{2+} ion. Is this a stable species?

Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and stability

Strategy:

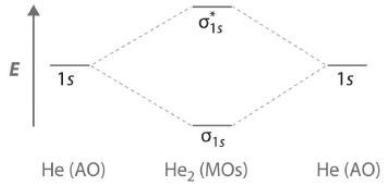
A Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for the system.

B Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.

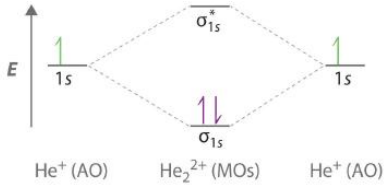
C Calculate the bond order and predict whether the species is stable.

Solution:

A Two He 1*s* atomic orbitals combine to give two molecular orbitals: a σ_{1s} bonding orbital at lower energy than the atomic orbitals and a σ_{1s}^* antibonding orbital at higher energy. The bonding in any diatomic molecule with two He atoms can be described using the following molecular orbital diagram:



B The He_2^{2+} ion has only two valence electrons (two from each He atom minus two for the +2 charge). We can also view He_2^{2+} as being formed from two He^+ ions, each of which has a single valence electron in the 1*s* atomic orbital. We can now fill the molecular orbital diagram:



The two electrons occupy the lowest-energy molecular orbital, which is the bonding (σ_{1s}) orbital, giving a $(\sigma_{1s})^2$ electron configuration. To avoid violating the Pauli principle, the electron spins must be paired. **C** So the bond order is

$$\frac{2-0}{2}=1$$

He_2^{2+} is therefore predicted to contain a single He–He bond. Thus it should be a stable species.

Exercise

Use a molecular orbital energy-level diagram to predict the valence-electron configuration and bond order of the H_2^{2-} ion. Is this a stable species?

Answer: H_2^{2-} has a valence electron configuration of $(\sigma_{1s})^2(\sigma_{1s}^*)^2$ with a bond order of 0. It is therefore predicted to be unstable.

So far, our discussion of molecular orbitals has been confined to the interaction of valence orbitals, which tend to lie farthest from the nucleus. When two atoms are close enough for their valence orbitals to overlap significantly, the filled inner electron shells are largely unperturbed; hence they do not need to be considered in a molecular orbital scheme. Also, when the inner orbitals are completely filled, they contain exactly enough electrons to completely fill both the bonding and antibonding molecular orbitals that arise from their interaction. Thus the interaction of filled shells always gives a bond order of 0, so filled shells are not a factor when predicting the stability of a species. This means that we can focus our attention on the molecular orbitals derived from valence atomic orbitals.

A molecular orbital diagram that can be applied to any **homonuclear diatomic molecule** with two identical alkali metal atoms (Li_2 and Cs_2, for example) is shown in part (a) in Figure 5.3.4, where M represents the metal atom. Only two energy levels are important for describing the valence electron molecular orbitals of these species: a σ_{ns} bonding molecular orbital and a σ^*_{ns} antibonding molecular orbital. Because each alkali metal (M) has an ns^1 valence electron configuration, the M_2 molecule has two valence electrons that fill the σ_{ns} bonding orbital. As a result, a bond order of 1 is predicted for all homonuclear diatomic species formed from the alkali metals (Li_2, Na_2, K_2, Rb_2, and Cs_2). The general features of these M_2 diagrams are identical to the diagram

for the H_2 molecule in Figure 5.3.2. Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.

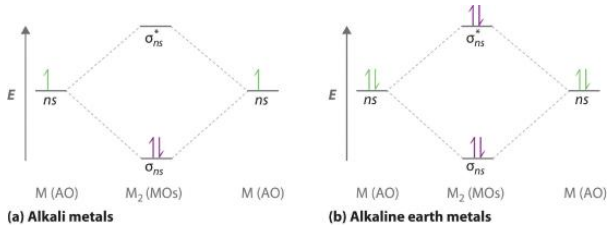


Figure 5.3.4 Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules
(a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σ_{ns} (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic molecules, the four valence electrons fill both the σ_{ns} (bonding) and the σ_{ns} (nonbonding) levels, leading to a predicted bond order of 0.*

Similarly, the molecular orbital diagrams for homonuclear diatomic compounds of the alkaline earth metals (such as Be_2), in which each metal atom has an ns^2 valence electron configuration, resemble the diagram for the He_2 molecule in part (c) in Figure 5.3.3 As shown in part (b) in Figure 5.3.4 , this is indeed the case. All the homonuclear alkaline earth diatomic molecules have four valence electrons, which fill both the σ_{ns} bonding orbital and the σ_{ns}* antibonding orbital and give a bond order of 0. Thus Be_2, Mg_2, Ca_2, Sr_2, and Ba_2 are all expected to be unstable, in agreement with experimental data.In the solid state, however, all the alkali metals and the alkaline earth metals exist as extended lattices held together by metallic bonding. At low temperatures, Be_2 is stable.

Example 5.3.2

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Na_2^- ion.

Given: chemical species

Asked for: molecular orbital energy-level diagram, valence electron configuration, bond order, and stability

Strategy:

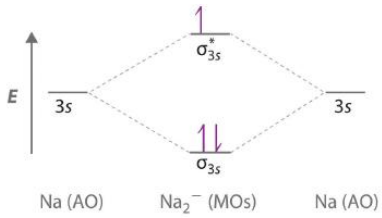
A Combine the two sodium valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for this system.

B Determine the total number of valence electrons in the Na_2^- ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.

C Calculate the bond order and predict whether the species is stable.

Solution:

A Because sodium has a [Ne]$3s^1$ electron configuration, the molecular orbital energy-level diagram is qualitatively identical to the diagram for the interaction of two 1*s* atomic orbitals. **B** The Na_2^- ion has a total of three valence electrons (one from each Na atom and one for the negative charge), resulting in a filled σ_{3s} molecular orbital, a half-filled σ_{3s*} and a $(\sigma_{3s})^2(\sigma^*_{3s})^1$ electron configuration.



C The bond order is (2-1)÷2=1/2 With a fractional bond order, we predict that the Na_2^- ion exists but is highly reactive.

Exercise

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Ca_2^+ ion.

Answer: Ca_2^+ has a $(\sigma_{4s})^2 (\sigma_{4s}^*)^1$ electron configurations and a bond order of 1/2 and should exist.

Molecular Orbitals Formed from *ns* and *np* Atomic Orbitals

Atomic orbitals other than *ns* orbitals can also interact to form molecular orbitals. Because individual *p*, *d*, and *f* orbitals are not spherically symmetrical, however, we need to define a coordinate system so we know which lobes are interacting in three-dimensional space. Recall from Section 2.5 that for each *np* subshell, for example, there are np_x, np_y, and np_z orbitals (Figure 2.5.6). All have the same energy and are therefore degenerate, but they have different spatial orientations.$\sigma_{np_z} = np_z\,(A) - np_z\,(B)$

Just as with *ns* orbitals, we can form molecular orbitals from *np* orbitals by taking their mathematical sum and difference. When two positive lobes with the appropriate spatial orientation overlap, as illustrated for two np_z atomic orbitals in part (a) in Figure 5.3.5, it is the mathematical *difference* of their wave functions that results in *constructive* interference, which in turn increases the electron probability density between the two atoms. The difference therefore corresponds to a molecular orbital called a σ_{np_z} *bonding molecular orbital* because, just as with the σ orbitals discussed previously, it is symmetrical about the internuclear axis (in this case, the *z*-axis):

$$\sigma_{np_z} = np_z\,(A) - np_z\,(B)$$

The other possible combination of the two np_z orbitals is the mathematical sum:

$$\sigma_{np_z} = np_z\,(A) + np_z\,(B)$$

In this combination, shown in part (b) in Figure 5.3.5, the positive lobe of one np_z atomic orbital overlaps the negative lobe of the other, leading to *destructive* interference of the two waves and creating a node between the two atoms. Hence this is an antibonding molecular orbital. Because it, too, is symmetrical about the internuclear axis, this molecular orbital is called a $\sigma_{np_z} = np_z\,(A) - np_z\,(B)$ *antibonding molecular orbital*. Whenever orbitals combine, *the bonding combination is always lower in energy* (more stable) than the atomic orbitals from which it was derived, and *the antibonding combination is higher in energy* (less stable).

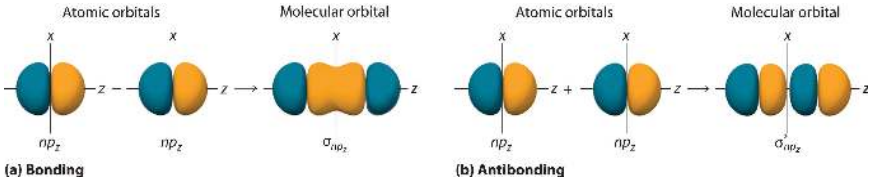


Figure 5.3.5 Formation of Molecular Orbitals from np_z Atomic Orbitals on Adjacent Atoms *(a) By convention, in a linear molecule or ion, the z-axis always corresponds to the internuclear axis, with +z to the right. As a result, the signs of the lobes of the np_z atomic orbitals on the two atoms alternate − + − +, from left to right. In this case, the σ (bonding) molecular orbital corresponds to the mathematical difference, in which the overlap of lobes with the same sign results in increased probability density between the nuclei. (b) In contrast, the σ* (antibonding) molecular orbital corresponds to the mathematical sum, in which the overlap of lobes with opposite signs results in a nodal plane of zero probability density perpendicular to the internuclear axis.*

Note the Pattern

Overlap of atomic orbital lobes with the *same sign* produces a bonding molecular orbital, regardless of whether it corresponds to the sum or the difference of the atomic orbitals.

The remaining *p* orbitals on each of the two atoms, np_x and np_y, do not point directly toward each other. Instead, they are perpendicular to the internuclear axis. If we arbitrarily label the axes as shown in Figure 5.3.6, we see that we have two pairs of *np* orbitals: the two np_x orbitals lying in the plane of the page, and two np_y orbitals perpendicular to the plane. Although these two pairs are equivalent in energy, the np_x orbital on one atom can interact with only the np_x orbital on the other, and the np_y orbital on one atom can interact with only the np_y on the other. These interactions are side-to-side rather than the head-to-head interactions characteristic of σ orbitals. Each pair of overlapping atomic orbitals again forms two molecular orbitals: one corresponds to the arithmetic sum of the two atomic orbitals and one to the difference. The sum of these side-to-side interactions increases the electron probability in the region above and below a line connecting the nuclei, so it is a bonding molecular orbital that is called a pi (π) orbitalA bonding molecular orbital formed from the side-to-side interactions of two or more parallel np atomic orbitals.. The

difference results in the overlap of orbital lobes with opposite signs, which produces a nodal plane perpendicular to the internuclear axis; hence it is an antibonding molecular orbital, called a pi star (π*) orbital An antibonding molecular orbital formed from the difference of the side-to-side interactions of two or more parallel *np* atomic orbitals, creating a nodal plane perpendicular to the internuclear axis..

$$\pi_{np_z} = np_x\,(A) + np_x\,(B)$$

$$\pi^{\star}_{np_z} = np_x\,(A) - np_x\,(B)$$

The two np_y orbitals can also combine using side-to-side interactions to produce a bonding π_{np_y} molecular orbital and an antibonding $\pi^{\star}_{np_y}$ molecular orbital. Because the np_x and np_y atomic orbitals interact in the same way (side-to-side) and have the same energy, the π_{np_z} and π_{np_y}molecular orbitals are a degenerate pair, as are the $\pi^{\star}_{np_z}$ and $\pi^{\star}_{np_y}$ molecular orbitals.

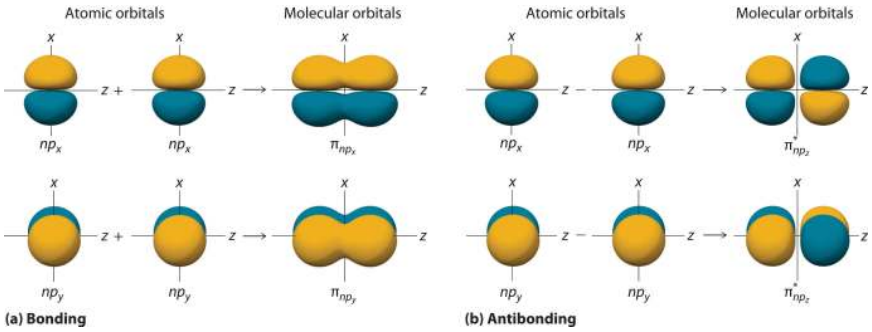


Figure 5.3.6 Formation of π Molecular Orbitals from np_x and np_y Atomic Orbitals on Adjacent Atoms*(a) Because the signs of the lobes of both the np_x and the np_y atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) In contrast, in both cases, the mathematical difference corresponds to a π* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.*

Figure 5.3.7 is an energy-level diagram that can be applied to two identical interacting atoms that have three *np* atomic orbitals each. There are six degenerate *p* atomic orbitals (three from each atom) that combine to form six molecular orbitals, three bonding and three antibonding. The bonding molecular orbitals are lower in energy than the atomic orbitals because of the increased stability associated with the formation of a bond. Conversely, the antibonding molecular orbitals are higher in energy, as shown. The energy difference between the σ and σ* molecular orbitals is significantly greater than the difference between the two π and π* sets. The reason for this is that the atomic orbital overlap and thus the strength of the interaction are greater for a σ bond than a π bond, which means that the σ molecular orbital is more stable (lower in energy) than the π molecular orbitals.

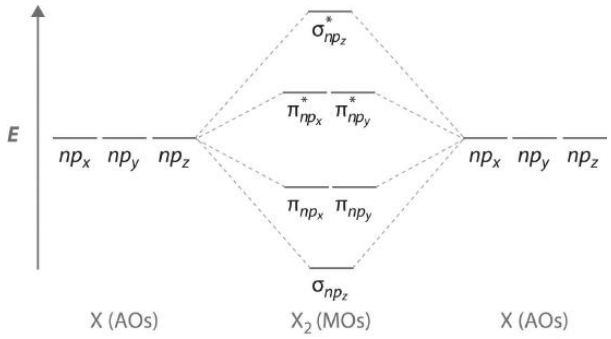


Figure 5.3.7 The Relative Energies of the σ and π Molecular Orbitals Derived from np_x, np_y, and np_z Orbitals on Identical Adjacent Atoms *Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals is greater than the energy difference between the π and π* orbitals.*

Although many combinations of atomic orbitals form molecular orbitals, we will discuss only one other interaction: an *ns* atomic orbital on one atom with an np_z atomic orbital on another. As shown in Figure 5.3.8 , the sum of the two atomic wave functions ($ns + np_z$) produces a σ bonding molecular orbital. Their difference ($ns - np_z$) produces a σ* antibonding molecular orbital, which has a nodal plane of zero probability density perpendicular to the internuclear axis.

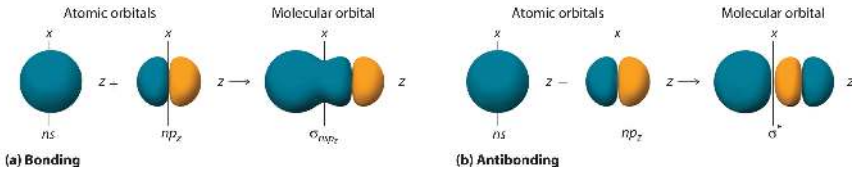


Figure 5.3.8 Formation of Molecular Orbitals from an *ns* Atomic Orbital on One Atom and an np_z Atomic Orbital on an Adjacent Atom *(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.*

Molecular Orbital Diagrams for Period 2 Homonuclear Diatomic Molecules

We now describe examples of systems involving period 2 homonuclear diatomic molecules, such as N_2, O_2, and F_2. When we draw a molecular orbital diagram for a molecule, there are four key points to remember:

1. The number of molecular orbitals produced is the same as the number of atomic orbitals used to create them (the law of conservation of orbitals A law that states that the number of molecular orbitals produced is the same as the number of atomic orbitals used to create them.).
2. As the overlap between two atomic orbitals increases, the difference in energy between the resulting bonding and antibonding molecular orbitals increases.
3. When two atomic orbitals combine to form a pair of molecular orbitals, the bonding molecular orbital is stabilized about as much as the antibonding molecular orbital is destabilized.
4. The interaction between atomic orbitals is greatest when they have the same energy.

Note the Pattern

The number of molecular orbitals is always equal to the total number of atomic orbitals we started with.

We illustrate how to use these points by constructing a molecular orbital energy-level diagram for F_2. We use the diagram in part (a) in Figure 5.3.9 ; the $n = 1$ orbitals (σ_{1s} and σ_{1s}*) are located well below those of the $n = 2$ level and are not shown. As illustrated in the diagram, the σ_{2s} and σ_{2s}* molecular orbitals are much lower in energy than the molecular orbitals derived from the 2*p* atomic orbitals because of the large difference in energy between the 2*s* and 2*p* atomic orbitals of fluorine. The lowest-energy molecular orbital derived from the three 2*p* orbitals on each F is σ_{2p_z} and the next most stable are the two degenerate orbitals, π_{2p_x} and π_{2p_y}. For each bonding orbital in the diagram, there is an antibonding orbital, and the antibonding orbital is destabilized by about as much as the corresponding bonding orbital is stabilized. As a result, the $\sigma^*_{2p_z}$ orbital is higher in energy than either of the degenerate $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ orbitals. We can now fill the orbitals, beginning with the one that is lowest in energy.

Each fluorine has 7 valence electrons, so there are a total of 14 valence electrons in the F_2 molecule. Starting at the lowest energy level, the electrons are placed in the orbitals according to the Pauli principle and Hund's rule. Two electrons each fill the σ_{2s} and σ_{2s}* orbitals, 2 fill the σ_{2p_z} orbital, 4 fill the two degenerate π orbitals, and 4 fill the two degenerate π^* orbitals, for a total of 14 electrons. To determine what type of bonding the molecular orbital approach predicts F_2 to have, we must calculate the bond order. According to our diagram, there are 8 bonding electrons and 6 antibonding electrons, giving a bond order of $(8 - 6) \div 2 = 1$. Thus F_2 is predicted to have a stable F–F single bond, in agreement with experimental data.

We now turn to a molecular orbital description of the bonding in O_2. It so happens that the molecular orbital description of this molecule provided an explanation for a long-standing puzzle that could not be explained using other bonding models. To obtain the molecular orbital energy-level diagram for O_2, we need to place 12 valence electrons (6 from each O atom) in the energy-level diagram shown in part (b) in Figure 5.3.9. We again fill the orbitals according to Hund's rule and the Pauli principle, beginning with the orbital that is lowest in energy. Two electrons each are needed to fill the σ_{2s} and σ_{2s}* orbitals, 2 more to fill the σ_{2p_z} orbital, and 4 to fill the degenerate $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ orbitals. According to Hund's rule, the last 2 electrons must be placed in separate π^* orbitals with their spins parallel, giving two unpaired electrons. This leads to a predicted bond order of $(8 - 4) \div 2 = 2$, which corresponds to a double bond, in agreement with experimental data (Table 4.5): the O–O bond length is 120.7 pm, and the bond energy is 498.4 kJ/mol at 298 K.

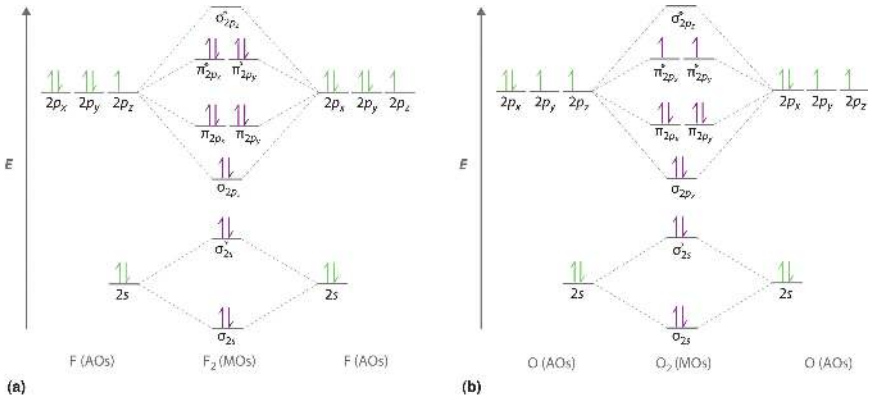


Figure 5.3.9 Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules *(a) For F_2, with 14 valence electrons (7 from each F atom), all of the energy levels except the highest, $\sigma^*_{2p_z}$ are filled. This diagram shows 8 electrons in bonding orbitals and 6 in antibonding orbitals, resulting in a bond order of 1. (b) For O_2, with 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $\left(\pi^*_{np_z}, \pi^*_{np_y}\right)$ pair of orbitals. Hund's rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O_2 molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2.*

None of the other bonding models can predict the presence of two unpaired electrons in O_2. Chemists had long wondered why, unlike most other substances, liquid O_2 is attracted into a magnetic field. As shown in Figure 5.3.10 , it actually remains suspended between the poles of a magnet until the liquid boils away. The only way to explain this behavior was for O_2 to have unpaired electrons, making it paramagnetic, exactly as predicted by molecular orbital theory. This result was one of the earliest triumphs of molecular orbital theory over the other bonding approaches we have discussed.



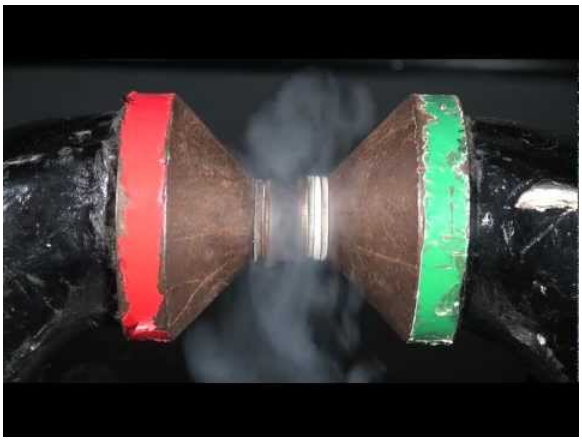
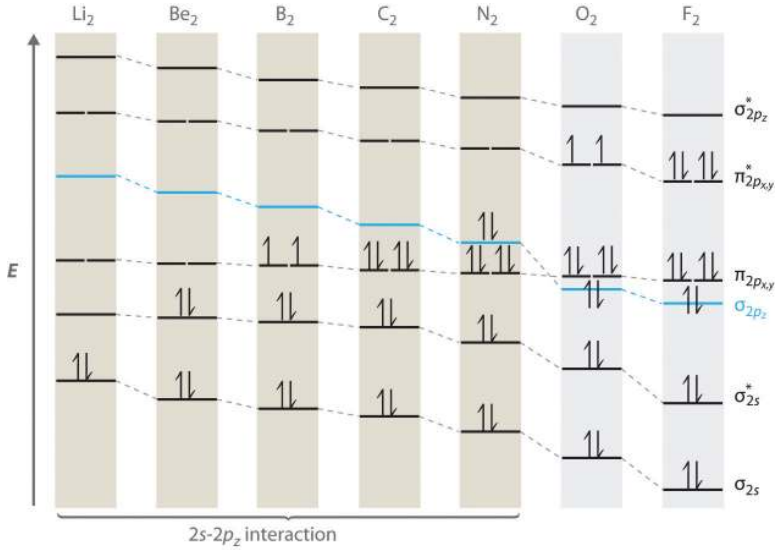


Figure 5.3.10 Liquid O_2 Suspended between the Poles of a Magnet

Because the O_2 molecule has two unpaired electrons, it is paramagnetic. Consequently, it is attracted into a magnetic field, which allows it to remain suspended between the poles of a powerful magnet until it evaporates.

The magnetic properties of O_2 are not just a laboratory curiosity; they are absolutely crucial to the existence of life. Because Earth's atmosphere contains 20% oxygen, all organic compounds, including those that compose our body tissues, should react rapidly with air to form H_2O, CO_2, and N_2 in an exothermic reaction. Fortunately for us, however, this reaction is very, very slow. The reason for the unexpected stability of organic compounds in an oxygen atmosphere is that virtually all organic compounds, as well as H_2O, CO_2, and N_2, have only paired electrons, whereas oxygen has two unpaired electrons. Thus the reaction of O_2 with organic compounds to give H_2O, CO_2, and N_2 would require that at least one of the electrons on O_2 change its spin during the reaction. This would require a large input of energy, an obstacle that chemists call a *spin barrier*. Consequently, reactions of this type are usually exceedingly slow. If they were not so slow, all organic substances, including this book and you, would disappear in a puff of smoke!

For period 2 diatomic molecules to the left of N_2 in the periodic table, a slightly different molecular orbital energy-level diagram is needed because the σ_{2p_z} molecular orbital is slightly *higher* in energy than the degenerate $\pi^*_{np_x}$ and $\pi^*_{np_y}$ orbitals. The difference in energy between the 2*s* and 2*p* atomic orbitals increases from Li_2 to F_2 due to increasing nuclear charge and poor screening of the 2*s* electrons by electrons in the 2*p* subshell. The bonding interaction between the 2*s* orbital on one atom and the 2*pz* orbital on the other is most important when the two orbitals have similar energies. This interaction decreases the energy of the σ_{2s} orbital and increases the energy of the σ_{2p_z} orbital. Thus for Li_2, Be_2, B_2, C_2, and N_2, the σ_{2p_z} orbital is higher in energy than the σ_{3p_z} orbitals, as shown in Figure 5.3.11 Experimentally, it is found that the energy gap between the *ns* and *np* atomic orbitals *increases* as the nuclear charge increases (Figure 5.3.11). Thus for example, the σ_{2p_z} molecular orbital is at a lower energy than the $\pi_{2p_{x,y}}$ pair.



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Figure 5.3.11 Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements *Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component atoms have been omitted. For Li_2 through N_2, the σ_{2p_z} orbital is higher in energy than the $\pi_{2p_{x,y}}$ orbitals. In contrast, the σ_{2p_z} orbital is lower in energy than the $\pi_{2p_{x,y}}$ orbitals for O_2 and F_2 due to the increase in the energy difference between the 2s and 2p atomic orbitals as the nuclear charge increases across the row.*

Completing the diagram for N_2 in the same manner as demonstrated previously, we find that the 10 valence electrons result in 8 bonding electrons and 2 antibonding electrons, for a predicted bond order of 3, a triple bond. Experimental data show that the N–N bond is significantly shorter than the F–F bond (109.8 pm in N_2 versus 141.2 pm in F_2), and the bond energy is much greater for N_2 than for F_2 (945.3 kJ/mol versus 158.8 kJ/mol, respectively). Thus the N_2 bond is much shorter and stronger than the F_2 bond, consistent with what we would expect when comparing a triple bond with a single bond.

Example 5.3.3

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in S_2, a bright blue gas at high temperatures.

Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and number of unpaired electrons

Strategy:

A Write the valence electron configuration of sulfur and determine the type of molecular orbitals formed in S_2. Predict the relative energies of the molecular orbitals based on how close in energy the valence atomic orbitals are to one another.

B Draw the molecular orbital energy-level diagram for this system and determine the total number of valence electrons in S_2.

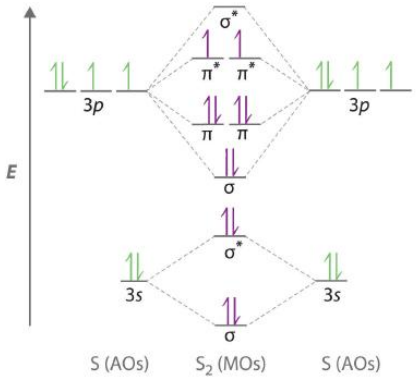
C Fill the molecular orbitals in order of increasing energy, being sure to obey the Pauli principle and Hund's rule.

D Calculate the bond order and describe the bonding.

Solution:

A Sulfur has a $[Ne]3s^23p^4$ valence electron configuration. To create a molecular orbital energy-level diagram similar to those in Figure 5.3.9 and Figure 5.3.11 , we need to know how close in energy the 3*s* and 3*p* atomic orbitals are because their energy separation will determine whether the $\pi_{3p_{x,y}}$ or the σ_{3p_z}> molecular orbital is higher in energy. Because the *ns*–*np* energy gap *increases* as the nuclear charge increases (Figure 5.3.11), the σ_{3p_z} molecular orbital will be lower in energy than the $\pi_{3p_{x,y}}$ pair.

B The molecular orbital energy-level diagram is as follows:



Each sulfur atom contributes 6 valence electrons, for a total of 12 valence electrons.

C Ten valence electrons are used to fill the orbitals through π_{3p_x} and π_{3p_y}, leaving 2 electrons to occupy the degenerate $\pi^*_{3p_x}$ and $\pi^*_{3p_y}$ pair. From Hund's rule, the remaining 2 electrons must occupy these orbitals separately with their spins aligned. With the numbers of electrons written as superscripts, the electron configuration of S_2 is $(\sigma_{3s})^2(\sigma^*_{3s})^2(\sigma_{3p_z})^2(\pi_{3p_{x,y}})^4(\pi^*_{3p_{x,y}})^2$ with 2 unpaired electrons. The bond order is $(8 - 4) \div 2 = 2$, so we predict an S=S double bond.

Exercise

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in the peroxide ion (O_2^{2-}).

Answer: $(\sigma_{2s})^2 (\sigma^*_{2s})^2 (\sigma_{2p_z})^2 (\pi_{2p_{x,y}})^4 (\pi^*_{2p_{x,y}})^4$ bond order of 1; no unpaired electrons

Molecular Orbitals for Heteronuclear Diatomic Molecules

Diatomic molecules with two different atoms are called heteronuclear diatomic molecules A molecule that consists of two atoms of different elements.. When two nonidentical atoms interact to form a chemical bond, the interacting atomic orbitals do not have the same energy. If, for example, element B is more electronegative than element A ($\chi_B > \chi_A$), the net result is a "skewed" molecular orbital energy-level diagram, such as the one shown for a hypothetical A–B molecule in Figure 5.3.12 . The atomic orbitals of element B are uniformly lower in energy than the corresponding atomic orbitals of element A because of the enhanced stability of the electrons in element B. The molecular orbitals are no longer symmetrical, and the energies of the bonding molecular orbitals are more similar to those of the atomic orbitals of B. Hence the electron density of bonding electrons is likely to be closer to the more electronegative atom. In this way, molecular orbital theory can describe a polar covalent bond.

Figure 5.3.12 Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$

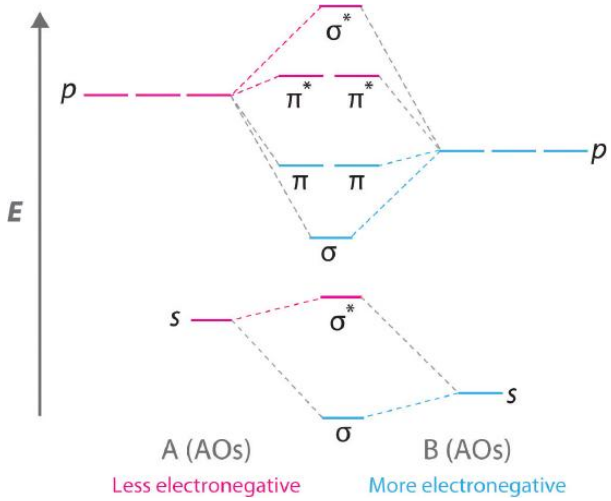


Figure 5.3.12 Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$ *The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. On average, they are closer to the B atom, resulting in a polar covalent bond.*

Note the Pattern

A molecular orbital energy-level diagram is always skewed toward the more electronegative atom.

An Odd Number of Valence Electrons: NO

Nitric oxide (NO) is an example of a heteronuclear diatomic molecule. The reaction of O_2 with N_2 at high temperatures in internal combustion engines forms nitric oxide, which undergoes a complex reaction with O_2 to produce NO_2, which in turn is responsible for the brown color we associate with air pollution. Recently, however, nitric oxide has also been recognized to be a vital biological messenger involved in regulating blood pressure and long-term memory in mammals.

Because NO has an odd number of valence electrons (5 from nitrogen and 6 from oxygen, for a total of 11), its bonding and properties cannot be successfully explained by either the Lewis electron-pair approach or valence bond theory. The molecular orbital energy-level diagram for NO (Figure 5.3.13) shows that the general pattern is similar to that for the O_2 molecule (see Figure 5.3.11). Because 10 electrons are sufficient to fill all the bonding molecular orbitals derived from 2*p* atomic orbitals, the 11th electron must occupy one of the degenerate π^* orbitals. The predicted bond order for NO is therefore (8-3) ÷ 2 = 2 1/2 . Experimental data, showing an N–O bond length of 115 pm and N–O bond energy of 631 kJ/mol, are consistent with this description. These values lie between those of the N_2 and O_2 molecules, which have triple and double bonds, respectively. As we

stated earlier, molecular orbital theory can therefore explain the bonding in molecules with an odd number of electrons, such as NO, whereas Lewis electron structures cannot.

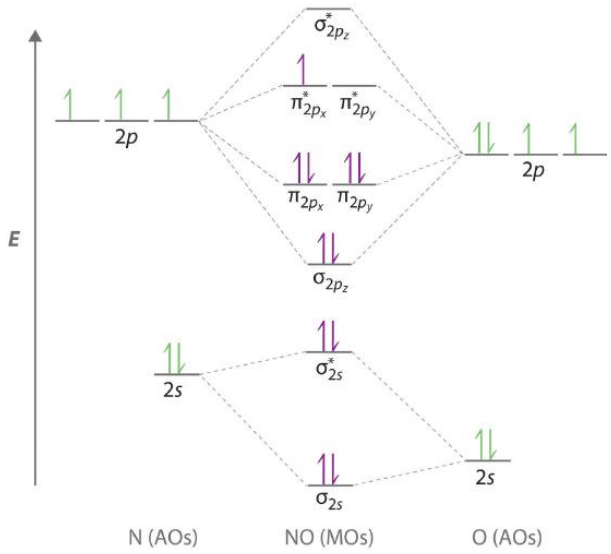


Figure 5.3.13 Molecular Orbital Energy-Level Diagram for NO*Because NO has 11 valence electrons, it is paramagnetic, with a single electron occupying the* $\left(\pi^*_{2p_z}, \pi^*_{2p_y}\right)$ *pair of orbitals.*

Molecular orbital theory can also tell us something about the *chemistry* of NO. As indicated in the energy-level diagram in Figure 5.3.13 , NO has a single electron in a relatively high-energy molecular orbital. We might therefore expect it to have similar reactivity as alkali metals such as Li and Na with their single valence electrons. In fact, NO is easily oxidized to the NO^+ cation, which is isoelectronic with N_2 and has a bond order of 3, corresponding to an N≡O triple bond.

Nonbonding Molecular Orbitals

Molecular orbital theory is also able to explain the presence of lone pairs of electrons. Consider, for example, the HCl molecule, whose Lewis electron structure has three lone pairs of electrons on the chlorine atom. Using the molecular orbital approach to describe the bonding in HCl, we can see from Figure 5.3.14 that the 1*s* orbital of atomic hydrogen is closest in energy to the 3*p* orbitals of chlorine. Consequently, the filled Cl 3*s* atomic orbital is not involved in bonding to any appreciable extent, and the only important interactions are those between the H 1*s* and Cl 3*p* orbitals. Of the three *p* orbitals, only one, designated as $3p_z$, can interact with the H 1*s* orbital. The $3p_x$ and $3p_y$ atomic orbitals have no net overlap with the 1*s* orbital on hydrogen, so they are not involved in bonding. Because the energies of the Cl 3*s*, $3p_x$, and $3p_y$ orbitals do not change when HCl forms, they are called nonbonding molecular orbitals A molecular orbital that forms when atomic orbitals or orbital lobes interact only very weakly, creating essentially no change in the electron probability density between the nuclei.. A nonbonding molecular orbital occupied by a pair of electrons is the molecular orbital equivalent of a lone pair of electrons. By definition, electrons in nonbonding orbitals have no effect on bond order, so they are not counted in the calculation of bond order. Thus the predicted bond order of HCl is (2 − 0) ÷ 2 = 1. Because the σ bonding molecular orbital is closer in energy to the Cl $3p_z$ than to the H 1*s* atomic orbital, the electrons in the σ orbital are concentrated closer to the chlorine atom than to hydrogen. A molecular orbital approach to bonding can therefore be used to describe the polarization of the H–Cl bond to give $H^{\delta+}-\!-Cl^{\delta-}$ as described in Chapter 4.1

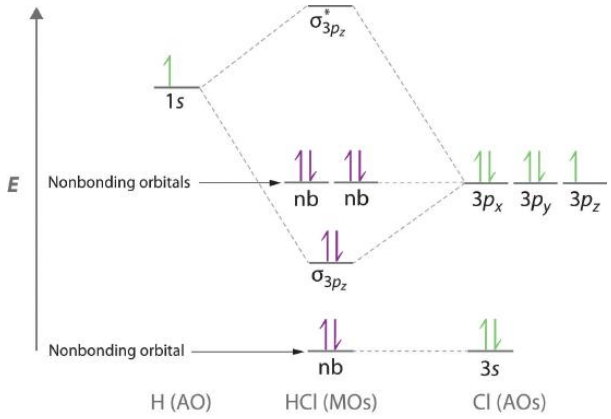


Figure 5.3.14 Molecular Orbital Energy-Level Diagram for HCl *The hydrogen 1s atomic orbital interacts most strongly with the $3p_z$ orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.*

Note the Pattern

Electrons in nonbonding molecular orbitals have no effect on bond order.

Example 5.3.4

Use a "skewed" molecular orbital energy-level diagram like the one in Figure 5.3.12 to describe the bonding in the cyanide ion (CN^-). What is the bond order?

Given: chemical species

Asked for: "skewed" molecular orbital energy-level diagram, bonding description, and bond order

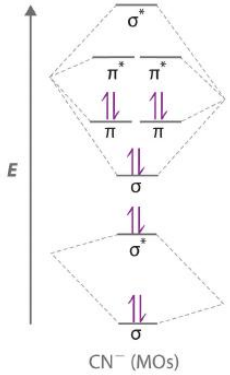
Strategy:

A Calculate the total number of valence electrons in CN^-. Then place these electrons in a molecular orbital energy-level diagram like Figure 5.3.12 in order of increasing energy. Be sure to obey the Pauli principle and Hund's rule while doing so.

B Calculate the bond order and describe the bonding in CN^-.

Solution:

A The CN^- ion has a total of 10 valence electrons: 4 from C, 5 from N, and 1 for the −1 charge. Placing these electrons in an energy-level diagram like Figure 5.3.12 fills the five lowest-energy orbitals, as shown here:



Because $\chi_N > \chi_C$, the atomic orbitals of N (on the right) are lower in energy than those of C. **B** The resulting valence electron configuration gives a predicted bond order of $(8 - 2) \div 2 = 3$, indicating that the CN^- ion has a triple bond, analogous to that in N_2.

Exercise

Use a qualitative molecular orbital energy-level diagram to describe the bonding in the hypochlorite ion (OCl^-). What is the bond order?

Answer: All molecular orbitals except the highest-energy σ* are filled, giving a bond order of 1.

Although the molecular orbital approach reveals a great deal about the bonding in a given molecule, the procedure quickly becomes computationally intensive for molecules of even moderate complexity. Furthermore, because the computed molecular orbitals extend over the entire molecule, they are often difficult to represent in a way that is easy to visualize. Therefore we do not use a pure molecular orbital approach to describe the bonding in molecules or ions with more than two atoms. Instead, we use a valence bond approach and a molecular orbital approach to explain, among other things, the concept of resonance, which cannot adequately be explained using other methods.

Summary

A **molecular orbital (MO)** is an allowed spatial distribution of electrons in a molecule that is associated with a particular orbital energy. Unlike an atomic orbital (AO), which is centered on a single atom, a molecular orbital extends over all the atoms in a molecule or ion. Hence the **molecular orbital theory** of bonding is a *delocalized* approach. Molecular orbitals are constructed using **linear combinations of atomic orbitals (LCAOs)**, which are usually the mathematical sums and differences of wave functions that describe overlapping atomic orbitals. Atomic orbitals interact to form three types of molecular orbitals.

1. Orbitals or orbital lobes with the same sign interact to give increased electron probability along the plane of the internuclear axis because of *constructive* reinforcement of the wave functions. Consequently, electrons in such molecular orbitals help to hold the positively charged nuclei together. Such orbitals are **bonding molecular orbitals**, and they are always lower in energy than the parent atomic orbitals.
2. Orbitals or orbital lobes with opposite signs interact to give decreased electron probability density between the nuclei because of *destructive* interference of the wave functions. Consequently, electrons in such molecular orbitals are primarily located outside the internuclear region, leading to increased repulsions between the positively charged nuclei. These orbitals are called **antibonding molecular orbitals**, and they are always higher in energy than the parent atomic orbitals.
3. Some atomic orbitals interact only very weakly, and the resulting molecular orbitals give essentially no change in the electron probability density between the nuclei. Hence electrons in such orbitals have no effect on the bonding in a molecule or ion. These orbitals are **nonbonding molecular orbitals**, and they have approximately the same energy as the parent atomic orbitals.

A completely bonding molecular orbital contains no nodes (regions of zero electron probability) perpendicular to the internuclear axis, whereas a completely **antibonding molecular orbital** contains at least one node perpendicular to the internuclear axis. A **sigma (σ) orbital** (bonding) or a **sigma star (σ*) orbital** (antibonding) is symmetrical about the internuclear axis. Hence all cross-sections perpendicular to that axis are circular. Both a **pi (π) orbital** (bonding) and a **pi star (π*) orbital** (antibonding) possess a nodal plane that contains the nuclei, with electron density localized on both sides of the plane.

The energies of the molecular orbitals versus those of the parent atomic orbitals can be shown schematically in an **energy-level diagram**. The electron configuration of a molecule is shown by placing the correct number of electrons in the appropriate energy-level diagram, starting with the lowest-energy orbital and obeying the Pauli principle; that is, placing only two electrons with opposite spin in each orbital. From the completed energy-level diagram, we can calculate the **bond order**, defined as one-half the net number of bonding electrons. In bond orders, electrons in antibonding molecular orbitals cancel electrons in bonding molecular orbitals, while electrons in nonbonding orbitals have no effect and are not counted. Bond orders of 1, 2, and 3 correspond to single, double, and triple bonds, respectively. Molecules with predicted bond orders of 0 are generally less stable than the isolated atoms and do not normally exist.

Molecular orbital energy-level diagrams for diatomic molecules can be created if the electron configuration of the parent atoms is known, following a few simple rules. Most important, the number of molecular orbitals in a molecule is the same as the number of atomic orbitals that interact. The difference between bonding and antibonding molecular orbital combinations is proportional to the overlap of the parent orbitals and decreases as the energy difference between the parent atomic orbitals increases. With such an approach, the electronic structures of virtually all commonly encountered **homonuclear diatomic molecules**, molecules with two identical atoms, can be understood. The molecular orbital approach correctly predicts that the O_2 molecule has two unpaired electrons and hence is attracted into a magnetic field. In contrast, most substances have only paired electrons. A similar procedure can be applied to molecules with two dissimilar atoms, called **heteronuclear diatomic molecules**, using a molecular orbital

energy-level diagram that is skewed or tilted toward the more electronegative element. Molecular orbital theory is able to describe the bonding in a molecule with an odd number of electrons such as NO and even to predict something about its chemistry.

Key Takeaway

- Molecular orbital theory, a delocalized approach to bonding, can often explain a compound's color, why a compound with unpaired electrons is stable, semiconductor behavior, and resonance, none of which can be explained using a localized approach.

Conceptual Problems

1. What is the distinction between an atomic orbital and a molecular orbital? How many electrons can a molecular orbital accommodate?
2. Why is the molecular orbital approach to bonding called a *delocalized* approach?
3. How is the energy of an electron affected by interacting with more than one positively charged atomic nucleus at a time? Does the energy of the system increase, decrease, or remain unchanged? Why?
4. Constructive and destructive interference of waves can be used to understand how bonding and antibonding molecular orbitals are formed from atomic orbitals. Does constructive interference of waves result in increased or decreased electron probability density between the nuclei? Is the result of constructive interference best described as a bonding molecular orbital or an antibonding molecular orbital?
5. What is a "node" in molecular orbital theory? How is it similar to the nodes found in atomic orbitals?
6. What is the difference between an *s* orbital and a σ orbital? How are the two similar?
7. Why is a σ_{1s} molecular orbital lower in energy than the two *s* atomic orbitals from which it is derived? Why is a σ^*_{1s} molecular orbital higher in energy than the two *s* atomic orbitals from which it is derived?
8. What is meant by the term *bond order* in molecular orbital theory? How is the bond order determined from molecular orbital theory different from the bond order obtained using Lewis electron structures? How is it similar?
9. What is the effect of placing an electron in an antibonding orbital on the bond order, the stability of the molecule, and the reactivity of a molecule?
10. How can the molecular orbital approach to bonding be used to predict a molecule's stability? What advantages does this method have over the Lewis electron-pair approach to bonding?
11. What is the relationship between bond length and bond order? What effect do antibonding electrons have on bond length? on bond strength?
12. Draw a diagram that illustrates how atomic *p* orbitals can form both σ and π molecular orbitals. Which type of molecular orbital typically results in a stronger bond?
13. What is the minimum number of nodes in σ, π, σ*, and π*? How are the nodes in bonding orbitals different from the nodes in antibonding orbitals?
14. It is possible to form both σ and π molecular orbitals with the overlap of a *d* orbital with a *p* orbital, yet it is possible to form only σ molecular orbitals between *s* and *d* orbitals. Illustrate why this is so with a diagram showing the three types of overlap between this set of orbitals. Include a fourth image that shows why *s* and *d* orbitals cannot combine to form a π molecular orbital.
15. Is it possible for an np_x orbital on one atom to interact with an np_y orbital on another atom to produce molecular orbitals? Why or why not? Can the same be said of np_y and np_z orbitals on adjacent atoms?
16. What is meant by *degenerate orbitals* in molecular orbital theory? Is it possible for σ molecular orbitals to form a degenerate pair? Explain your answer.
17. Why are bonding molecular orbitals lower in energy than the parent atomic orbitals? Why are antibonding molecular orbitals higher in energy than the parent atomic orbitals?

18. What is meant by the *law of conservation of orbitals*?
19. Atomic orbitals on different atoms have different energies. When atomic orbitals from nonidentical atoms are combined to form molecular orbitals, what is the effect of this difference in energy on the resulting molecular orbitals?
20. If two atomic orbitals have different energies, how does this affect the orbital overlap and the molecular orbitals formed by combining the atomic orbitals?
21. Are the Al–Cl bonds in $AlCl_3$ stronger, the same strength, or weaker than the Al–Br bonds in $AlBr_3$? Why?
22. Are the Ga–Cl bonds in $GaCl_3$ stronger, the same strength, or weaker than the Sb–Cl bonds in $SbCl_3$? Why?
23. What is meant by a *nonbonding* molecular orbital, and how is it formed? How does the energy of a nonbonding orbital compare with the energy of bonding or antibonding molecular orbitals derived from the same atomic orbitals?
24. Many features of molecular orbital theory have analogs in Lewis electron structures. How do Lewis electron structures represent
    1. nonbonding electrons?
    2. electrons in bonding molecular orbitals?
25. How does electron screening affect the energy difference between the 2*s* and 2*p* atomic orbitals of the period 2 elements? How does the energy difference between the 2*s* and 2*p* atomic orbitals depend on the effective nuclear charge?
26. For σ versus π, π versus σ*, and σ* versus π*, which of the resulting molecular orbitals is lower in energy?
27. The energy of a σ molecular orbital is usually lower than the energy of a π molecular orbital derived from the same set of atomic orbitals. Under specific conditions, however, the order can be reversed. What causes this reversal? In which portion of the periodic table is this kind of orbital energy reversal most likely to be observed?
28. Is the σ_{2p_z} molecular orbital stabilized or destabilized by interaction with the σ_{2s} molecular orbital in N_2? in O_2? In which molecule is this interaction most important?
29. Explain how the Lewis electron-pair approach and molecular orbital theory differ in their treatment of bonding in O_2.
30. Why is it crucial to our existence that O_2 is paramagnetic?
31. Will NO or CO react more quickly with O_2? Explain your answer.
32. How is the energy-level diagram of a heteronuclear diatomic molecule, such as CO, different from that of a homonuclear diatomic molecule, such as N_2?
33. How does molecular orbital theory describe the existence of polar bonds? How is this apparent in the molecular orbital diagram of HCl?

Answers

1. An atomic orbital is a region of space around an atom that has a non-zero probability for an electron with a particular energy. Analogously, a molecular orbital is a region of space in a molecule that has a non-zero probability for an electron with a particular energy. Both an atomic orbital and a molecular orbital can contain two electrons.
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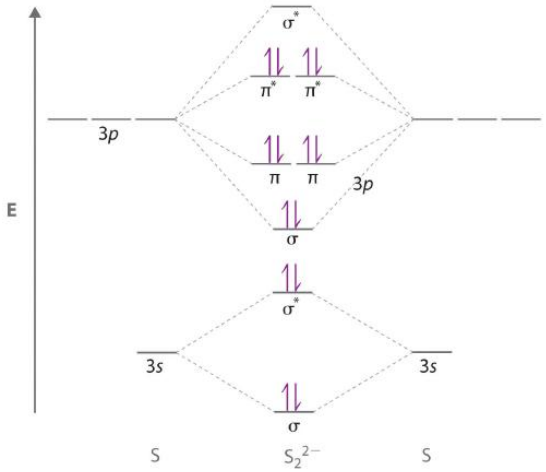
10.
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15. No. Because an np_x orbital on one atom is perpendicular to an np_y orbital on an adjacent atom, the net overlap between the two is zero. This is also true for np_y and np_z orbitals on adjacent atoms.
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Numerical Problems

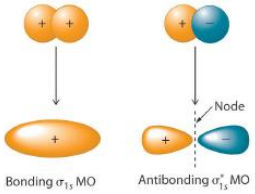
1. Use a qualitative molecular orbital energy-level diagram to describe the bonding in S_2^{2-}. What is the bond order? How many unpaired electrons does it have?
2. Use a qualitative molecular orbital energy-level diagram to describe the bonding in F_2^{2+}. What is the bond order? How many unpaired electrons does it have?
3. If three atomic orbitals combine to form molecular orbitals, how many molecular orbitals are generated? How many molecular orbitals result from the combination of four atomic orbitals? From five?
4. If two atoms interact to form a bond, and each atom has four atomic orbitals, how many molecular orbitals will form?
5. Sketch the possible ways of combining two 1*s* orbitals on adjacent atoms. How many molecular orbitals can be formed by this combination? Be sure to indicate any nodal planes.
6. Sketch the *four* possible ways of combining two 2*p* orbitals on adjacent atoms. How many molecular orbitals can be formed by this combination? Be sure to indicate any nodal planes.
7. If a diatomic molecule has a bond order of 2 and six bonding electrons, how many antibonding electrons must it have? What would be the corresponding Lewis electron structure (disregarding lone pairs)? What would be the effect of a one-electron reduction on the bond distance?

8. What is the bond order of a diatomic molecule with six bonding electrons and no antibonding electrons? If an analogous diatomic molecule has six bonding electrons and four antibonding electrons, which has the stronger bond? the shorter bond distance? If the highest occupied molecular orbital in both molecules is bonding, how will a one-electron oxidation affect the bond length?
9. Qualitatively discuss how the bond distance in a diatomic molecule would be affected by adding an electron to
    1. an antibonding orbital.
    2. a bonding orbital.
10. Explain why the oxidation of O_2 decreases the bond distance, whereas the oxidation of N_2 *increases* the N–N distance. Could Lewis electron structures be employed to answer this problem?
11. Draw a molecular orbital energy-level diagram for Na_2^+. What is the bond order in this ion? Is this ion likely to be a stable species? If not, would you recommend an oxidation or a reduction to improve stability? Explain your answer. Based on your answers, will Na_2^+, Na_2, or Na_2^- be the most stable? Why?
12. Draw a molecular orbital energy-level diagram for Xe_2^+, showing only the valence orbitals and electrons. What is the bond order in this ion? Is this ion likely to be a stable species? If not, would you recommend an oxidation or a reduction to improve stability? Explain your answer. Based on your answers, will Xe_2^{2+}, Xe_2^+, or Xe_2 be most stable? Why?
13. Draw a molecular orbital energy-level diagram for O_2^{2-} and predict its valence electron configuration, bond order, and stability.
14. Draw a molecular orbital energy-level diagram for C_2^{2-} and predict its valence electron configuration, bond order, and stability.
15. If all the *p* orbitals in the valence shells of two atoms interact, how many molecular orbitals are formed? Why is it not possible to form three π orbitals (and the corresponding antibonding orbitals) from the set of six *p* orbitals?
16. Draw a complete energy-level diagram for B_2. Determine the bond order and whether the molecule is paramagnetic or diamagnetic. Explain your rationale for the order of the molecular orbitals.
17. Sketch a molecular orbital energy-level diagram for each ion. Based on your diagram, what is the bond order of each species?
    1. NO^+
    2. NO^-
18. The diatomic molecule BN has never been detected. Assume that its molecular orbital diagram would be similar to that shown for CN^- in Section 5.3 but that the $<(\sigma _{2p_{z}} \)$ molecular orbital is higher in energy than the $\pi_{2p_{x,y}}$ molecular orbitals.
    1. Sketch a molecular orbital diagram for BN.
    2. Based on your diagram, what would be the bond order of this molecule?
    3. Would you expect BN to be stable? Why or why not?
19. Of the species BN, CO, C_2, and N_2, which are isoelectronic?
20. Of the species CN^-, NO^+, B_2^{2-}, and O_2^+, which are isoelectronic?

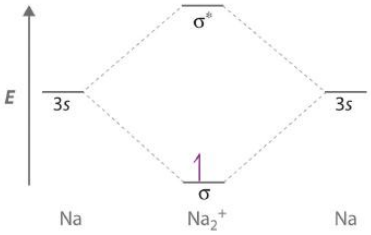
Answers



Each S atom contributes 6 valence electrons
+ 2 e⁻ for charge = 14 e⁻

1. The bond order is 1, and the ion has no unpaired electrons.
2.
3. The number of molecular orbitals is always equal to the number of atomic orbitals you start with. Thus, combining three atomic orbitals gives three molecular orbitals, and combining four or five atomic orbitals will give four or five molecular orbitals, respectively.
4.
5. 

   Combining two atomic *s* orbitals gives two molecular orbitals, a σ (bonding) orbital with no nodal planes, and a σ* (antibonding) orbital with a nodal plane perpendicular to the internuclear axis.
6.
7.
8.
9. 1. Adding an electron to an antibonding molecular orbital will decrease the bond order, thereby increasing the bond distance.
   2. Adding an electron to a bonding molecular orbital will increase the bond order, thereby decreasing the bond distance.
10.
11. Sodium contains only a single valence electron in its 3*s* atomic orbital. Combining two 3*s* atomic orbitals gives two molecular orbitals; as shown in the diagram, these are a σ (bonding) orbital and a σ* (antibonding) orbital.



Although each sodium atom contributes one valence electron, the +1 charge indicates that one electron has been removed. Placing the single electron in the lowest energy molecular orbital gives a σ_{3s}^1 electronic configuration and a bond order of 0.5. Consequently, Na_2^+ should be a stable species. Oxidizing Na_2^+ by one electron to give Na_2^{2+} would remove the electron in the σ_{3s} molecular orbital, giving a bond order of 0. Conversely, reducing Na_2^+ by one electron to give Na_2 would put an additional electron into the σ_{3s} molecular orbital, giving a bond order of 1. Thus, reduction to Na_2 would produce a more stable species than oxidation to Na_2^{2+}. The Na_2^- ion would have two electrons in the bonding σ_{3s} molecular orbital and one electron in the σ_{3s}* antibonding molecular orbital, giving a bond order of 0.5. Thus, Na_2 is the most stable of the three species.

12.

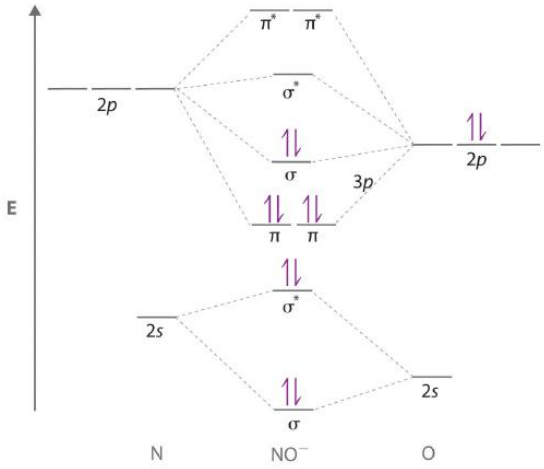
13.

14.

15.

16.

17.



1. The NO^+ ion has 10 valence electrons, which fill all the molecular orbitals up to and including the σ_{2p}. With eight electrons in bonding molecular orbitals and two electrons in antibonding orbitals, the bond order in NO^+ is $(8 - 2)/2 = 3$.
2. The NO^- ion contains two more electrons, which fill the σ_{2p}^* molecular orbital. The bond order in NO^- is $(8 - 4)/2 = 2$.

18.

19. BN and C_2 are isoelectronic, with 12 valence electrons, while N_2 and CO are isoelectronic, with 14 valence electrons.

20.

Contributors

- Anonymous

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Chapter 5.4: Polyatomic Systems, Multiple Bonds, Resonance

Learning Objective

- To explain resonance structures using molecular orbitals.

So far in our molecular orbital descriptions we have not dealt with polyatomic systems with multiple bonds. To do so, we can use an approach in which we describe σ bonding using localized electron-pair bonds formed by hybrid atomic orbitals, and π bonding using molecular orbitals formed by unhybridized *np* atomic orbitals.

Multiple Bonds

We begin our discussion by considering the bonding in ethylene (C_2H_4). Experimentally, we know that the H–C–H and H–C–C angles in ethylene are approximately 120°. This angle suggests that the carbon atoms are sp^2 hybridized, which means that a singly occupied sp^2 orbital on one carbon overlaps with a singly occupied *s* orbital on each H and a singly occupied sp^2 lobe on the other C. Thus each carbon forms a set of three σ bonds: two C–H (sp^2 + *s*) and one C–C (sp^2 + sp^2) (part (a) in Figure 5.4.1). The sp^2 hybridization can be represented as follows:

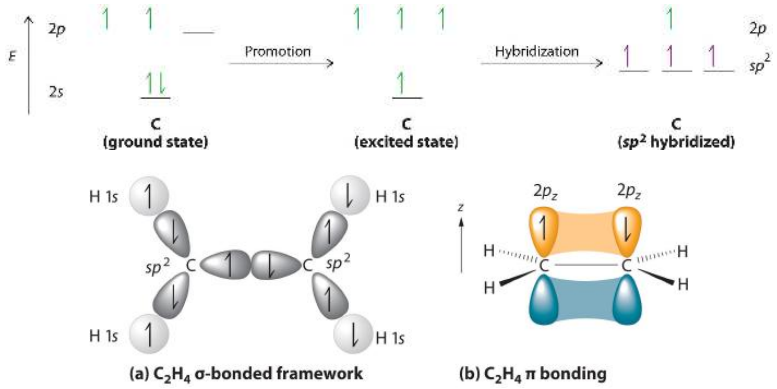


Figure 5.4.1 Bonding in Ethylene *(a) The σ-bonded framework is formed by the overlap of two sets of singly occupied carbon sp^2 hybrid orbitals and four singly occupied hydrogen 1s orbitals to form electron-pair bonds. This uses 10 of the 12 valence electrons to form a total of five σ bonds (four C–H bonds and one C–C bond). (b) One singly occupied unhybridized $2p_z$ orbital remains on each carbon atom to form a carbon–carbon π bond. (Note: by convention, in planar molecules the axis perpendicular to the molecular plane is the z-axis.)*

After hybridization, each carbon still has one unhybridized $2p_z$ orbital that is perpendicular to the hybridized lobes and contains a single electron (part (b) in Figure 5.4.1). The two singly occupied $2p_z$ orbitals can overlap to form a π bonding orbital and a π* antibonding orbital, which produces the energy-level diagram shown in Figure 5.4.2 With the formation of a π bonding orbital, electron density increases in the plane between the carbon nuclei. The π* orbital lies outside the internuclear region and has a nodal plane perpendicular to the internuclear axis. Because each $2p_z$ orbital has a single electron, there are only two electrons, enough to fill only the bonding (π) level, leaving the π* orbital empty. Consequently, the C–C bond in ethylene consists of a σ bond and a π bond, which together give a C=C double bond. Our model is supported by the facts that the measured carbon–carbon bond is shorter than that in ethane (133.9 pm versus 153.5 pm) and the bond is stronger (728 kJ/mol versus 376 kJ/mol in ethane). The two CH_2 fragments are coplanar, which maximizes the overlap of the two singly occupied $2p_z$ orbitals.

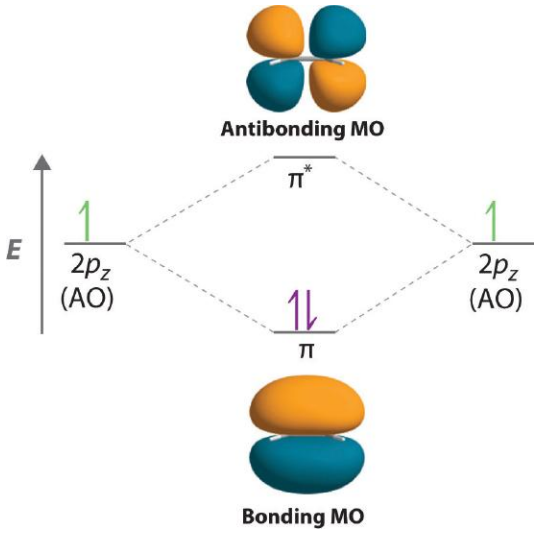
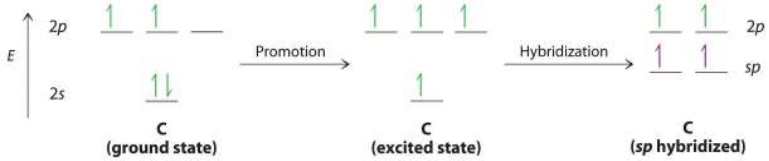


Figure 5.4.2 Molecular Orbital Energy-Level Diagram for π Bonding in Ethylene *As in the diatomic molecules discussed previously, the singly occupied $2p_z$ orbital in ethylene can overlap to form a bonding/antibonding pair of π molecular orbitals. The two electrons remaining are enough to fill only the bonding π orbital. With one σ bond plus one π bond, the carbon–carbon bond order in ethylene is 2.*

Triple bonds, as in acetylene (C_2H_2), can also be explained using a combination of hybrid atomic orbitals and molecular orbitals. The four atoms of acetylene are collinear, which suggests that each carbon is *sp* hybridized. If one *sp* lobe on each carbon atom is used to form a C–C σ bond and one is used to form the C–H σ bond, then each carbon will still have two unhybridized 2*p* orbitals (a $2p_{x,y}$ pair), each with one electron (part (a) in Figure 5.4.4).



The two 2*p* orbitals on each carbon can align with the corresponding 2*p* orbitals on the adjacent carbon to simultaneously form a *pair* of π bonds (part (b) in Figure 5.4.4). Because each of the unhybridized 2*p* orbitals has a single electron, four electrons are available for π bonding, which is enough to occupy only the bonding molecular orbitals. Acetylene must therefore have a carbon–carbon triple bond, which consists of a C–C σ bond and two mutually perpendicular π bonds. Acetylene does in fact have a shorter carbon–carbon bond (120.3 pm) and a higher bond energy (965 kJ/mol) than ethane and ethylene, as we would expect for a triple bond.

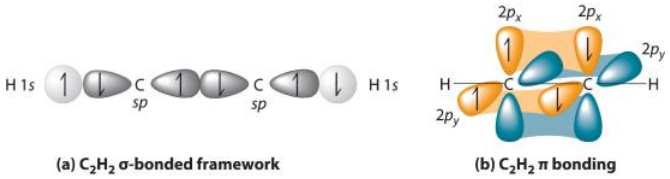


Figure 5.4.4 Bonding in Acetylene *(a) In the formation of the σ-bonded framework, two sets of singly occupied carbon sp hybrid orbitals and two singly occupied hydrogen 1s orbitals overlap. (b) In the formation of two carbon–carbon π bonds in acetylene, two singly occupied unhybridized $2p_{x,y}$ orbitals on each carbon atom overlap. With one σ bond plus two π bonds, the carbon–carbon bond order in acetylene is 3.*

Note the Pattern

In complex molecules, hybrid orbitals and valence bond theory can be used to describe σ bonding, and unhybridized *π* orbitals and molecular orbital theory can be used to describe π bonding.

Example 5.4.1

Describe the bonding in HCN using a combination of hybrid atomic orbitals and molecular orbitals. The HCN molecule is linear.

Given: chemical compound and molecular geometry

Asked for: bonding description using hybrid atomic orbitals and molecular orbitals

Strategy:

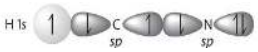
A From the geometry given, predict the hybridization in HCN. Use the hybrid orbitals to form the σ-bonded framework of the molecule and determine the number of valence electrons that are used for σ bonding.

B Determine the number of remaining valence electrons. Use any remaining unhybridized *p* orbitals to form π and π* orbitals.

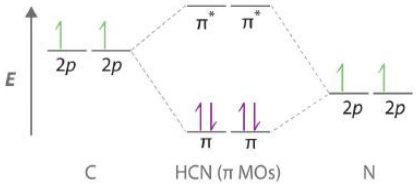
C Fill the orbitals with the remaining electrons in order of increasing energy. Describe the bonding in HCN.

Solution:

A Because HCN is a linear molecule, it is likely that the bonding can be described in terms of *sp* hybridization at carbon. Because the nitrogen atom can also be described as *sp* hybridized, we can use one *sp* hybrid on each atom to form a C–N σ bond. This leaves one *sp* hybrid on each atom to either bond to hydrogen (C) or hold a lone pair of electrons (N). Of 10 valence electrons (5 from N, 4 from C, and 1 from H), 4 are used for σ bonding:



B We are now left with 2 electrons on N (5 valence electrons minus 1 bonding electron minus 2 electrons in the lone pair) and 2 electrons on C (4 valence electrons minus 2 bonding electrons). We have two unhybridized 2*p* atomic orbitals left on carbon and two on nitrogen, each occupied by a single electron. These four 2*p* atomic orbitals can be combined to give four molecular orbitals: two π (bonding) orbitals and two π* (antibonding) orbitals. **C** With 4 electrons available, only the π orbitals are filled. The overall result is a triple bond (1 σ and 2 π) between C and N.



Exercise

Describe the bonding in formaldehyde ($H_2C{=}O$), a trigonal planar molecule, using a combination of hybrid atomic orbitals and molecular orbitals.

Answer:

σ-bonding framework: Carbon and oxygen are sp^2 hybridized. Two sp^2 hybrid orbitals on oxygen have lone pairs, two sp^2 hybrid orbitals on carbon form C–H bonds, and one sp^2 hybrid orbital on C and O forms a C–O σ bond.

π bonding: Unhybridized, singly occupied 2*p* atomic orbitals on carbon and oxygen interact to form π (bonding) and π* (antibonding) molecular orbitals. With two electrons, only the π (bonding) orbital is occupied.

Molecular Orbitals and Resonance Structures

In Chapter 4 , we used resonance structures to describe the bonding in molecules such as ozone (O_3) and the nitrite ion (NO_2^-). We showed that ozone can be represented by either of these Lewis electron structures:



Although the VSEPR model correctly predicts that both species are bent, it gives no information about their bond orders.

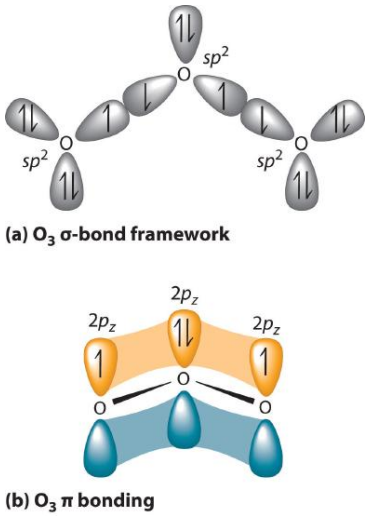


Figure 5.4.5 Bonding in Ozone *(a) In the formation of the σ-bonded framework, three sets of oxygen sp^2 hybrid orbitals overlap to give two O–O σ bonds and five lone pairs, two on each terminal O and one on the central O. The σ bonds and lone pairs account for 14 of the 18 valence electrons of O_3. (b) One unhybridized $2p_z$ orbital remains on each oxygen atom that is available for π bonding. The unhybridized $2p_z$ orbital on each terminal O atom has a single electron, whereas the unhybridized $2p_z$ orbital on the central O atom has 2 electrons*

.

Experimental evidence indicates that ozone has a bond angle of 117.5°. Because this angle is close to 120°, it is likely that the central oxygen atom in ozone is trigonal planar and sp^2 hybridized. If we assume that the terminal oxygen atoms are also sp^2 hybridized, then we obtain the σ-bonded framework shown in Figure 5.4.5 . Two of the three sp^2 lobes on the central O are used to form O–O sigma bonds, and the third has a lone pair of electrons. Each terminal oxygen atom has two lone pairs of electrons that are also in sp^2 lobes. In addition, each oxygen atom has one unhybridized 2*p* orbital perpendicular to the molecular plane. The σ bonds and lone pairs account for a total of 14 electrons (five lone pairs and two σ bonds, each containing 2 electrons). Each oxygen atom in ozone has 6 valence electrons, so O_3 has a total of 18 valence electrons. Subtracting 14 electrons from the total gives us 4 electrons that must occupy the three unhybridized 2*p* orbitals.

With a molecular orbital approach to describe the π bonding, three 2*p* atomic orbitals give us three molecular orbitals, as shown in Figure 5.4.6 . One of the molecular orbitals is a π bonding molecular orbital, which is shown as a banana-shaped region of electron density above and below the molecular plane. This region has *no* nodes perpendicular to the O_3 plane. The molecular orbital with the highest energy has two nodes that bisect the O–O σ bonds; it is a π* antibonding orbital. The third molecular orbital contains a single node that is perpendicular to the O_3 plane and passes through the central O atom; it is a nonbonding molecular orbital. Because electrons in nonbonding orbitals are neither bonding nor antibonding, they are ignored in calculating bond orders.

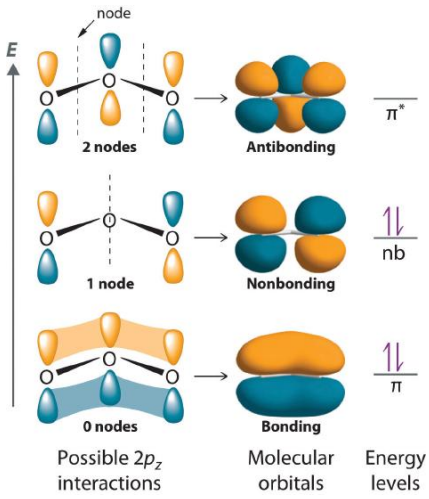


Figure 5.4.6 π Bonding in Ozone *The three unhybridized $2p_z$ atomic orbitals interact with one another to form three molecular orbitals: one π bonding orbital at lower energy, one π* antibonding orbital at higher energy, and a nonbonding orbital in between. Placing four electrons in this diagram fills the bonding and nonbonding orbitals. With one filled π bonding orbital holding three atoms together, the net π bond order is 1/2 per O–O bond. The combined σ/π bond order is thus 1 1/2 for each O-O bond....*

We can now place the remaining four electrons in the three energy levels shown in Figure 5.4.6 , thereby filling the π bonding and the nonbonding levels. The result is a single π bond holding *three* oxygen atoms together, or 1/2 π bonds per O–O. We therefore predict the overall O–O bond order to be 1 1/2 (1/2 π bond plus 1 σ bond), just as predicted using resonance structures. The molecular orbital approach, however, shows that the π nonbonding orbital is localized on the *terminal* O atoms, which suggests that they are more electron rich than the central O atom. The reactivity of ozone is consistent with the predicted charge localization.

Note the Pattern

Resonance structures are a crude way of describing molecular orbitals that extend over more than two atoms.

Example 5.4.2

Describe the bonding in the nitrite ion in terms of a combination of hybrid atomic orbitals and molecular orbitals. Lewis dot structures and the VSEPR model predict that the NO_2^- ion is bent.

Given: chemical species and molecular geometry

Asked for: bonding description using hybrid atomic orbitals and molecular orbitals

Strategy:

A Calculate the number of valence electrons in NO_2^-. From the structure, predict the type of atomic orbital hybridization in the ion.

B Predict the number and type of molecular orbitals that form during bonding. Use valence electrons to fill these orbitals and then calculate the number of electrons that remain.

C If there are unhybridized orbitals, place the remaining electrons in these orbitals in order of increasing energy. Calculate the bond order and describe the bonding.

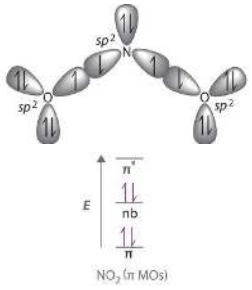
Solution:

A The lone pair of electrons on nitrogen and a bent structure suggest that the bonding in NO_2^- is similar to the bonding in ozone. This conclusion is supported by the fact that nitrite also contains 18 valence electrons (5 from N and 6 from each O, plus 1 for the −1 charge). The bent structure implies that the nitrogen is sp^2 hybridized.

B If we assume that the oxygen atoms are sp^2 hybridized as well, then we can use two sp^2 hybrid orbitals on each oxygen and one sp^2 hybrid orbital on nitrogen to accommodate the five lone pairs of electrons. Two sp^2 hybrid orbitals on nitrogen form σ bonds with the remaining sp^2 hybrid orbital on each oxygen. The σ bonds and lone pairs account for 14 electrons. We are left with three unhybridized 2*p* orbitals, one on each atom, perpendicular to the plane of the molecule, and 4 electrons. Just as with ozone, these

three 2*p* orbitals interact to form bonding, nonbonding, and antibonding π molecular orbitals. The bonding molecular orbital is spread over the nitrogen and both oxygen atoms.

C Placing 4 electrons in the energy-level diagram fills both the bonding and nonbonding molecular orbitals and gives a π bond order of 1/2 per N–O bond. The overall N–O bond order is 1 1/2 consistent with a resonance structure.



Exercise

Describe the bonding in the formate ion (HCO_2^-), in terms of a combination of hybrid atomic orbitals and molecular orbitals.

Answer: Like nitrite, formate is a planar polyatomic ion with 18 valence electrons. The σ bonding framework can be described in terms of sp^2 hybridized carbon and oxygen, which account for 14 electrons. The three unhybridized 2*p* orbitals (on C and both O atoms) form three π molecular orbitals, and the remaining 4 electrons occupy both the bonding and nonbonding π molecular orbitals. The overall C–O bond order is therefore 1 1/2

Summary

To describe the bonding in more complex molecules with multiple bonds, we can use an approach that uses hybrid atomic orbitals to describe the σ bonding and molecular orbitals to describe the π bonding. In this approach, unhybridized *np* orbitals on atoms bonded to one another are allowed to interact to produce bonding, antibonding, or nonbonding combinations. For π bonds between two atoms (as in ethylene or acetylene), the resulting molecular orbitals are virtually identical to the π molecular orbitals in diatomic molecules such as O_2 and N_2. Applying the same approach to π bonding between three or four atoms requires combining three or four unhybridized *np* orbitals on adjacent atoms to generate π bonding, antibonding, and nonbonding molecular orbitals extending over all of the atoms. Filling the resulting energy-level diagram with the appropriate number of electrons explains the bonding in molecules or ions that previously required the use of resonance structures in the Lewis electron-pair approach.

Key Takeaway

- Polyatomic systems with multiple bonds can be described using hybrid atomic orbitals for σ bonding and molecular orbitals to describe π bonding.

Conceptual Problems

1. What information is obtained by using the molecular orbital approach to bonding in O_3 that is not obtained using the VSEPR model? Can this information be obtained using a Lewis electron-pair approach?
2. How is resonance explained using the molecular orbital approach?
3. Indicate what information can be obtained by each method:

	Lewis Electron Structures	VSEPR Model	Valence Bond Theory	Molecular Orbital Theory
Geometry				
Resonance				
Orbital Hybridization				
Reactivity				
Expanded Valences				
Bond Order				

Numerical Problems

1. Using both a hybrid atomic orbital and molecular orbital approaches, describe the bonding in BCl_3 and CS_3^{2-}.
2. Use both a hybrid atomic orbital and molecular orbital approaches to describe the bonding in CO_2 and N_3^-.

Contributors

- Anonymous

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Learning Objective

- To name covalent compounds that contain up to three elements.

As with ionic compounds, the system that chemists have devised for naming covalent compounds enables us to write the molecular formula from the name and vice versa. In this and the following section, we describe the rules for naming simple organic compounds.

Hydrocarbons

Approximately one-third of the compounds produced industrially are organic compounds. All living organisms are composed of organic compounds, as is most of the food you consume, the medicines you take, the fibers in the clothes you wear, and the plastics in the materials you use. Among the few organic compounds we have discussed are methane (CH_4) and methanol (CH_3OH). These and other organic compounds appear frequently in discussions and examples throughout this text.

The simplest class of organic compounds is the hydrocarbonsThe simplest class of organic molecules, consisting of only carbon and hydrogen., which consist entirely of carbon and hydrogen. Petroleum and natural gas are complex, naturally occurring mixtures of many different hydrocarbons that furnish raw materials for the chemical industry. The four major classes of hydrocarbons are the alkanesA saturated hydrocarbon with only carbon–hydrogen and carbon–carbon single bonds., which contain only carbon–hydrogen and carbon–carbon single bonds; the alkenesAn unsaturated hydrocarbon with at least one carbon–carbon double bond., which contain at least one carbon–carbon double bond; the alkynesAn unsaturated hydrocarbon with at least one carbon–carbon triple bond., which contain at least one carbon–carbon triple bond; and the aromatic hydrocarbonsAn unsaturated hydrocarbon consisting of a ring of six carbon atoms with alternating single and double bonds., which usually contain rings of six carbon atoms that can be drawn with alternating single and double bonds. Alkanes are also called *saturated* hydrocarbons, whereas hydrocarbons that contain multiple bonds (alkenes, alkynes, and aromatics) are *unsaturated*.

Alkanes

The simplest alkane is methane (CH_4), a colorless, odorless gas that is the major component of natural gas. In larger alkanes whose carbon atoms are joined in an unbranched chain (*straight-chain alkanes*), each carbon atom is bonded to at most two other carbon atoms. The structures of two simple alkanes are shown in Figure 6.4.3 , and the names and condensed structural formulas for the first 10 straight-chain alkanes are in Table 6.4.2. The names of all alkanes end in *-ane*, and their boiling points increase as the number of carbon atoms increases. In all of these compounds the hybridization of the atomic orbitals of carbon is sp^3 and the molecular geometry around each carbon atom is tetrahedral

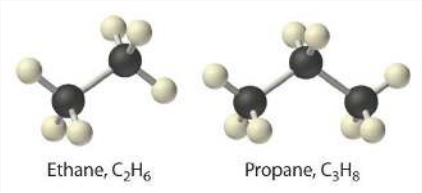


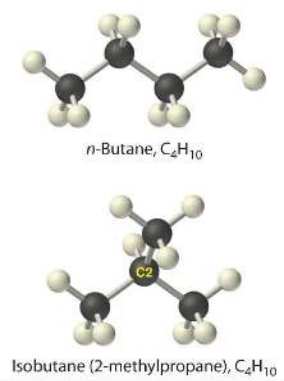
Figure 6.4.3 Straight-Chain Alkanes with Two and Three Carbon Atoms

Table 6.4.2 The First 10 Straight-Chain Alkanes

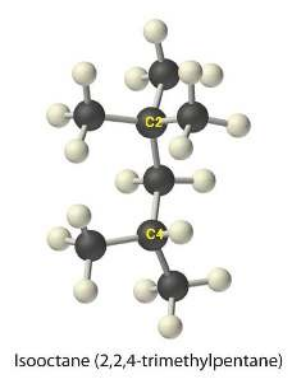
Table 6.4.2 The First 10 Straight-Chain Alkanes

Name	Number of Carbon Atoms	Molecular Formula	Condensed Structural Formula	Boiling Point (°C)	Uses
methane	1	CH_4	CH_4	−162	natural gas constituent
ethane	2	C_2H_6	CH_3CH_3	−89	natural gas constituent
propane	3	C_3H_8	$CH_3CH_2CH_3$	−42	bottled gas
butane	4	C_4H_{10}	$CH_3CH_2CH_2CH_3$ or $CH_3(CH_2)_2CH_3$	0	lighters, bottled gas
pentane	5	C_5H_{12}	$CH_3(CH_2)_3CH_3$	36	solvent, gasoline
hexane	6	C_6H_{14}	$CH_3(CH_2)_4CH_3$	69	solvent, gasoline
heptane	7	C_7H_{16}	$CH_3(CH_2)_5CH_3$	98	solvent, gasoline
octane	8	C_8H_{18}	$CH_3(CH_2)_6CH_3$	126	gasoline
nonane	9	C_9H_{20}	$CH_3(CH_2)_7CH_3$	151	gasoline
decane	10	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	174	kerosene

Alkanes with four or more carbon atoms can have more than one arrangement of atoms. The carbon atoms can form a single unbranched chain, or the primary chain of carbon atoms can have one or more shorter chains that form branches. For example, butane (C_4H_{10}) has two possible structures. *Normal* butane (usually called *n*-butane) is $CH_3CH_2CH_2CH_3$, in which the carbon atoms form a single unbranched chain. In contrast, the condensed structural formula for *isobutane* is $(CH_3)_2CHCH_3$, in which the primary chain of three carbon atoms has a one-carbon chain branching at the central carbon. Three-dimensional representations of both structures are as follows:



The systematic names for branched hydrocarbons use the lowest possible number to indicate the position of the branch along the longest straight carbon chain in the structure. Thus the systematic name for isobutane is 2-methylpropane, which indicates that a methyl group (a branch consisting of $–CH_3$) is attached to the second carbon of a propane molecule. Similarly, you will learn in Section 6.6 that one of the major components of gasoline is commonly called isooctane; its structure is as follows:



As you can see, the longest chain in this compound has five carbon atoms, so it is a derivative of pentane. There are two methyl group branches at one carbon atom and one methyl group at another. Using the lowest possible numbers for the branches gives 2,2,4-trimethylpentane for the systematic name of this compound.

Alkenes

The simplest alkenes are *ethylene*, C_2H_4 or $CH_2{=}CH_2$, and *propylene*, C_3H_6 or $CH_3CH{=}CH_2$ (part (a) in Figure 6.4.4). The names of alkenes that have more than three carbon atoms use the same stems as the names of the alkanes (Table 6.4.2) but end in *-ene* instead of *-ane*. The hybridization around any of the carbon attached to a double bond is sp^2 . The molecular geometry around that carbon atom is trigonal planar.

Once again, more than one structure is possible for alkenes with four or more carbon atoms. For example, an alkene with four carbon atoms has three possible structures. One is $CH_2{=}CHCH_2CH_3$ (1-butene), which has the double bond between the first and second carbon atoms in the chain. The other two structures have the double bond between the second and third carbon atoms and are forms of $CH_3CH{=}CHCH_3$ (2-butene). All four carbon atoms in 2-butene lie in the same plane, so there are two possible structures (part (a) in Figure 6.4.4). If the two methyl groups are on the same side of the double bond, the compound is *cis*-2-butene (from the Latin *cis*, meaning “on the same side”). If the two methyl groups are on opposite sides of the double bond, the compound is *trans*-2-butene (from the Latin *trans*, meaning “across”). These are distinctly different molecules: *cis*-2-butene melts at −138.9°C, whereas *trans*-2-butene melts at −105.5°C.

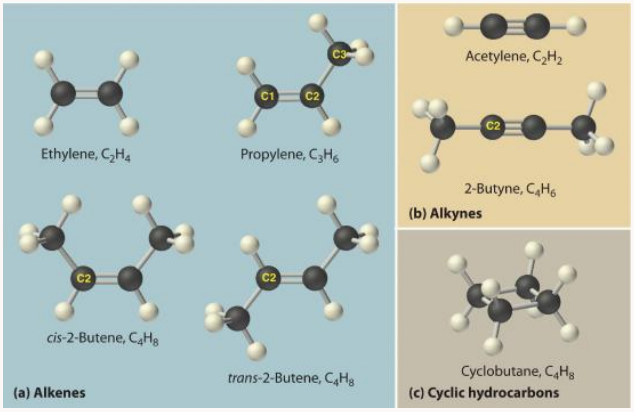
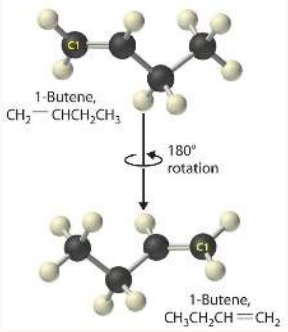


Figure 6.4.4 Some Simple (a) Alkenes, (b) Alkynes, and (c) Cyclic Hydrocarbons *The positions of the carbon atoms in the chain are indicated by C1 or C2.*

Just as a number indicates the positions of branches in an alkane, the number in the name of an alkene specifies the position of the *first* carbon atom of the double bond. The name is based on the lowest possible number starting from *either end* of the carbon chain, so $CH_3CH_2CH{=}CH_2$ is called 1-butene, *not* 3-butene. Note that $CH_2{=}CHCH_2CH_3$ and $CH_3CH_2CH{=}CH_2$ are different ways of writing the *same molecule* (1-butene) in two different orientations.



The name of a compound does *not* depend on its orientation. As illustrated for 1-butene, both condensed structural formulas and molecular models show different orientations of the same molecule. Don't let orientation fool you; you must be able to recognize the same structure no matter what its orientation.

Note the Pattern

The positions of groups or multiple bonds are always indicated by the lowest number possible.

Alkynes

The simplest alkyne is *acetylene*, C_2H_2 or HC≡CH (part (b) in Figure 6.4.4). Because a mixture of acetylene and oxygen burns with a flame that is hot enough (>3000°C) to cut metals such as hardened steel, acetylene is widely used in cutting and welding torches. The names of other alkynes are similar to those of the corresponding alkanes but end in *-yne*. For example, $HC{\equiv}CCH_3$ is *propyne*, and $CH_3C{\equiv}CCH_3$ is *2-butyne* because the multiple bond begins on the second carbon atom. The hybridization of a carbon atom attached to the triple bond is *sp*, and the geometric shape is linear

Note the Pattern

The number of bonds between carbon atoms in a hydrocarbon is indicated in the suffix:

- alk*ane*: only carbon–carbon single bonds
- alk*ene*: at least one carbon–carbon double bond
- alk*yne*: at least one carbon–carbon triple bond

Cyclic Hydrocarbons

In a cyclic hydrocarbonA hydrocarbon in which the ends of the carbon chain are connected to form a ring of covalently bonded carbon atoms., the ends of a hydrocarbon chain are connected to form a ring of covalently bonded carbon atoms. Cyclic hydrocarbons are named by attaching the prefix *cyclo-* to the name of the alkane, the alkene, or the alkyne. The simplest cyclic alkanes are *cyclopropane* (C_3H_6) a flammable gas that is also a powerful anesthetic, and *cyclobutane* (C_4H_8) (part (c) in Figure 6.4.4). The most common way to draw the structures of cyclic alkanes is to sketch a polygon with the same number of vertices as there are carbon atoms in the ring; each vertex represents a CH_2 unit. The structures of the cycloalkanes that contain three to six carbon atoms are shown schematically in Figure 6.4.5.

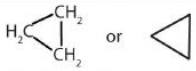
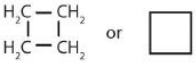
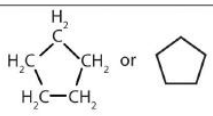
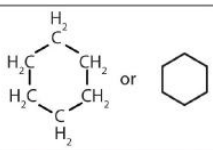
Name	Molecular Formula	Structural Formula
cyclopropane	C_3H_6	
cyclobutane	C_4H_8	
cyclopentane	C_5H_{10}	
cyclohexane	C_6H_{12}	

Figure 6.4.5 The Simple Cycloalkanes

Aromatic Hydrocarbons

Alkanes, alkenes, alkynes, and cyclic hydrocarbons are generally called aliphatic hydrocarbonsAlkanes, alkenes, alkynes, and cyclic hydrocarbons (hydrocarbons that are not aromatic).. The name comes from the Greek *aleiphar*, meaning "oil," because the first examples were extracted from animal fats. In contrast, the first examples of **aromatic hydrocarbons**, also called *arenes*, were obtained by the distillation and degradation of highly scented (thus *aromatic*) resins from tropical trees.

The simplest aromatic hydrocarbon is *benzene* (C_6H_6), which was first obtained from a coal distillate. The word *aromatic* now refers to benzene and structurally similar compounds. As shown in part (a) in Figure 6.4.6, it is possible to draw the structure of benzene in two different but equivalent ways, depending on which carbon atoms are connected by double bonds or single bonds. We learned that this is a consequence of the p orbitals on each carbon forming a bonding molecular π orbital which extends over the planar carbon chain. *Toluene* is similar to benzene, except that one hydrogen atom is replaced by a $–CH_3$ group; it has the formula C_7H_8 (part (b) in Figure 6.4.6). As you will soon learn, the chemical behavior of aromatic compounds differs from the behavior of aliphatic compounds. Benzene and toluene are found in gasoline, and benzene is the starting material for preparing substances as diverse as aspirin and nylon. Notice that the C atoms in aromatic molecules are sp^2 hybridized and the molecules are planar.

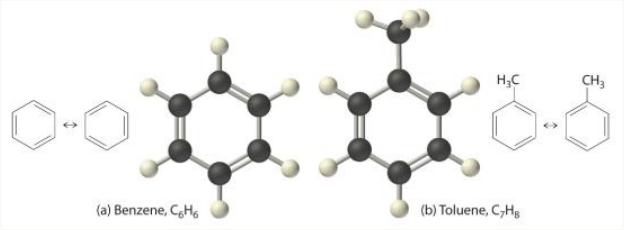


Figure 6.4.6 Two Aromatic Hydrocarbons: (a) Benzene and (b) Toluene

Figure 6.4.7 illustrates two of the molecular structures possible for hydrocarbons that have six carbon atoms. As you can see, compounds with the same molecular formula can have very different structures. The hybridization of the carbon atoms in these cases is sp^3 and the molecular geometry around each C atom is tetrahedral

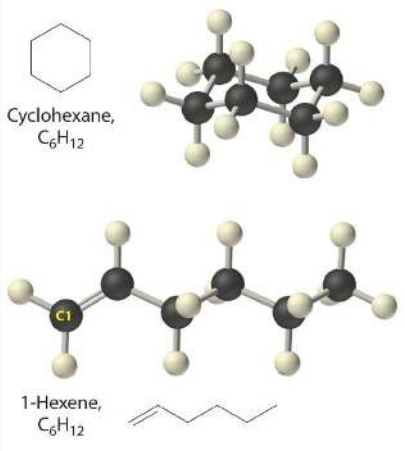


Figure 6.4.7 Two Hydrocarbons with the Molecular Formula C_6H_{12}

Example 10

Write the condensed structural formula for each hydrocarbon.

1. *n*-heptane
2. 2-pentene
3. 2-butyne
4. cyclooctene

Given: name of hydrocarbon

Asked for: condensed structural formula

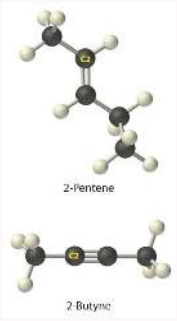
Strategy:

A Use the prefix to determine the number of carbon atoms in the molecule and whether it is cyclic. From the suffix, determine whether multiple bonds are present.

B Identify the position of any multiple bonds from the number(s) in the name and then write the condensed structural formula.

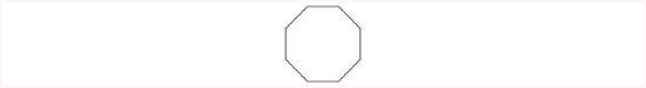
Solution:

1. **A** The prefix *hept-* tells us that this hydrocarbon has seven carbon atoms, and *n-* indicates that the carbon atoms form a straight chain. The suffix *-ane* tells that it is an alkane, with no carbon–carbon double or triple bonds. **B** The condensed structural formula is $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$, which can also be written as $CH_3(CH_2)_5CH_3$.
2. **A** The prefix *pent-* tells us that this hydrocarbon has five carbon atoms, and the suffix *-ene* indicates that it is an alkene, with a carbon–carbon double bond. **B** The 2- tells us that the double bond begins on the second carbon of the five-carbon atom chain. The condensed structural formula of the compound is therefore $CH_3CH{=}CHCH_2CH_3$.



3. **A** The prefix *but-* tells us that the compound has a chain of four carbon atoms, and the suffix *-yne* indicates that it has a carbon–carbon triple bond. **B** The 2- tells us that the triple bond begins on the second carbon of the four-carbon atom chain. So the condensed structural formula for the compound is $CH_3C{\equiv}CCH_3$.

4. **A** The prefix *cyclo-* tells us that this hydrocarbon has a ring structure, and *oct-* indicates that it contains eight carbon atoms, which we can draw as



The suffix *-ene* tells us that the compound contains a carbon–carbon double bond, but where in the ring do we place the double bond? **B** Because all eight carbon atoms are identical, it doesn't matter. We can draw the structure of cyclooctene as



Exercise

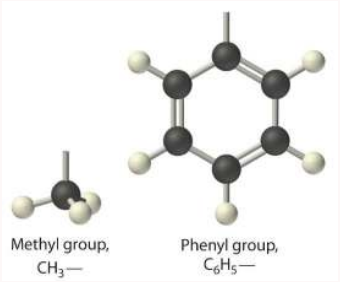
Write the condensed structural formula for each hydrocarbon.

1. *n*-octane
2. 2-hexene
3. 1-heptyne
4. cyclopentane

Answer:

1. $CH_3(CH_2)_6CH_3$
2. $CH_3CH{=}CHCH_2CH_2CH_3$
3. $HC{\equiv}C(CH_2)_4CH_3$
4. 

The general name for a group of atoms derived from an alkane is an *alkyl group*. The name of an alkyl group is derived from the name of the alkane by adding the suffix *-yl*. Thus the $–CH_3$ fragment is a *methyl* group, the $–CH_2CH_3$ fragment is an *ethyl* group, and so forth, where the dash represents a single bond to some other atom or group. Similarly, groups of atoms derived from aromatic hydrocarbons are *aryl groups*, which sometimes have unexpected names. For example, the $–C_6H_5$ fragment is derived from benzene, but it is called a *phenyl* group. In general formulas and structures, alkyl and aryl groups are often abbreviated as RThe abbreviation used for alkyl groups and aryl groups in general formulas and structures..

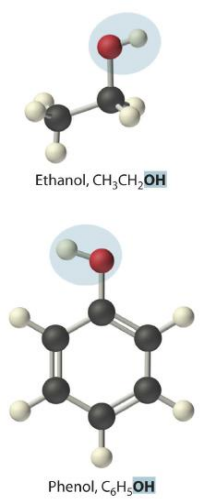


Structures of alkyl and aryl groups. *The methyl group is an example of an alkyl group, and the phenyl group is an example of an aryl group.*

Alcohols

Replacing one or more hydrogen atoms of a hydrocarbon with an –OH group gives an alcoholA class of organic compounds obtained by replacing one or more of the hydrogen atoms of a hydrocarbon with an −OH group., represented as ROH. The simplest alcohol (CH_3OH) is called either *methanol* (its systematic name) or *methyl alcohol* (its common name) (see Figure 6.4.4). Methanol is the antifreeze in automobile windshield washer fluids, and it is also used as an efficient fuel for racing cars, most notably in the Indianapolis 500. Ethanol (or ethyl alcohol, CH_3CH_2OH) is familiar as the alcohol in fermented or distilled

beverages, such as beer, wine, and whiskey; it is also used as a gasoline additive. The simplest alcohol derived from an aromatic hydrocarbon is C_6H_5OH, *phenol* (shortened from *phenyl* alcohol), a potent disinfectant used in some sore throat medications and mouthwashes.



Ethanol, which is easy to obtain from fermentation processes, has successfully been used as an alternative fuel for several decades. Although it is a "green" fuel when derived from plants, it is an imperfect substitute for fossil fuels because it is less efficient than gasoline. Moreover, because ethanol absorbs water from the atmosphere, it can corrode an engine's seals. Thus other types of processes are being developed that use bacteria to create more complex alcohols, such as octanol, that are more energy efficient and that have a lower tendency to absorb water. As scientists attempt to reduce mankind's dependence on fossil fuels, the development of these so-called *biofuels* is a particularly active area of research.

Summary

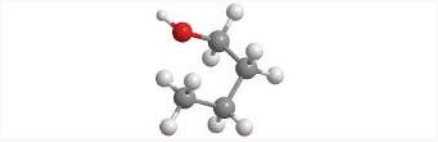
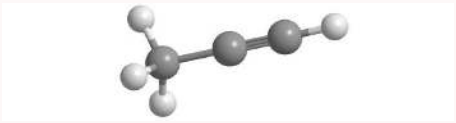
Covalent inorganic compounds are named by a procedure similar to that used for ionic compounds, using prefixes to indicate the numbers of atoms in the molecular formula. The simplest organic compounds are the **hydrocarbons**, which contain *only* carbon and hydrogen. **Alkanes** contain only carbon–hydrogen and carbon–carbon single bonds, **alkenes** contain at least one carbon–carbon double bond, and **alkynes** contain one or more carbon–carbon triple bonds. Hydrocarbons can also be **cyclic**, with the ends of the chain connected to form a ring. Collectively, alkanes, alkenes, and alkynes are called **aliphatic hydrocarbons**. **Aromatic hydrocarbons**, or *arenes*, are another important class of hydrocarbons that contain rings of carbon atoms related to the structure of benzene (C_6H_6). A derivative of an alkane or an arene from which one hydrogen atom has been removed is called an *alkyl group* or an *aryl group*, respectively. **Alcohols** are another common class of organic compound, which contain an –OH group covalently bonded to either an alkyl group or an aryl group (often abbreviated **R**).

Key Takeaway

- Covalent inorganic compounds are named using a procedure similar to that used for ionic compounds, whereas hydrocarbons use a system based on the number of bonds between carbon atoms.

Conceptual Problems

1. Benzene (C_6H_6) is an organic compound, and KCl is an ionic compound. The sum of the masses of the atoms in each empirical formula is approximately the same. How would you expect the two to compare with regard to each of the following? What species are present in benzene vapor?
    1. melting point
    2. type of bonding
    3. rate of evaporation
    4. structure
2. Can an inorganic compound be classified as a hydrocarbon? Why or why not?

3. Is the compound $NaHCO_3$ a hydrocarbon? Why or why not?
4.
5. 1. 
   2. 
6. For each structural formula, write the condensed formula and the name of the compound.
   1. 
7. Would you expect PCl_3 to be an ionic compound or a covalent compound? Explain your reasoning.
8. What distinguishes an aromatic hydrocarbon from an aliphatic hydrocarbon?
9. The following general formulas represent specific classes of hydrocarbons. Refer to Table 6.4.2 and Table 6.8 and Figure 6.4.4 and identify the classes.
   1. C_nH_{2n+2}
   2. C_nH_{2n}
   3. C_nH_{2n-2}
10. Using R to represent an alkyl or aryl group, show the general structure of an
    1. alcohol.
    2. phenol.

Answer

1.
2.
3.
4.
5.
6.
7.
8.
9.
10.
11. 1. ROH (where R is an alkyl group)
    2. ROH (where R is an aryl group)

Numerical Problems

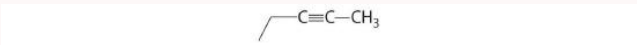
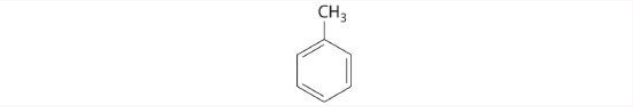
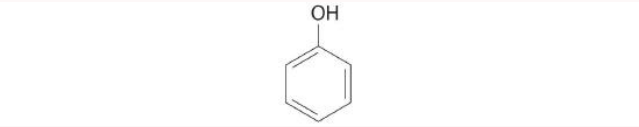
1. Draw the structure of each compound.
   1. propyne
   2. ethanol
   3. *n*-hexane

4. cyclopropane
5. benzene

2. Draw the structure of each compound.

1. 1-butene
2. 2-pentyne
3. cycloheptane
4. toluene
5. phenol

Answers

1. 1. 
   2. 
   3. 
   4. 
   5. 

Contributors

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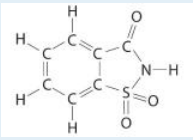
Chapter 5.6: End of Chapter Material

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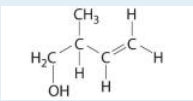
APPLICATION PROBLEMS

Problems marked with a ♦ involve multiple concepts.

1. ♦ Sulfur hexafluoride (SF_6) is a very stable gas that is used in a wide range of applications because it is nontoxic, nonflammable, and noncorrosive. Unfortunately, it is also a very powerful "greenhouse gas" that is about 22,000 times more effective at causing global warming than the same mass of CO_2.
   a. Draw the Lewis electron structure of SF_6 and determine the number of electron groups around the central atom, the molecular geometry, and the hybridization of the central atom.
   b. Suggest a reason for the extremely high stability of SF_6.
   c. Despite its rather high molecular mass (146.06 g/mol) and highly polar S–F bonds, SF_6 is a gas at room temperature (boiling point = −63°C). Why?
2. ♦ The elevated concentrations of chlorine monoxide (ClO) that accompany ozone depletions in Earth's atmosphere can be explained by a sequence of reactions. In the first step, chlorine gas is split into chlorine atoms by sunlight. Each chlorine atom then catalyzes the decomposition of ozone through a chlorine monoxide intermediate.
   a. Write balanced chemical equations showing this sequence of reactions.
   b. Sketch the molecular orbital energy-level diagram of ClO.
   c. Does ClO contain any unpaired electrons?
   d. Based on your molecular orbital diagram, is ClO likely to be a stable species? Explain your answer.
3. ♦ Saccharin is an artificial sweetener that was discovered in 1879. For several decades, it was used by people who had to limit their intake of sugar for medical reasons. Because it was implicated as a carcinogen in 1977, however, warning labels are now required on foods and beverages containing saccharin. The structure of this sweetener is as follows:



   a. Give the hybridization of all five atoms shown in bold in the structure. Note: all five atoms in the five-membered ring are coplanar.
   b. The carbon–oxygen bond is drawn as a double bond. If the nitrogen and the carbon attached to the C=O group each contribute one electron to the bonding, use both a Lewis electron structure and a hybrid orbital approach to explain the presence of the double bond.
   c. If sulfur and carbon each contribute one electron to nitrogen, how many lone pairs are present on the nitrogen?
   d. What is the geometry of the sulfur atom?
   e. The Lewis electron structure supports a single bond between the carbon and the nitrogen and a double bond between the carbon and the oxygen. In actuality, the C–O bond is longer than expected for a double bond, and the C–N bond is shorter. The nitrogen is also planar. Based on this information, what is the likely hybridization of the nitrogen? Using the concepts of molecular orbital theory, propose an explanation for this observation.
4. ♦ Pheromones are chemical signals used for communication between members of the same species. For example, the bark beetle uses an aggregation pheromone to signal other bark beetles to congregate at a particular site in a tree. Bark beetle infestations can cause severe damage because the beetles carry a fungal infection that spreads rapidly and can kill the tree. One of the components of this aggregation pheromone has the following structure:



   a. Give the hybridization of all atoms except hydrogen in this pheromone.
   b. How many σ bonds are present in this molecule? How many π bonds are there?
   c. Describe the bonding in this molecule using a combination of the localized and delocalized approaches.

5. Carbon monoxide is highly poisonous because it binds more strongly than O_2 to the iron in red blood cells, which transport oxygen in the blood. Consequently, a victim of CO poisoning suffocates from a lack of oxygen. Draw a molecular orbital energy-level diagram for CO. What is the highest occupied molecular orbital? Are any of the molecular orbitals degenerate? If so, which ones?

ANSWER



1. a. There are six electron groups, the molecular geometry is octahedral, and the hybridization of S is sp^3d^2.
   b. With six fluorine atoms packed around the central sulfur atom, there is no room for another species to approach the sulfur to initiate a reaction. The polar S–F bonds are also expected to be quite strong, so breaking an S–F bond to initiate a reaction is unlikely under most conditions.
   c. SF_6 is a gas at room temperature because it has no net dipole moment; the individual S–F bond dipoles cancel one another in this highly symmetrical structure. The absence of a dipole moment results in very weak interactions between SF_6 molecules, and as a result SF_6 is a gas rather than a liquid or a solid at room temperature.
2.
3.
4.
5.

Contributors

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SECTION OVERVIEW

Unit 3: States of Matter

Chapter 6: Gases

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CHAPTER OVERVIEW

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Chapter 6.1: Gaseous Elements and Compounds

Learning Objective

- To describe the characteristics of a gas.

The three common phases (or states) of matter are gases, liquids, and solids. Gases have the lowest density of the three, are highly compressible, and completely fill any container in which they are placed. Gases behave this way because their intermolecular forces are relatively weak, so their molecules are constantly moving independently of the other molecules present. Solids, in contrast, are relatively dense, rigid, and incompressible because their intermolecular forces are so strong that the molecules are essentially locked in place. Liquids are relatively dense and incompressible, like solids, but they flow readily to adapt to the shape of their containers, like gases. We can therefore conclude that the sum of the intermolecular forces in liquids are between those of gases and solids. Figure 6.1.1 compares the three states of matter and illustrates the differences at the molecular level.

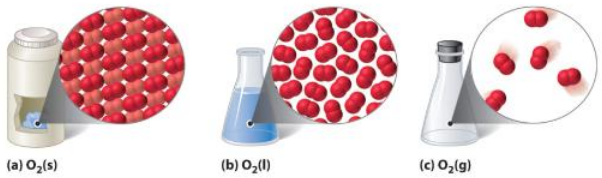


Figure 6.1.1 A Diatomic Substance (O_2) in the Solid, Liquid, and Gaseous States *(a) Solid O_2 has a fixed volume and shape, and the molecules are packed tightly together. (b) Liquid O_2 conforms to the shape of its container but has a fixed volume; it contains relatively densely packed molecules. (c) Gaseous O_2 fills its container completely—regardless of the container's size or shape—and consists of widely separated molecules.*

The state of a given substance depends strongly on conditions. For example, H_2O is commonly found in all three states: solid ice, liquid water, and water vapor (its gaseous form). Under most conditions, we encounter water as the liquid that is essential for life; we drink it, cook with it, and bathe in it. When the temperature is cold enough to transform the liquid to ice, we can ski or skate on it, pack it into a snowball or snow cone, and even build dwellings with it. Water vaporThe distinction between a gas and a vapor is subtle: the term *vapor* refers to the gaseous form of a substance that is a liquid or a solid under normal conditions (25°C, 1.0 atm). Nitrogen (N_2) and oxygen (O_2) are thus referred to as gases, but gaseous water in the atmosphere is called water vapor. is a component of the air we breathe, and it is produced whenever we heat water for cooking food or making coffee or tea. Water vapor at temperatures greater than 100°C is called steam. Steam is used to drive large machinery, including turbines that generate electricity. The properties of the three states of water are summarized in Table 6.1.1.

Table 6.1.1 Properties of Water at 1.0 atm

Temperature	State	Density (g/cm^3)
≤0°C	solid (ice)	0.9167 (at 0.0°C)
0°C–100°C	liquid (water)	0.9997 (at 4.0°C)
≥100°C	vapor (steam)	0.005476 (at 127°C)

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

Figure 6.1.2 shows the locations in the periodic table of those elements that are commonly found in the gaseous, liquid, and solid states. Except for hydrogen, the elements that occur naturally as gases are on the right side of the periodic table. Of these, all the noble gases (group 18) are monatomic gases, whereas the other gaseous elements are diatomic molecules (H_2, N_2, O_2, F_2, and Cl_2). Oxygen can also form a second allotrope, the highly reactive triatomic molecule ozone (O_3), which is also a gas. In contrast, bromine (as Br_2) and mercury (Hg) are liquids under normal conditions (25°C and 1.0 atm, commonly referred to as "room

temperature and pressure"). Gallium (Ga), which melts at only 29.76°C, can be converted to a liquid simply by holding a container of it in your hand or keeping it in a non-air-conditioned room on a hot summer day. The rest of the elements are all solids under normal conditions.

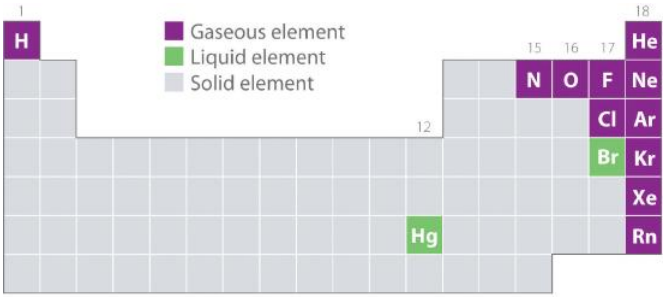


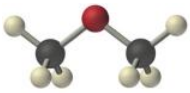
Figure 6.1.2 Elements That Occur Naturally as Gases, Liquids, and Solids at 25°C and 1 atm *The noble gases and mercury occur as monatomic species, whereas all other gases and bromine are diatomic molecules.*

Many of the elements and compounds we have encountered so far are typically found as gases; some of the more common ones are listed in Table 6.1.2 . Gaseous substances include many binary hydrides, such as the hydrogen halides (HX); hydrides of the chalcogens; hydrides of the group 15 elements N, P, and As; hydrides of the group 14 elements C, Si, and Ge; and diborane (B_2H_6). In addition, many of the simple covalent oxides of the nonmetals are gases, such as CO, CO_2, NO, NO_2, SO_2, SO_3, and ClO_2. Many low-molecular-mass organic compounds are gases as well, including all the hydrocarbons with four or fewer carbon atoms and simple molecules such as dimethyl ether [$(CH_3)_2O$], methyl chloride (CH_3Cl), formaldehyde (CH_2O), and acetaldehyde (CH_3CHO). Finally, most of the commonly used refrigerants, such as the chlorofluorocarbons (CFCs) and the hydrochlorofluorocarbons (HCFCs), which were discussed in Chapter 5, are gases.

Table 6.1.2 Some Common Substances That Are Gases at 25°C and 1.0 atm

Elements	Compounds	
He (helium)	HF (hydrogen fluoride)	C_2H_4 (ethylene)
Ne (neon)	HCl (hydrogen chloride)	C_2H_2 (acetylene)
Ar (argon)	HBr (hydrogen bromide)	C_3H_8 (propane)
Kr (krypton)	HI (hydrogen iodide)	C_4H_{10} (butane)
Xe (xenon)	HCN (hydrogen cyanide)*	CO (carbon monoxide)
Rn (radon)	H_2S (hydrogen sulfide)	CO_2 (carbon dioxide)
H_2 (hydrogen)	NH_3 (ammonia)	NO (nitric oxide)
N_2 (nitrogen)	PH_3 (phosphine)	N_2O (nitrous oxide)
O_2 (oxygen)	CH_4 (methane)	NO_2 (nitrogen dioxide)
O_3 (ozone)	C_2H_6 (ethane)	SO_2 (sulfur dioxide)
F_2 (fluorine)		
Cl_2 (chlorine)		

*HCN boils at 26°C at 1 atm, so it is included in this table.



Dimethyl ether

All of the gaseous substances mentioned previously (other than the monatomic noble gases) contain covalent or polar covalent bonds and are nonpolar or polar molecules. In contrast, the strong electrostatic attractions in ionic compounds, such as NaBr (boiling point = 1390°C) or LiF (boiling point = 1673°C), prevent them from existing as gases at room temperature and pressure. In addition, the lightest members of any given family of compounds are most likely gases, and the boiling points of polar compounds are generally greater than those of nonpolar compounds of similar molecular mass. Therefore, in a given series of compounds, the lightest and least polar members are the ones most likely to be gases. With relatively few exceptions, however, compounds with more than about five atoms from period 2 or below are too heavy to exist as gases under normal conditions.

Note the Pattern

Gaseous substances often contain covalent or polar covalent bonds, exist as nonpolar or slightly polar molecules, have relatively low molecular masses, and contain five or fewer atoms from periods 1 or 2.

While gases have a wide array of uses, a particularly grim use of a gaseous substance is believed to have been employed by the Persians on the Roman city of Dura in eastern Syria in the third century AD. The Persians dug a tunnel underneath the city wall to enter and conquer the city. Archeological evidence suggests that when the Romans responded with counter-tunnels to stop the siege, the Persians ignited bitumen and sulfur crystals to produce a dense, poisonous gas. It is likely that bellows or chimneys distributed the toxic fumes. The remains of about 20 Roman soldiers were discovered at the base of the city wall at the entrance to a tunnel that was less than 2 m high and 11 m long. Because it is highly unlikely that the Persians could have slaughtered so many Romans at the entrance to such a confined space, archeologists speculate that the ancient Persians used chemical warfare to successfully conquer the city.

Example 6.1.1

Which compounds would you predict to be gases at room temperature and pressure?

1. cyclohexene
2. lithium carbonate
3. cyclobutane
4. vanadium(III) oxide
5. benzoic acid ($C_6H_5CO_2H$)

Given: compounds

Asked for: physical state

Strategy:

A Decide whether each compound is ionic or covalent. An ionic compound is most likely a solid at room temperature and pressure, whereas a covalent compound may be a solid, a liquid, or a gas.

B Among the covalent compounds, those that are relatively nonpolar and have low molecular masses are most likely gases at room temperature and pressure.

Solution:

A Lithium carbonate is Li_2CO_3, containing Li^+ and CO_3^{2-} ions, and vanadium(III) oxide is V_2O_3, containing V^{3+} and O^{2-} ions. Both are primarily ionic compounds that are expected to be solids. The remaining three compounds are all covalent.

B Benzoic acid has more than four carbon atoms and is polar, so it is not likely to be a gas. Both cyclohexene and cyclobutane are essentially nonpolar molecules, but cyclobutane (C_4H_8) has a significantly lower molecular mass than cyclohexene (C_6H_{10}), which again has more than four carbon atoms. We therefore predict that cyclobutane is most likely a gas at room temperature and pressure, while cyclohexene is a liquid. In fact, with a boiling point of only 12°C, compared to 83°C for cyclohexene, cyclobutane is indeed a gas at room temperature and pressure.

Exercise

Which compounds would you predict to be gases at room temperature and pressure?

1. *n*-butanol
2. ammonium fluoride (NH_4F)
3. ClF
4. ethylene oxide



5. $HClO_4$

Answer: c; d

Summary

Bulk matter can exist in three states: gas, liquid, and solid. Gases have the lowest density of the three, are highly compressible, and fill their containers completely. Elements that exist as gases at room temperature and pressure are clustered on the right side of the periodic table; they occur as either monatomic gases (the noble gases) or diatomic molecules (some halogens, N_2, O_2). Many inorganic and organic compounds with four or fewer nonhydrogen atoms are also gases at room temperature and pressure. All gaseous substances are characterized by weak interactions between the constituent molecules or atoms.

Key Takeaway

- The molecules in gaseous substances often contain covalent or polar covalent bonds, are nonpolar or slightly polar molecules, and have relatively low molecular masses.

Conceptual Problems

1. Explain the differences between the microscopic and the macroscopic properties of matter. Is the boiling point of a compound a microscopic or macroscopic property? molecular mass? Why?
2. Determine whether the melting point, the dipole moment, and electrical conductivity are macroscopic or microscopic properties of matter and explain your reasoning.
3. How do the microscopic properties of matter influence the macroscopic properties? Can you relate molecular mass to boiling point? Why or why not? Can polarity be related to boiling point?
4. For a substance that has gas, liquid, and solid phases, arrange these phases in order of increasing
    1. density.
    2. strength of intermolecular interactions.
    3. compressibility.
    4. molecular motion.
    5. order in the arrangement of the molecules or atoms.
5. Explain what is wrong with this statement: “The state of matter largely determines the molecular properties of a substance.”
6. Describe the most important factors that determine the state of a given compound. What external conditions influence whether a substance exists in any one of the three states of matter?
7. Which elements of the periodic table exist as gases at room temperature and pressure? Of these, which are diatomic molecules and which are monatomic? Which elements are liquids at room temperature and pressure? Which portion of the periodic table contains elements whose binary hydrides are most likely gases at room temperature?
8. Is the following observation correct? “Almost all nonmetal binary hydrides are gases at room temperature, but metal hydrides are all solids.” Explain your reasoning.
9. Is the following observation correct? “All the hydrides of the chalcogens are gases at room temperature and pressure except the binary hydride of oxygen, which is a liquid.” Explain your reasoning. Would you expect 1-chloropropane to be a gas?

iodopropane? Why?

5. The molecular properties of a substance control its state of matter under a given set of conditions, *not* the other way around. The presence of strong intermolecular forces favor a condensed state of matter (liquid or solid), while very weak intermolecular interaction favor the gaseous state. In addition, the shape of the molecules dictates whether a condensed phase is a liquid or a solid.

10. Explain why ionic compounds are not gases under normal conditions.

Answers

1.
2. solid.
3. interaction favor the gaseous state. In addition, the shape of the molecules dictates whether a condensed phase is a liquid or a
4. presence of strong intermolecular forces favor a condensed state of matter (liquid or solid), while very weak intermolecular
5. The molecular properties of a substance control its state of matter under a given set of conditions, *not* the other way around. The
6.
7. Elements that exist as gases are mainly found in the upper right corner and on the right side of the periodic table. The following elements exist as gases: H, He, N, O, F, Ne, Cl, Ar, Kr, Xe, and Rn. Thus, half of the halogens, all of the noble gases, and the lightest chalcogens and picnogens are gases. Of these, all except the noble gases exist as diatomic molecules. Only two elements exist as liquids at a normal room temperature of 20°C–25°C: mercury and bromine. The upper right portion of the periodic table also includes most of the elements whose binary hydrides are gases. In addition, the binary hydrides of the elements of Groups 14–16 are gases.
8.
9.
10.

Contributors

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Chapter 6.2: Gas Pressure

Learning Objective

- To describe and measure the pressure of a gas.

At the macroscopic level, a complete physical description of a sample of a gas requires four quantities: *temperature* (expressed in kelvins), *volume* (expressed in liters), *amount* (expressed in moles), and *pressure* (in atmospheres). As we explain in this section and Section 6.3, these variables are *not* independent. If we know the values of any *three* of these quantities, we can calculate the fourth and thereby obtain a full physical description of the gas. Temperature, volume, and amount have been discussed in previous chapters. We now discuss pressure and its units of measurement.

Units of Pressure

Any object, whether it is your computer, a person, or a sample of gas, exerts a force on any surface with which it comes in contact. The air in a balloon, for example, exerts a force against the interior surface of the balloon, and a liquid injected into a mold exerts a force against the interior surface of the mold, just as a chair exerts a force against the floor because of its mass and the effects of gravity. If the air in a balloon is heated, the increased kinetic energy of the gas eventually causes the balloon to burst because of the increased pressure(*P*)The amount of force (F)(A)P = F/A of the gas, the force (*F*) per unit area (*A*) of surface:

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

Pressure is dependent on *both* the force exerted *and* the size of the area to which the force is applied. We know from Equation 6.2.1 that applying the same force to a smaller area produces a higher pressure. When we use a hose to wash a car, for example, we can increase the pressure of the water by reducing the size of the opening of the hose with a thumb.

The units of pressure are derived from the units used to measure force and area. In the English system, the units of force are pounds and the units of area are square inches, so we often see pressure expressed in pounds per square inch (lb/in^2, or psi), particularly among engineers. For scientific measurements, however, the SI units for force are preferred. The SI unit for pressure, derived from the SI units for force (newtons) and area (square meters), is the newton per square meter (N/m^2), which is called the pascal (Pa)The SI unit for pressure. The pascal is newtons per square meter: N/m^2, after the French mathematician Blaise Pascal (1623–1662):

$$1\ Pa = 1\ N/m^2$$

To convert from pounds per square inch to pascals, multiply psi by 6894.757 [1 Pa = 1 psi (6894.757)].

Blaise Pascal (1623–1662)

In addition to his talents in mathematics (he invented modern probability theory), Pascal did research in physics and was an author and a religious philosopher as well. His accomplishments include invention of the first syringe and the first digital calculator and development of the principle of hydraulic pressure transmission now used in brake systems and hydraulic lifts.

Example 6.2.1

Assuming a paperback book has a mass of 2.00 kg, a length of 27.0 cm, a width of 21.0 cm, and a thickness of 4.5 cm, what pressure does it exert on a surface if it is

1. lying flat?
2. standing on edge in a bookcase?

Given: mass and dimensions of object

Asked for: pressure

Strategy:

A Calculate the force exerted by the book and then compute the area that is in contact with a surface.

B Substitute these two values into Equation 6.2.1 to find the pressure exerted on the surface in each orientation.

Solution:

The force exerted by the book does *not* depend on its orientation. Recall that the force exerted by an object is $F = ma$, where m is its mass and a is its acceleration. In Earth's gravitational field, the acceleration is due to gravity (9.8067 m/s^2 at Earth's surface). In SI units, the force exerted by the book is therefore

$F = ma$ = (2.00 kg)(9.8067 m/s^2) = 19.6 (kg·m)/s^2 = 19.6 N

1. **A** We calculated the force as 19.6 N. When the book is lying flat, the area is (0.270 m)(0.210 m) = 0.0567 m^2. **B** The pressure exerted by the text lying flat is thus

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

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

   $$(21.0\ cm)\,(4.5\ cm) = (0.210\ m)\,(0.045\ m) = 9.5 \times \times 10^{-3}\ m^2$$

   B The pressure exerted by the book in this position is thus

   $$P = \frac{19.6\ N}{9.5 \times 10^{-3}\ m^2} = 2.1 \times 10^3\ Pa$$

   Thus the *pressure* exerted by the book varies by a factor of about six depending on its orientation, although the *force* exerted by the book does not vary.

Exercise

What pressure does a 60.0 kg student exert on the floor

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

Answers:

1. 3.27 × 10^4 Pa (4.74 lb/in.^{2})
2. 5.9 × 10^6 Pa (8.5 × 10^2 lb/in.^{2})

Atmospheric Pressure

Just as we exert pressure on a surface because of gravity, so does our atmosphere. We live at the bottom of an ocean of gases that becomes progressively less dense with increasing altitude. Approximately 99% of the mass of the atmosphere lies within 30 km of Earth's surface, and half of it is within the first 5.5 km (Figure 6.2.1). Every point on Earth's surface experiences a net pressure called *atmospheric pressure*. The pressure exerted by the atmosphere is considerable: a 1.0 m^2 column, measured from sea level to the top of the atmosphere, has a mass of about 10,000 kg, which gives a pressure of about 100 kPa:

$$Pressure = \frac{(1.0 \times 10^4\ kg)\,(9,807\ \cancel{m}/s^2)}{1.0\ \cancel{m^2}} = 0.98 \times 10^5\ Pa = 98\ kPa$$

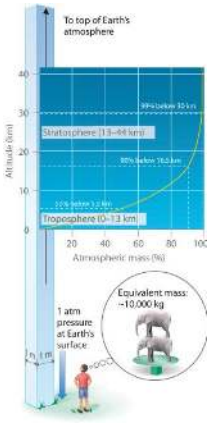


Figure 6.2.1 Atmospheric Pressure *Each square meter of Earth's surface supports a column of air that is more than 200 km high and weighs about 10,000 kg at Earth's surface, resulting in a pressure at the surface of 1.01 × 10^5 N/m^2. This corresponds to a pressure of 101 kPa = 760 mmHg = 1 atm.*

In English units, this is about 14 lb/in.^{2}, but we are so accustomed to living under this pressure that we never notice it. Instead, what we notice are *changes* in the pressure, such as when our ears pop in fast elevators in skyscrapers or in airplanes during rapid changes in altitude. We make use of atmospheric pressure in many ways. We can use a drinking straw because sucking on it removes air and thereby reduces the pressure inside the straw. The atmospheric pressure pushing down on the liquid in the glass then forces the liquid up the straw.

Atmospheric pressure can be measured using a barometerA device used to measure atmospheric pressure., a device invented in 1643 by one of Galileo's students, Evangelista Torricelli (1608–1647). A barometer may be constructed from a long glass tube that is closed at one end. It is filled with mercury and placed upside down in a dish of mercury without allowing any air to enter the tube. Some of the mercury will run out of the tube, but a relatively tall column remains inside (Figure 6.2.1). Why doesn't all the mercury run out? Gravity is certainly exerting a downward force on the mercury in the tube, but it is opposed by the pressure of the atmosphere pushing down on the surface of the mercury in the dish, which has the net effect of pushing the mercury up into the tube. Because there is no air above the mercury inside the tube in a properly filled barometer (it contains a *vacuum*), there is no pressure pushing down on the column. Thus the mercury runs out of the tube until the pressure exerted by the mercury column itself exactly balances the pressure of the atmosphere. Under normal weather conditions at sea level, the two forces are balanced when the top of the mercury column is approximately 760 mm above the level of the mercury in the dish, as shown in Figure 6.2.2 This value varies with meteorological conditions and altitude. In Denver, Colorado, for example, at an elevation of about 1 mile, or 1609 m (5280 ft), the height of the mercury column is 630 mm rather than 760 mm.

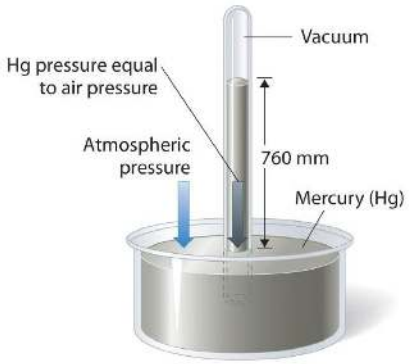


Figure 6.2.2 A Mercury Barometer*The pressure exerted by the atmosphere on the surface of the pool of mercury supports a column of mercury in the tube that is about 760 mm tall. Because the boiling point of mercury is quite high (356.73°C), there is very little mercury vapor in the space above the mercury column.*

Mercury barometers have been used to measure atmospheric pressure for so long that they have their own unit for pressure: the millimeter of mercury (mmHg)A unit of pressure, often called the TorrA unit of pressure. One Torr is the same as 1 mmHg., after Torricelli. It is annoying that some chemistry books insist on using mmHg rather than Torr or even better, the SI unit, bar. 1 bar is 100 kPa.

While mercury barometers were the workhorses for pressure measurement into the last quarter of the 20th century, they have been replaced by electronic gauges. One motivation was safety. Mercury and mercury vapor are heavy metal poisons.

The oldest and simplest replacement for mercury barometers are aneroid gauges. The simplest version of an aneroid gauge (Figure 6.2.3) has a thin metal diaphram which expands and contracts. The diaphragm is connected to a dial by a mechanical linkage. Aneroid gauges can either be absolute or differential. Differential aneroid gauges compare the pressure in the gauge housing to that being measured. A common use for aneroid gauges was airplane altimeters.

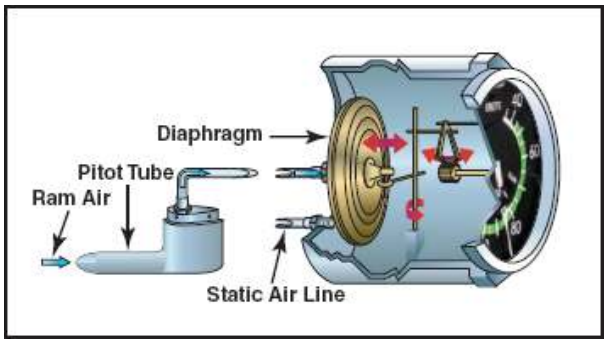


Figure 6.2.2 An Aneroid Barometer *An Aneroid Barometer uses the expansion/contraction of a metal diaphragm to move the indicator dial. This drawing from the Wikipedia shows a simple aneroid barometer used for an airplane altimeter.*

Most modern pressure sensors are based on strain gauge which convert pressure into a strain on a semiconductor element. The strain is converted into an electrical signal by the piezoelectric effect as a change in resistance monitored by a resistance bridge. Alternatively pressure is related to the change in frequency of a quartz crystal oscillator. Modern balances are also based on this later principle.

A very accurate type of pressure sensor uses a metal diaphragm as one part of a capacitor. As the pressure changes the diaphragm moves altering the capacitance. Handbooks are available from sensor manufacturers with details including OMEGA and WIKA.

Below atmospheric pressures another type of gauge is used based on measuring temperature change of a hot wire as a function of pressure. This is best suited to pressures below atmospheric. Older types called thermocouple or Pirani gauges measure only up to a few Torr. Modern variations called convection gauges can measure up to atmospheric pressure

A summary of the various types of pressure gauge in use today can be found in a technical note at the Kurt Lesker site

Standard atmospheric pressureThe atmospheric pressure required to support a column of mercury exactly 760 mm tall, which is also referred to as 1 atmosphere (atm). is the atmospheric pressure required to support a column of mercury exactly 760 mm tall; this pressure is also referred to as 1 atmosphere (atm)Also referred to as standard atmospheric pressure, it is the atmospheric pressure required to support a column of mercury exactly 760 mm tall.. These units are also related to the pascal:

$$1\ atm = 760\ mmHg = 760\ torr = 1.01325 \times \times 10^5\ Pa = 101.325\ kPa$$

Thus a pressure of 1 atm equals 760 mmHg exactly and is approximately equal to 100 kPa.

Pressure gauges specify whether the measurement is absolute (relative to zero pressure) or gauge (relative to the standard atmosphere). One must be careful about which kind a gauge is when buying or using one..

Example 6.2.2

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

1. atmospheres.
2. kilopascals.

Given: pressure in millimeters of mercury

Asked for: pressure in atmospheres and kilopascals

Strategy:

Use the conversion factors in Equation 6.2.4 to convert from millimeters of mercury to atmospheres and kilopascals.

Solution:

From Equation 6.2,4, we have 1 atm = 760 mmHg = 101.325 kPa. The pressure at 14,000 ft in atm is thus

$$P = \left(454 \ \cancel{mmHg}\right)\left(\frac{1 \ atm}{760 \ \cancel{mmHg}}\right) = 0.597 \ atm$$

The pressure in kPa is given by

$$P = \left(0.597 \ \cancel{atm}\right)\left(\frac{101.325 \ kPa}{1 \ \cancel{atm}}\right) = 80.5 \ kPa$$

Exercise

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

1. millimeters of mercury.
2. kilopascals.

Answer: a. 234 mmHg; b. 31.2 kPa

Manometers

Barometers measure atmospheric pressure, but manometersA device used to measure the pressures of samples of gases contained in an apparatus. measure the pressures of samples of gases contained in an apparatus. The key feature of a manometer is a U-shaped tube containing mercury (or occasionally another nonvolatile liquid). A closed-end manometer is shown schematically in part (a) in Figure 6.2.4 . When the bulb contains no gas (i.e., when its interior is a near vacuum), the heights of the two columns of mercury are the same because the space above the mercury on the left is a near vacuum (it contains only traces of mercury vapor). If a gas is released into the bulb on the right, it will exert a pressure on the mercury in the right column, and the two columns of mercury will no longer be the same height. The *difference* between the heights of the two columns is equal to the pressure of the gas.

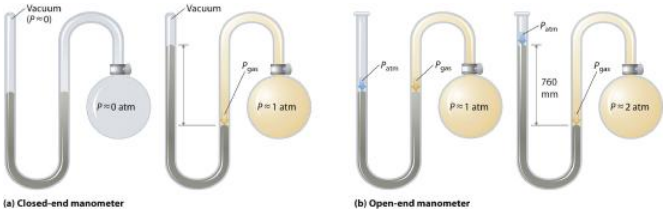


Figure 6.2.4 The Two Types of Manometer *(a) In a closed-end manometer, the space above the mercury column on the left (the reference arm) is essentially a vacuum (P ≈ 0), and the difference in the heights of the two columns gives the pressure of the gas contained in the bulb directly. (b) In an open-end manometer, the left (reference) arm is open to the atmosphere (P ≈ 1 atm), and the difference in the heights of the two columns gives the difference between atmospheric pressure and the pressure of the gas in the bulb.*

If the tube is open to the atmosphere instead of closed, as in the open-end manometer shown in part (b) in Figure 6.2.3, then the two columns of mercury have the same height only if the gas in the bulb has a pressure equal to the atmospheric pressure. If the gas in the bulb has a *higher* pressure, the mercury in the open tube will be forced up by the gas pushing down on the mercury in the other arm of the U-shaped tube. The pressure of the gas in the bulb is therefore the sum of the atmospheric pressure (measured with a barometer) and the difference in the heights of the two columns. If the gas in the bulb has a pressure *less* than that of the atmosphere, then the height of the mercury will be greater in the arm attached to the bulb. In this case, the pressure of the gas in the bulb is the atmospheric pressure minus the difference in the heights of the two columns.

The other types of pressure sensors, aneroid gauges, semiconductor strain gauges and capacitance manometers all can be used as manometers. Unfortunately most chemistry books have not kept up with the times and still refer only to measurements made with mercury barometers and manometers. They also, almost uniformly use units of mm of Hg, rather than the proper unit of Torr (1 Torr = 1 mm Hg), or even better bar.

Example 6.2.3

Suppose you want to construct a closed-end manometer to measure gas pressures in the range 0.000–0.200 atm. Because of the toxicity of mercury, you decide to use water rather than mercury. How tall a column of water do you need? (At 25°C, the density of

water is 0.9970 g/cm^3; the density of mercury is 13.53 g/cm^3.)

Given: pressure range and densities of water and mercury

Asked for: column height

Strategy:

A Calculate the height of a column of mercury corresponding to 0.200 atm in Torr. This is the height needed for a mercury-filled column.

B From the given densities, use a proportion to compute the height needed for a water-filled column.

Solution:

A In millimeters of mercury, a gas pressure of 0.200 atm is

$$P = (0.200\ \cancel{atm}) \left(\frac{760\ Torr}{1\ \cancel{atm}} \right) = 152\ Torr$$

Using a mercury manometer, you would need a mercury column at least 152 mm high.

B Because water is less dense than mercury, you need a *taller* column of water to achieve the same pressure as a given column of mercury. The height needed for a water-filled column corresponding to a pressure of 0.200 atm is proportional to the ratio of the density of mercury (d_{Hg})(d_{H2O})

$$(height_{H_2O})\,(d_{H_2O}) = (height_{Hg})\,(d_{Hg})$$

$$height_{H_2O} = (height_{Hg})\,\frac{d_{Hg}}{d_{H_2O}}$$

$$= (152\ mmHg) \left(\frac{13.53\ \cancel{g/cm^2}}{0.9970\ \cancel{g/cm^2}} \right)$$

$$= 2.06 \times 10^3\ mm\ H_2O$$

This answer makes sense: it takes a taller column of a less dense liquid to achieve the same pressure.

Exercise

Suppose you want to design a barometer to measure atmospheric pressure in an environment that is always hotter than 30°C. To avoid using mercury, you decide to use gallium, which melts at 29.76°C; the density of liquid gallium at 25°C is 6.114 g/cm^3. How tall a column of gallium do you need if P = 1.00 atm?

Answer: 1.68 m

The answer to Example 4 also tells us the maximum depth of a farmer's well if a simple suction pump will be used to get the water out. If a column of water 2.06 m high corresponds to 0.200 atm, then 1.00 atm corresponds to a column height of

$$\frac{h}{2.06\ m} = \frac{1.00\ \cancel{atm}}{0.200\ \cancel{atm}}$$

$$h = 10.3\ m$$

A suction pump is just a more sophisticated version of a straw: it creates a vacuum above a liquid and relies on atmospheric pressure to force the liquid up a tube. If 1 atm pressure corresponds to a 10.3 m (33.8 ft) column of water, then it is physically impossible for atmospheric pressure to raise the water in a well higher than this. Until electric pumps were invented to push water mechanically from greater depths, this factor greatly limited where people could live because obtaining water from wells deeper than about 33 ft was difficult.

Summary

Four quantities must be known for a complete physical description of a sample of a gas: *temperature*, *volume*, *amount*, and *pressure*. **Pressure** is force per unit area of surface; the SI unit for pressure is the **pascal (Pa)**, defined as 1 newton per square meter (N/m^2). The pressure exerted by an object is proportional to the force it exerts and inversely proportional to the area on which the force is exerted. The pressure exerted by Earth's atmosphere, called *atmospheric pressure*, is about 101 kPa or 14.7 $lb/in.^2$ at sea level. Atmospheric pressure can be measured with a **barometer**, a closed, inverted tube filled with mercury. The height of the mercury column is proportional to atmospheric pressure, which is often reported in units of **millimeters of mercury (mmHg)**, also called **torr**. **Standard atmospheric pressure**, the pressure required to support a column of mercury 760 mm tall, is yet another unit of pressure: 1 **atmosphere (atm)**. A **manometer** is an apparatus used to measure the pressure of a sample of a gas.

Key Takeaway

- Pressure is defined as the force exerted per unit area; it can be measured using a barometer or manometer.

Key Equation

Definition of pressure

Equation 6.2.1: $P = F/A$

Conceptual Problems

1. What four quantities must be known to completely describe a sample of a gas? What units are commonly used for each quantity?
2. If the applied force is constant, how does the pressure exerted by an object change as the area on which the force is exerted decreases? In the real world, how does this relationship apply to the ease of driving a small nail versus a large nail?
3. As the force on a fixed area increases, does the pressure increase or decrease? With this in mind, would you expect a heavy person to need smaller or larger snowshoes than a lighter person? Explain.
4. What do we mean by *atmospheric pressure*? Is the atmospheric pressure at the summit of Mt. Rainier greater than or less than the pressure in Miami, Florida? Why?
5. Which has the highest atmospheric pressure—a cave in the Himalayas, a mine in South Africa, or a beach house in Florida? Which has the lowest?
6. Mars has an average atmospheric pressure of 0.007 atm. Would it be easier or harder to drink liquid from a straw on Mars than on Earth? Explain your answer.
7. Is the pressure exerted by a 1.0 kg mass on a 2.0 m^2 area greater than or less than the pressure exerted by a 1.0 kg mass on a 1.0 m^2 area? What is the difference, if any, between the pressure of the atmosphere exerted on a 1.0 m^2 piston and a 2.0 m^2 piston?
8. If you used water in a barometer instead of mercury, what would be the major difference in the instrument?

Answer

3. Because pressure is defined as the force per unit area ($P = F/A$), increasing the force on a given area increases the pressure. A heavy person requires larger snowshoes than a lighter person. Spreading the force exerted on the heavier person by gravity (that is, their weight) over a larger area decreases the pressure exerted per unit of area, such as a square inch, and makes them less likely to sink into the snow.

Numerical Problems

1. Calculate the pressure in atmospheres and kilopascals exerted by a fish tank that is 2.0 ft long, 1.0 ft wide, and 2.5 ft high and contains 25.0 gal of water in a room that is at 20°C; the tank itself weighs 15 lb (d_{H_2O}= 1.00 g/cm^3 at 20°C). If the tank were 1

ft long, 1 ft wide, and 5 ft high, would it exert the same pressure? Explain your answer.

2. Calculate the pressure in pascals and in atmospheres exerted by a carton of milk that weighs 1.5 kg and has a base of 7.0 cm × 7.0 cm. If the carton were lying on its side (height = 25 cm), would it exert more or less pressure? Explain your reasoning.
3. If atmospheric pressure at sea level is 1.0×10^5 Pa, what is the mass of air in kilograms above a 1.0 cm^2 area of your skin as you lie on the beach? If atmospheric pressure is 8.2×10^4 Pa on a mountaintop, what is the mass of air in kilograms above a 4.0 cm^2 patch of skin?
4. Complete the following table:

atm	kPa	mmHg	torr
1.40			
		723	
	43.2		

5. The SI unit of pressure is the pascal, which is equal to 1 N/m^2. Show how the product of the mass of an object and the acceleration due to gravity result in a force that, when exerted on a given area, leads to a pressure in the correct SI units. What mass in kilograms applied to a 1.0 cm^2 area is required to produce a pressure of
    1. 1.0 atm?
    2. 1.0 torr?
    3. 1 mmHg?
    4. 1 kPa?
6. If you constructed a manometer to measure gas pressures over the range 0.60–1.40 atm using the liquids given in the following table, how tall a column would you need for each liquid? The density of mercury is 13.5 g/cm^3. Based on your results, explain why mercury is still used in barometers, despite its toxicity.

	Liquid Density (20°C)	Column Height (m)
isopropanol	0.785	
coconut oil	0.924	
glycerine	1.259	

Answer

1. 5.4 kPa or 5.3×10^{-2} atm; 11 kPa, 1.1×10^{-3} atm; the same force acting on a smaller area results in a greater pressure.
2.
3.
4.
5.
6.

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Chapter 6.3: The Ideal Gas Law

Learning Objective

- To use the ideal gas law to describe the behavior of a gas.

Motivating the Ideal Gas Law

In a gas, molecules freely move, filling any volume that they occupy. The kinetic energy of the molecules greatly exceeds any potential energy of attraction or repulsion between molecules and the size of the molecules are miniscule compared to the average space between them. Contrast this with solids, where the molecules are held in place by the attractive forces and the comparatively small kinetic energy only results in the molecules jiggling in place when thermally excited. Again, in a solid, the molecules are packed so closely together that the volume of the solid is essentially that of the sum of the molecular volumes of all of the molecules in it. Liquids represent a situation where molecular attraction and kinetic energy are balanced and the spacing between molecules is higher than in solids but much less than in gases.

At high temperatures and low pressures, where the kinetic energy and the spacing between molecules are both large, one may neglect both the miniscule attractive forces and molecular volume. Under such conditions the properties of the gas, the pressure, P, volume, V, number of moles, n, and the temperature, T are independent of the mixture of molecules in the gas. In that limit the behavior of the gas is called ideal, and governed by the ideal gas law

No gases are truly ideal, but while no model is perfect, some are useful, and under most commonly encountered conditions, the ideal gas law is very useful indeed to describe the behavior of gases. It is also easy to predict that the conditions where the ideal gas law would have trouble describing the behavior of a gas would be low temperature (small molecular kinetic energy) and high pressure (little space between molecules). The behavior of gases under such conditions becomes increasingly like that of liquids and will be discussed in the next chapter.

The Ideal Gas Law

The ideal gas law

$$PV = nRT$$

relates the pressure, volume, temperature and number of moles in a gas to each other. R is a constant called the gas constant. The ideal gas law is what is called an equation of state because it is a complete description of the gas's thermodynamic state. No other information is needed to calculate any other thermodynamic variable, and, since the equation relates four variables, a knowledge of any three of them is sufficient.

Pressure, volume and number of moles, the latter sometime called extent, share an important property, they can never be negative. What would a negative volume be, or an absolute negative pressure or extent? The concepts do not even exist. This means that temperature in the ideal gas law is similarly limited. **It can never be negative.**

We can determine what zero temperature on the ideal gas scale is by holding the number of moles and the pressure constant and extrapolate the temperature measured in Celcius to what its value would be at zero volume

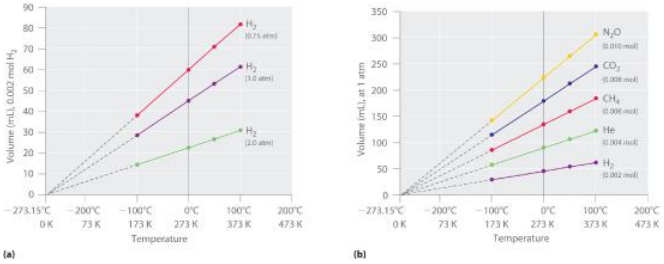


Figure 6.3.1 *The Relationship between Volume and Temperature (a) In these plots of volume versus temperature for equal-sized samples of H_2 at three different pressures, the solid lines show the experimentally measured data down to −100°C, and the broken lines show the extrapolation of the data to V = 0. The temperature scale is given in both degrees Celsius and Kelvin. Although the slopes of the lines decrease with increasing pressure, all of the lines extrapolate to the same temperature at V = 0 (−273.15°C = 0*

K). (b) In these plots of volume versus temperature for different amounts of selected gases at 1 atm pressure, all the plots extrapolate to a value of V = 0 at −273.15°C, regardless of the identity or the amount of the gas.

The extrapolated temperature corresponding to zero volume at constant pressure and amount is -273.15 °C, which is called absolute zero because no lower temperature is possible (unless, of course you can come up with a negative volumes, but you cannot). For convenience we set the degrees on the Kelvin scale to the size of the degree on the Celcius scale. In other words

$$1\ K = 1^oC$$

Note the Pattern

Before we can use the ideal gas law, however, we need to know the value of the gas constant *R*. Its form depends on the units used for the other quantities in the expression. If *V* is expressed in liters (L), *P* in atmospheres (atm), *T* in kelvins (K), and *n* in moles (mol), then

$$R = 0.08206\ L \cdot atm/\left(K \cdot \cdot mol\right)$$

Because the product *PV* has the units of energy, *R* can also have units of J/(K·mol) or cal/(K·mol):

$$R = 8.3145\ J/\left(K \cdot mol\right) = 1.9872 cal/\left(K \cdot mol\right)$$

Scientists have chosen a particular set of conditions to use as a reference: 0°C (273.15 K) and 1 atm pressure, referred to as standard temperature and pressure (STP) The conditions 0°C (273.15 K) and 1 atm pressure for a gas.

We can calculate the volume of 1.000 mol of an ideal gas under standard conditions using the variant of the ideal gas law given in Equation 6.3.1:

$$V = \frac{nRT}{P} = \frac{\left(1.000\ \cancel{mol}\left(0.082057\ L \cdot \cancel{atm}/\cancel{K} \cdot \cancel{mol}\right)\right)\left(273.15\ \cancel{K}\right)}{1.000\ \cancel{atm}} = 22.31\ L$$

Thus the volume of 1 mol of an ideal gas at 0°C and 1 atm pressure is 22.41 L, approximately equivalent to the volume of three basketballs. The quantity 22.41 L is called the standard molar volumeThe volume of 1 mol of an ideal gas at STP (0°C and 1 atm pressure), which is 22.41 L. of an ideal gas. The molar volumes of several real gases at STP are given in Table 6.3.1, which shows that the deviations from ideal gas behavior are quite small. Thus the ideal gas law does a good job of approximating the behavior of real gases at STP.

Table 6.3.1 *Molar Volumes of Selected Gases at Standard Temperature (0°C) and Pressure (1 atm)*

Gas	Molar Volume (L)
He	22.434
Ar	22.397
H_2	22.433
N_2	22.402
O_2	22.397
CO_2	22.260
NH_3	22.079

Applying the Ideal Gas Law

The ideal gas law allows us to calculate the value of the fourth variable for a gaseous sample if we know the values of any three of the four variables (*P*, *V*, *T*, and *n*). It also allows us to predict the *final state* of a sample of a gas (i.e., its final temperature, pressure, volume, and amount) following any changes in conditions if the parameters (*P*, *V*, *T*, and *n*) are specified for an *initial state*. Some applications are illustrated in the following examples. The approach used throughout is always to start with the same equation—the ideal gas law—and then determine which quantities are given and which need to be calculated. Let's begin with simple cases in which we are given three of the four parameters needed for a complete physical description of a gaseous sample.

Example 6.3.1

The balloon that Charles used for his flight in 1783 was destroyed, but we can estimate that its volume was 31,150 L (1100 ft^3), given the dimensions recorded at the time. If the temperature at ground level was 86°F (30°C) and the atmospheric pressure was 745 mmHg, how many moles of hydrogen gas were needed to fill the balloon?

Given: volume, temperature, and pressure

Asked for: amount of gas

Strategy:

A Solve the ideal gas law for the unknown quantity, in this case *n*.

B Make sure that all quantities are given in units that are compatible with the units of the gas constant. If necessary, convert them to the appropriate units, insert them into the equation you have derived, and then calculate the number of moles of hydrogen gas needed.

Solution:

A We are given values for *P*, *T*, and *V* and asked to calculate *n*. If we solve the ideal gas law (Equation 6.3.1) for *n*, we obtain

$$n = \frac{PV}{RT}$$

B *P* and *T* are given in units that are not compatible with the units of the gas constant [*R* = 0.082057 (L·atm)/(K·mol)]. We must therefore convert the temperature to kelvins and the pressure to atmospheres:

$$745 \cancel{\text{ Torr}} \times \frac{1 \text{ atm}}{760 \cancel{\text{ Torr}}} = 0.980 \text{ atm} \qquad \text{(Chapter 6.3.1)}$$

$$T = 273 + 30 = 303\text{K} \qquad \text{(Chapter 6.3.2)}$$

Substituting these values into the expression we derived for *n*, we obtain

$$n = \frac{PV}{RT} = \frac{0.980 \cancel{\text{ atm}} \times 31150 \cancel{\text{ L}}}{0.08206 \frac{\cancel{\text{atm}} \cdot \cancel{\text{L}}}{\text{mol} \cdot \cancel{\text{K}}} \times 303 \cancel{\text{ K}}} = 1.23 \times 10^3 \text{ mol} \qquad \text{(Chapter 6.3.3)}$$

Exercise

Suppose that an “empty” aerosol spray-paint can has a volume of 0.406 L and contains 0.025 mol of a propellant gas such as CO_2. What is the pressure of the gas at 25°C?

Answer: 1.5 atm

In Example 5, we were given three of the four parameters needed to describe a gas under a particular set of conditions, and we were asked to calculate the fourth. We can also use the ideal gas law to calculate the effect of *changes* in any of the specified conditions on any of the other parameters, as shown in Example 6.

Using the Ideal Gas Law to Calculate Gas Densities and Molar Masses

The ideal gas law can also be used to calculate molar masses of gases from experimentally measured gas densities. To see how this is possible, we first rearrange the ideal gas law to obtain

$$\frac{n}{V} = \frac{P}{RT} \qquad (6.3.6)$$

The left side has the units of moles per unit volume (mol/L). The number of moles of a substance equals its mass (*m*, in grams) divided by its molar mass (*M*, in grams per mole):

$$n = \frac{m}{M} \qquad (6.3.7)$$

Substituting this expression for *n* into Equation 6.3.6 gives

$$\frac{m}{MV} = \frac{P}{RT} \tag{6.3.8}$$

Because m/V is the density d of a substance, we can replace m/V by d and rearrange to give

$$d = \frac{m}{V} = \frac{MP}{RT} \tag{6.3.9}$$

The distance between particles in gases is large compared to the size of the particles, so their densities are much lower than the densities of liquids and solids. Consequently, gas density is usually measured in grams per liter (g/L) rather than grams per milliliter (g/mL).

Example 6.3.2

Calculate the density of butane at 25°C and a pressure of 750 mmHg.

Given: compound, temperature, and pressure

Asked for: density

Strategy:

A Calculate the molar mass of butane and convert all quantities to appropriate units for the value of the gas constant.

B Substitute these values into Equation 6.3.9 to obtain the density.

Solution:

A The molar mass of butane (C_4H_{10}) is

$$(4)(12.011) + (10)(1.0079) = 58.123\ g/mol$$

Using 0.082057 (L·atm)/(K·mol) for R means that we need to convert the temperature from degrees Celsius to kelvins (T = 25 + 273 = 298 K) and the pressure from millimeters of mercury to atmospheres:

$$P = 750\ \text{mmHg} \times \frac{1\ \text{atm}}{760\ \text{Torr}} = 0.987\ \text{atm} \tag{Chapter 6.3.4}$$

B Substituting these values into Equation 6.3.9 gives

$$d = \frac{58.123\ \text{g/mol} \times 0.987\ \text{atm}}{0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 298\ \text{K}} = 2.35\ \text{g/L} \tag{Chapter 6.3.5}$$

Exercise

Radon (Rn) is a radioactive gas formed by the decay of naturally occurring uranium in rocks such as granite. It tends to collect in the basements of houses and poses a significant health risk if present in indoor air. Many states now require that houses be tested for radon before they are sold. Calculate the density of radon at 1.00 atm pressure and 20°C and compare it with the density of nitrogen gas, which constitutes 80% of the atmosphere, under the same conditions to see why radon is found in basements rather than in attics.

Answer: radon, 9.23 g/L; N_2, 1.17 g/L

A common use of Equation 6.3.9 is to determine the molar mass of an unknown gas by measuring its density at a known temperature and pressure. This method is particularly useful in identifying a gas that has been produced in a reaction, and it is not difficult to carry out. A flask or glass bulb of known volume is carefully dried, evacuated, sealed, and weighed empty. It is then filled with a sample of a gas at a known temperature and pressure and re-weighed. The difference in mass between the two readings is the mass of the gas. The volume of the flask is usually determined by weighing the flask when empty and when filled with a liquid of known density such as water. The use of density measurements to calculate molar masses is illustrated in Example 10.

Example 6.3.3

The reaction of a copper penny with nitric acid results in the formation of a red-brown gaseous compound containing nitrogen and oxygen. A sample of the gas at a pressure of 727 mmHg and a temperature of 18°C weighs 0.289 g in a flask with a volume of

157.0 mL. Calculate the molar mass of the gas and suggest a reasonable chemical formula for the compound.

Given: pressure, temperature, mass, and volume

Asked for: molar mass and chemical formula

Strategy:

A Solve Equation 6.3.9 for the molar mass of the gas and then calculate the density of the gas from the information given.

B Convert all known quantities to the appropriate units for the gas constant being used. Substitute the known values into your equation and solve for the molar mass.

C Propose a reasonable empirical formula using the atomic masses of nitrogen and oxygen and the calculated molar mass of the gas.

Solution:

A Solving Equation 6.3.9 for the molar mass gives

$$M = \frac{mRT}{PV} = \frac{dRT}{P} \tag{Chapter 6.3.6}$$

Density is the mass of the gas divided by its volume:

$$d = \frac{m}{V} = \frac{0.289\text{g}}{0.17\text{L}} = 1.84\text{g/L} \tag{Chapter 6.3.7}$$

B We must convert the other quantities to the appropriate units before inserting them into the equation:

$$T = 18 + 273 = 291K \tag{Chapter 6.3.8}$$

$$P = 727\text{Torr} \times \frac{1\text{atm}}{760\text{Torr}} = 0.957\text{atm} \tag{Chapter 6.3.9}$$

The molar mass of the unknown gas is thus

$$d = \frac{1.84\text{ g/L} \times 0.08206\dfrac{\text{L}\cdot\text{atm}}{\text{K}\cdot\text{mol}} \times 291\text{ K}}{0.957\text{ atm}} = 45.9\text{g/mol} \tag{Chapter 6.3.10}$$

C The atomic masses of N and O are approximately 14 and 16, respectively, so we can construct a list showing the masses of possible combinations:

$$M(\text{NO}) = 14 + 16 = 30\text{ g/mol} \tag{Chapter 6.3.11}$$

$$M(\text{N}_2\text{O}) = (2)(14) + 16 = 44\text{ g/mol} \tag{Chapter 6.3.12}$$

$$M(\text{NO}_2) = 14 + (2)(16) = 46\text{ g/mol} \tag{Chapter 6.3.13}$$

The most likely choice is NO_2 which is in agreement with the data. The red-brown color of smog also results from the presence of NO_2 gas.

Exercise

You are in charge of interpreting the data from an unmanned space probe that has just landed on Venus and sent back a report on its atmosphere. The data are as follows: pressure, 90 atm; temperature, 557°C; density, 58 g/L. The major constituent of the atmosphere (>95%) is carbon. Calculate the molar mass of the major gas present and identify it.

Answer: 44 g/mol; CO_2

Summary

The empirical relationships among the volume, the temperature, the pressure, and the amount of a gas can be combined into the **ideal gas law**, $PV = nRT$. The proportionality constant, R, is called the **gas constant** and has the value 0.08206 (L·atm)/(K·mol), 8.3145 J/(K·mol), or 1.9872 cal/(K·mol), depending on the units used. The ideal gas law describes the behavior of an **ideal gas**, a hypothetical substance whose behavior can be explained quantitatively by the ideal gas law and the kinetic molecular theory of gases. **Standard temperature and pressure (STP)** is 0°C and 1 atm. The volume of 1 mol of an ideal gas at STP is 22.41 L, the **standard molar volume**. All of the empirical gas relationships are special cases of the ideal gas law in which two of the four parameters are held constant. The ideal gas law allows us to calculate the value of the fourth quantity (P, V, T, or n) needed to describe a gaseous sample when the others are known and also predict the value of these quantities following a change in conditions if the original conditions (values of P, V, T, and n) are known. The ideal gas law can also be used to calculate the density of a gas if its molar mass is known or, conversely, the molar mass of an unknown gas sample if its density is measured.

Key Takeaway

- The ideal gas law is derived from empirical relationships among the pressure, the volume, the temperature, and the number of moles of a gas; it can be used to calculate any of the four properties if the other three are known.

Key Equations

Ideal gas law

Equation 6.3.1: $PV = nRT$

where $R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} = 8.3145 \frac{\text{J}}{\text{K} \cdot \text{mol}}$

Density of a gas

Equation 6.3.9: $d = \frac{MP}{RT}$

Conceptual Problems

1. For an ideal gas, is volume directly proportional or inversely proportional to temperature? What is the volume of an ideal gas at absolute zero?
2. What is meant by STP? If a gas is at STP, what further information is required to completely describe the state of the gas?
3. Given the following initial and final values, what additional information is needed to solve the problem using the ideal gas law?

Given	Solve for
V_1, T_1, T_2, n_1	n_2
P_1, P_2, T_2, n_2	n_1
T_1, T_2	V_2
P_1, n_1	P_2

4. Given the following information and using the ideal gas law, what equation would you use to solve the problem?

Given	Solve for
P_1, P_2, T_1	T_2
V_1, n_1, n_2	V_2
T_1, T_2, V_1, V_2, n_2	n_1

5. Using the ideal gas law as a starting point, derive the relationship between the density of a gas and its molar mass. Which would you expect to be denser—nitrogen or oxygen? Why does radon gas accumulate in basements and mine shafts?
6. Use the ideal gas law to derive an equation that relates the remaining variables for a sample of an ideal gas if the following are held constant.
    1. amount and volume
    2. pressure and amount
    3. temperature and volume
    4. temperature and amount
    5. pressure and temperature
7. Tennis balls that are made for Denver, Colorado, feel soft and do not bounce well at lower altitudes. Use the ideal gas law to explain this observation. Will a tennis ball designed to be used at sea level be harder or softer and bounce better or worse at higher altitudes?

Answer

1.
2.
3.
4.
5.
6. 1. P/T = constant
    2. V/T = constant (Charles' law)
    3. P/n = constant
    4. PV = constant (Boyle's law)
    5. V/n = constant (Avogadro's law)
7.

Numerical Problems

1. Calculate the number of moles in each sample at STP.
    1. 1580 mL of NO_2
    2. 847 cm^3 of HCl
    3. 4.792 L of H_2
    4. a 15.0 cm × 6.7 cm × 7.5 cm container of ethane
2. Calculate the number of moles in each sample at STP.
    1. 2200 cm^3 of CO_2
    2. 1200 cm^3 of N_2
    3. 3800 mL of SO_2
    4. 13.75 L of NH_3
3. Calculate the mass of each sample at STP.
    1. 36 mL of HI
    2. 550 L of H_2S
    3. 1380 cm^3 of CH_4
4. Calculate the mass of each sample at STP.
    1. 3.2 L of N_2O
    2. 65 cm^3 of Cl_2
    3. 3600 mL of HBr
5. Calculate the volume in liters of each sample at STP.

1. 1.68 g of Kr
2. 2.97 kg of propane (C_3H_8)
3. 0.643 mg of $(CH_3)_2O$

6. Calculate the volume in liters of each sample at STP.
   1. 3.2 g of Xe
   2. 465 mg of CS_2
   3. 5.34 kg of acetylene (C_2H_2)
7. Calculate the volume of each gas at STP.
   1. 1.7 L at 28°C and 96.4 kPa
   2. 38.0 mL at 17°C and 103.4 torr
   3. 650 mL at −15°C and 723 mmHg
8. Calculate the volume of each gas at STP.
   1. 2.30 L at 23°C and 740 mmHg
   2. 320 mL at 13°C and 97.2 kPa
   3. 100.5 mL at 35°C and 1.4 atm
9. One method for preparing hydrogen gas is to pass HCl gas over hot aluminum; the other product of the reaction is $AlCl_3$. If you wanted to use this reaction to fill a balloon with a volume of 28,500 L at sea level and a temperature of 78°F, what mass of aluminum would you need? What volume of HCl at STP would you need?
10. An 3.50 g sample of acetylene is burned in excess oxygen according to the following reaction:

    $2\ C_2H_2(g) + 5\ O_2(g) \rightarrow 4\ CO_2(g) + 2\ H_2O(l)$

    At STP, what volume of $CO_2(g)$ is produced?
11. Calculate the density of ethylene (C_2H_4) under each set of conditions.
    1. 7.8 g at 0.89 atm and 26°C
    2. 6.3 mol at 102.6 kPa and 38°C
    3. 9.8 g at 3.1 atm and −45°C
12. Determine the density of O_2 under each set of conditions.
    1. 42 g at 1.1 atm and 25°C
    2. 0.87 mol at 820 mmHg and 45°C
    3. 16.7 g at 2.4 atm and 67°C
13. At 140°C, the pressure of a diatomic gas in a 3.0 L flask is 635 kPa. The mass of the gas is 88.7 g. What is the most likely identity of the gas?
14. What volume must a balloon have to hold 6.20 kg of H_2 for an ascent from sea level to an elevation of 20,320 ft, where the temperature is −37°C and the pressure is 369 mmHg?
15. What must be the volume of a balloon that can hold 313.0 g of helium gas and ascend from sea level to an elevation of 1.5 km, where the temperature is 10.0°C and the pressure is 635.4 mmHg?
16. The average respiratory rate for adult humans is 20 breaths per minute. If each breath has a volume of 310 mL of air at 20°C and 0.997 atm, how many moles of air does a person inhale each day? If the density of air is 1.19 kg/m^3, what is the average molecular mass of air?

Answers

1. 1. 7.05×10^{-2} mol
   2. 3.78×10^{-2} mol
   3. 0.2138 mol

4. 3.4×10^{-2} mol

2.

3. 1. 0.21 g HI;
   2. 840 g H_2S;
   3. 0.988 g CH_4

4.

5. 1. 0.449 L Kr
   2. 1510 L C_3H_8
   3. 3.13×10^{-4} L $(CH_3)_2O$

6.

7. 1. 1.5 L
   2. 4.87 mL
   3. 650 mL

8.

9. 281 mmHg

10.

11.

12. 1. 1.0 g/L
    2. 1.1 g/L
    3. 4.6 g/L

13.

14.

15.

16. 2174

17.

Contributors

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Chapter 6.4: The Combined Gas Law

Learning Objective

- To understand the relationships among pressure, temperature, volume, and the amount of a gas.

We often encounter cases where two of the variables *P*, *V*, n and *T* are allowed to vary for a given sample of gas, and we are interested in the change in the value of the third under the new conditions. If we rearrange the ideal gas law so that *P*, *V*, and *T*, the quantities that change, are on one side and the constant terms (*R* and *n* for a given sample of gas) are on the other, we obtain

$$\frac{PV}{T} = nR = constant$$

Thus the quantity *PV*/n*T* is constant

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

In many of these problems one considers the changes in a sample of gas where the number of moles does not change. In such a case one can write the relationship as

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

If two of the parameters specifying the thermodynamic state of the gas sample are held constant, one recovers simple proportional relationships among the other two which were experimentally observed centuries ago by

Robert Boyle

$$V \propto \frac{1}{P}\,(at\ constant\ n,\ V)$$

expresses the idea that at constant composition (e.g. the number of moles of gas) and temperature the product PV is a constant.

Jacques Charles and Joseph-Louis Gay-Lussac

$$V \propto T\,(at\ constant\ n, P)$$

expresses the idea that at constant composition (e.g. the number of moles of gas) and pressure the ratio V/T is a constant. Using Boyle's law this also can be written as P/T being constant

Amedeo Avogadro

$$V \propto n\,(at\ constant\ T, P)$$

In its original formulation, Avogadro's law stated that equal volumes of gas at constant temperature and pressure held the same number of molecules

Brief descriptions of these scientists work are found at the end of this section.

Example 6.4.1

Charles originally observed the change of volume with temperature in balloon ascents and descents that he made. Suppose that Charles had changed his plans and carried out his initial flight not in August but on a cold day in January, when the temperature at ground level was −10°C. How large a balloon would he have needed to contain the same amount of hydrogen gas at the same pressure as in Example 5?

Given: temperature, pressure, amount, and volume in August; temperature in January

Asked for: volume in January

Strategy:

A Use the results from Example 5 for August as the initial conditions and then calculate the *change in volume* due to the change in temperature from 86°F to 14°F. Begin by constructing a table showing the initial and final conditions.

B Rearrange the ideal gas law to isolate those quantities that differ between the initial and final states on one side of the equation, in this case *V* and *T*.

C Equate the ratios of those terms that change for the two sets of conditions. Making sure to use the appropriate units, insert the quantities and solve for the unknown parameter.

Solution:

A To see exactly which parameters have changed and which are constant, prepare a table of the initial and final conditions:

	August (initial)	January (final)
T	30°C = 303 K	−10°C = 263 K
P	0.980 atm	0.980 atm
n	1.23×10^3 mol H_2	1.23×10^3 mol H_2
V	31,150 L	?

Thus we are asked to calculate the effect of a change in temperature on the volume of a fixed amount of gas at constant pressure.

B Both n and P are the same in both cases ($n_i = n_f, P_i = P_f$). Therefore, Equation 6.4.3 can be simplified to:

$$\frac{V_i}{T_i} = \frac{V_f}{T_f} \tag{Chapter 6.4.1}$$

This is the relationship first noted by Charles.

C Solving the equation for V_f, we get:

$$V_f = V_i \times \frac{T_f}{T_i} = 31150\ \text{L} \times \frac{263\ \text{K}}{303\ \text{K}} = 2.70 \times 10^4\ \text{L} \tag{Chapter 6.4.2}$$

It is important to check your answer to be sure that it makes sense, just in case you have accidentally inverted a quantity or multiplied rather than divided. In this case, the temperature of the gas decreases. Because we know that gas volume decreases with decreasing temperature, the final volume must be less than the initial volume, so the answer makes sense. We could have calculated the new volume by plugging all the given numbers into the ideal gas law, but it is generally much easier and faster to focus on only the quantities that change.

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Exercise

At a laboratory party, a helium-filled balloon with a volume of 2.00 L at 22°C is dropped into a large container of liquid nitrogen (T = −196°C). What is the final volume of the gas in the balloon?

Answer: 0.52 L

Example 8 illustrates the relationship originally observed by Charles. We could work through similar examples illustrating the inverse relationship between pressure and volume noted by Boyle (PV = constant) and the relationship between volume and amount observed by Avogadro (V/n = constant). We will not do so for all cases, however, because it is more important to note that the historically important gas laws are only special cases of the ideal gas law in which two quantities are varied while the other two remain fixed. The method used in Example 8 can be applied in *any* such case, as we demonstrate in Example 9 (which also shows why heating a closed container of a gas, such as a butane lighter cartridge or an aerosol can, may cause an explosion).

Example 6.4.2

Aerosol cans are prominently labeled with a warning such as “Do not incinerate this container when empty.” Assume that you did not notice this warning and tossed the “empty” aerosol can in Exercise 5 (0.025 mol in 0.406 L, initially at 25°C and 1.5 atm

internal pressure) into a fire at 750°C. What would be the pressure inside the can (if it did not explode)?

Given: initial volume, amount, temperature, and pressure; final temperature

Asked for: final pressure

Strategy:

Follow the strategy outlined in Example 8.

Solution:

Prepare a table to determine which parameters change and which are held constant:

	Initial	Final
V	0.406 L	0.406 L
n	0.025 mol	0.025 mol
T	25°C = 298 K	750°C = 1023 K
P	1.5 atm	?

Once again, two parameters are constant while one is varied, and we are asked to calculate the fourth. As before, we begin with the ideal gas law and rearrange it as necessary to get all the constant quantities on one side. In this case, because V and n are constant, we rearrange to obtain

$$P = \left(\frac{nR}{V}\right)(T) = constant \times T$$

Dividing both sides by T, we obtain an equation analogous to the one in Example 6, $P/T = nR/V$ = constant. Thus the ratio of P to T does not change if the amount and volume of a gas are held constant. We can thus write the relationship between any two sets of values of P and T for the same sample of gas at the same volume as

$$\frac{P_i}{T_i} = \frac{P_f}{T_f}$$

In this example, P_i = 1.5 atm, T_i = 298 K, and T_f = 1023 K, and we are asked to find P_f. Solving for P_f and substituting the appropriate values, we obtain

$$P_f = P_i \times \frac{T_f}{T_i} = 1.5 \text{ atm} \times \frac{1023 \text{ K}}{298 \text{ K}} = 5.1 \text{ atm} \quad \text{(Chapter 6.4.3)}$$

This pressure is more than enough to rupture a thin sheet metal container and cause an explosion!

Exercise

Suppose that a fire extinguisher, filled with CO_2 to a pressure of 20.0 atm at 21°C at the factory, is accidentally left in the sun in a closed automobile in Tucson, Arizona, in July. The interior temperature of the car rises to 160°F (71.1°C). What is the internal pressure in the fire extinguisher?

Answer: 23.4 atm

Example 6.4.3

We saw in Example 5 that Charles used a balloon with a volume of 31,150 L for his initial ascent and that the balloon contained 1.23×10^3 mol of H_2 gas initially at 30°C and 745 Torr. Suppose that Gay-Lussac had also used this balloon for his record-breaking ascent to 23,000 ft and that the pressure and temperature at that altitude were 312 Torr and −30°C, respectively. To what volume would the balloon have had to expand to hold the same amount of hydrogen gas at the higher altitude?

Given: initial pressure, temperature, amount, and volume; final pressure and temperature

Asked for: final volume

Strategy:

Follow the strategy outlined in Example 6.

Solution:

Begin by setting up a table of the two sets of conditions:

	Initial	Final
P	745 Torr = 0.980 atm	312 Torr = 0.411 atm
T	30°C = 303 K	−30°C = 243 K
n	1.23×10^3 mol H_2	1.23×10^3 mol H_2
V	31,150 L	?

Thus all the quantities except V_2 are known. Solving Equation 6.4.3 for V_2 and substituting the appropriate values give

$$V_f = V_i \times \frac{P_i}{P_f}\frac{T_f}{T_i} \qquad \text{(Chapter 6.4.4)}$$

$$= 3.115 \times 10^4 \text{ L} \times \frac{0.980 \cancel{\text{ atm}}}{0.411 \cancel{\text{ atm}}}\frac{243 \cancel{\text{ K}}}{303 \cancel{\text{ K}}} = 5.96 \times 10^4 \text{ L}$$

Does this answer make sense? Two opposing factors are at work in this problem: decreasing the pressure tends to *increase* the volume of the gas, while decreasing the temperature tends to *decrease* the volume of the gas. Which do we expect to predominate? The pressure drops by more than a factor of two, while the absolute temperature drops by only about 20%. Because the volume of a gas sample is directly proportional to both T and $1/P$, the variable that changes the most will have the greatest effect on V. In this case, the effect of decreasing pressure predominates, and we expect the volume of the gas to increase, as we found in our calculation.

We could also have solved this problem by solving the ideal gas law for V and then substituting the relevant parameters for an altitude of 23,000 ft:

$$V = \frac{nRT}{P} = \frac{\left(1.23 \times 10^3 \cancel{\text{ mol}}\right)\left[0.082057 \left(L \cdot \cancel{\text{atm}}\right) / \left(\cancel{K} \cdot \cancel{\text{mol}}\right)\right]\left(243 \cancel{K}\right)}{0.411 \cancel{\text{ atm}}} = 5.97 \times 10^4 L$$

Except for a difference caused by rounding to the last significant figure, this is the same result we obtained previously. *There is often more than one "right" way to solve chemical problems.*

Exercise

A steel cylinder of compressed argon with a volume of 0.400 L was filled to a pressure of 145 atm at 10°C. At 1.00 atm pressure and 25°C, how many 15.0 mL incandescent light bulbs could be filled from this cylinder? (Hint: find the number of moles of argon in each container.)

Answer: 4.07×10^3

The Relationship between Pressure and Volume

As the pressure on a gas increases, the volume of the gas decreases because the gas particles are forced closer together. Conversely, as the pressure on a gas decreases, the gas volume increases because the gas particles can now move farther apart. Weather balloons get larger as they rise through the atmosphere to regions of lower pressure because the volume of the gas has increased; that is, the atmospheric gas exerts less pressure on the surface of the balloon, so the interior gas expands until the internal and external pressures are equal.

Robert Boyle (1627–1691)

Boyle, the youngest (and 14th!) child of the Earl of Cork, was an important early figure in chemistry whose views were often at odds with accepted wisdom. Boyle's studies of gases are reported to have utilized a very tall J-tube that he set up in the entryway of his house, which was several stories tall. He is known for the gas law that bears his name and for his book, *The Sceptical Chymist*,

which was published in 1661 and influenced chemists for many years after his death. In addition, one of Boyle's early essays on morals is said to have inspired Jonathan Swift to write *Gulliver's Travels*.

The Irish chemist Robert Boyle (1627–1691) carried out some of the earliest experiments that determined the quantitative relationship between the pressure and the volume of a gas. Boyle used a J-shaped tube partially filled with mercury, as shown in Figure 6.4.1. In these experiments, a small amount of a gas or air is trapped above the mercury column, and its volume is measured at atmospheric pressure and constant temperature. More mercury is then poured into the open arm to increase the pressure on the gas sample. The pressure on the gas is atmospheric pressure *plus* the difference in the heights of the mercury columns, and the resulting volume is measured. This process is repeated until either there is no more room in the open arm or the volume of the gas is too small to be measured accurately. Data such as those from one of Boyle's own experiments may be plotted in several ways (Figure 6.4.2). A simple plot of V versus P gives a curve called a *hyperbola* and reveals an *inverse* relationship between pressure and volume: as the pressure is doubled, the volume decreases by a factor of two. This relationship between the two quantities is described as follows:

$$PV = constant$$

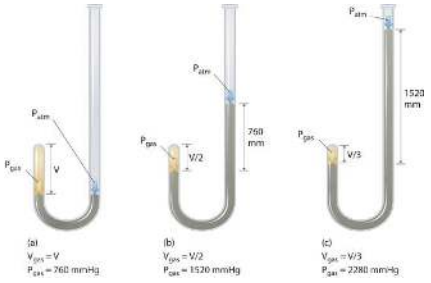
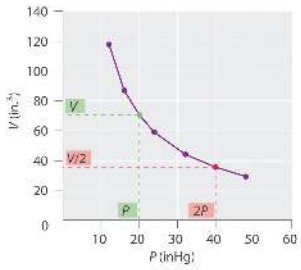


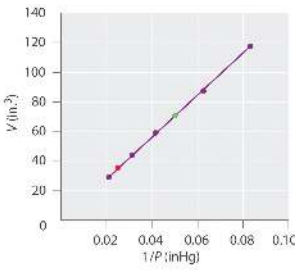
Figure 6.4.1 Boyle's Experiment Using a J-Shaped Tube to Determine the Relationship between Gas Pressure and Volume *(a) Initially the gas is at a pressure of 1 atm = 760 Torr (the mercury is at the same height in both the arm containing the sample and the arm open to the atmosphere); its volume is V. (b) If enough mercury is added to the right side to give a difference in height of 760 Torr between the two arms, the pressure of the gas is 760 mmHg (atmospheric pressure) + 760 mmHg = 1520 mmHg and the volume is V/2. (c) If an additional 760 Torr is added to the column on the right, the total pressure on the gas increases to 2280 Torr, and the volume of the gas decreases to V/3.*

P (inHg)	V (in.^{3})	PV
12.0	117.5	1410
16.0	87.2	1400
20.0	70.7	1410
24.0	58.8	1410
32.0	44.2	1410
40.0	35.3	1410
48.0	29.1	1400

(a) Data from Boyle's experiment



(b) Volume vs. pressure



(c) Volume vs. 1/pressure

Figure6.4.2 Plots of Boyle's Data *(a) Here are actual data from a typical experiment conducted by Boyle. Boyle used non-SI units to measure the volume (in.^{3} rather than cm^3) and the pressure (in. Hg rather than Torr). (b) This plot of pressure versus volume is a hyperbola. Because PV is a constant, decreasing the pressure by a factor of two results in a twofold increase in volume and vice versa. (c) A plot of volume versus 1/pressure for the same data shows the inverse linear relationship between the two quantities, as expressed by the equation V = constant/P.*

Dividing both sides by P gives an equation illustrating the inverse relationship between P and V:

$$V = \frac{constant}{P} = constant\left(\frac{1}{P}\right) \; or \; V \propto \frac{1}{P}$$

where the ∝ symbol is read "is proportional to." A plot of V versus $1/P$ is thus a straight line whose slope is equal to the constant in Equation 6.4.7. Dividing both sides of Equation 6.4.7 by V instead of P gives a similar relationship between P and $1/V$. The numerical value of the constant depends on the amount of gas used in the experiment and on the temperature at which the experiments are carried out. This relationship between pressure and volume is known as Boyle's lawA law that states that at

constant temperature, the volume of a fixed amount of a gas is inversely proportional to its pressure., after its discoverer, and can be stated as follows: *At constant temperature, the volume of a fixed amount of a gas is inversely proportional to its pressure.*

The Relationship between Temperature and Volume

Hot air rises, which is why hot-air balloons ascend through the atmosphere and why warm air collects near the ceiling and cooler air collects at ground level. Because of this behavior, heating registers are placed on or near the floor, and vents for air-conditioning are placed on or near the ceiling. The fundamental reason for this behavior is that gases expand when they are heated. Because the same amount of substance now occupies a greater volume, hot air is less dense than cold air. The substance with the lower density —in this case hot air—rises through the substance with the higher density, the cooler air.

The first experiments to quantify the relationship between the temperature and the volume of a gas were carried out in 1783 by an avid balloonist, the French chemist Jacques Alexandre César Charles (1746–1823). Charles's initial experiments showed that a plot of the volume of a given sample of gas versus temperature (in degrees Celsius) at constant pressure is a straight line. Similar but more precise studies were carried out by another balloon enthusiast, the Frenchman Joseph-Louis Gay-Lussac (1778–1850), who showed that a plot of V versus T was a straight line that could be extrapolated to a point at zero volume, a theoretical condition now known to correspond to −273.15°C (Figure 9.3.1) or absolute zero. A sample of a real gas cannot *really* have a volume of zero because any sample of matter must have *some* volume. Furthermore, at 1 atm pressure all gases liquefy at temperatures well above −273.15°C. However, the ideal gas model does allow for reaching absolute zero, but the second law of thermodynamics, which will be discussed in Unit 7, makes this impossible.

Jacques Alexandre César Charles (1746–1823) and Joseph-Louis Gay-Lussac (1778–1850)

In 1783, Charles filled a balloon ("aerostatic globe") with hydrogen (generated by the reaction of iron with more than 200 kg of acid over several days) and flew successfully for almost an hour. When the balloon descended in a nearby village, however, the terrified townspeople destroyed it. In 1804, Gay-Lussac managed to ascend to 23,000 ft (more than 7000 m) to collect samples of the atmosphere to analyze its composition as a function of altitude. In the process, he had trouble breathing and nearly froze to death, but he set an altitude record that endured for decades. (To put Gay-Lussac's achievement in perspective, recall that modern jetliners cruise at only 35,000 ft!)

We can state Charles's and Gay-Lussac's findings in simple terms: *At constant pressure, the volume of a fixed amount of gas is directly proportional to its absolute temperature (in Kelvin).* This relationship is often referred to as Charles's law

Charles's law is valid for virtually all gases at temperatures well above their boiling points. *Note that the temperature must be expressed in kelvins,* not *in degrees Celsius.*

The Relationship between Amount and Volume

We can demonstrate the relationship between the volume and the amount of a gas by filling a balloon; as we add more gas, the balloon gets larger. The specific quantitative relationship was discovered by the Italian chemist Amedeo Avogadro, who recognized the importance of Gay-Lussac's work on combining volumes of gases. In 1811, Avogadro postulated that, at the same temperature and pressure, equal volumes of gases contain the same number of gaseous particles. (This is the historic "Avogadro's hypothesis" introduced in Chapter 1 .) A logical corollary, sometimes called Avogadro's lawA law that states that at constant temperature and pressure, the volume of a sample of gas is directly proportional to the number of moles of gas in the sample., describes the relationship between the volume and the amount of a gas: *At constant temperature and pressure, the volume of a sample of gas is directly proportional to the number of moles of gas in the sample.* Stated mathematically,

$$V = (constant)\,(n) \text{ or } V \propto n \text{ (at constant } T \text{ and } P)$$

This relationship is valid for most gases at relatively low pressures, but deviations from strict linearity are observed at elevated pressures.

Summary

Boyle showed that the volume of a sample of a gas is inversely proportional to its pressure (**Boyle's law**), Charles and Gay-Lussac demonstrated that the volume of a gas is directly proportional to its temperature (in kelvins) at constant pressure (**Charles's law**), and Avogadro postulated that the volume of a gas is directly proportional to the number of moles of gas present (**Avogadro's law**).

Plots of the volume of gases versus temperature extrapolate to zero volume at −273.15°C, which is **absolute zero (0 K)**, the lowest temperature possible. Charles's law implies that the volume of a gas is directly proportional to its absolute temperature.

Key Takeaway

- The volume of a gas is inversely proportional to its pressure and directly proportional to its temperature and the amount of gas.

Conceptual Problems

1. Sketch a graph of the volume of a gas versus the pressure on the gas. What would the graph of V versus P look like if volume was directly proportional to pressure?
2. What properties of a gas are described by Boyle's law, Charles's law, and Avogadro's law? In each law, what quantities are held constant? Why does the constant in Boyle's law depend on the amount of gas used and the temperature at which the experiments are carried out?
3. Use Charles's law to explain why cooler air sinks.

4. Use Boyle's law to explain why it is dangerous to heat even a small quantity of water in a sealed container.

For an ideal gas, is volume directly proportional or inversely proportional to temperature? What is the volume of an ideal gas at absolute zero?

For a given amount of a gas, the volume, temperature, and pressure under any one set of conditions are related to the volume, the temperature, and the pressure under any other set of conditions by the equation

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Derive this equation from the ideal gas law. At constant temperature, this equation reduces to one of the laws discussed in Section 6.3; which one? At constant pressure, this equation reduces to one of the laws discussed in Section 6.3; which one?

Predict the effect of each change on one variable if the other variables are held constant.

1. If the number of moles of gas increases, what is the effect on the temperature of the gas?
2. If the temperature of a gas decreases, what is the effect on the pressure of the gas?
3. If the volume of a gas increases, what is the effect on the temperature of the gas?
4. If the pressure of a gas increases, what is the effect on the number of moles of the gas?

What would the ideal gas law be if the following were true?

1. volume were proportional to pressure
2. temperature were proportional to amount
3. pressure were inversely proportional to temperature
4. volume were inversely proportional to temperature
5. both pressure and volume were inversely proportional to temperature

Given the following initial and final values, what additional information is needed to solve the problem using the ideal gas law?

Given	Solve for
V_1, T_1, T_2, n_1	n_2
P_1, P_2, T_2, n_2	n_1
T_1, T_2	V_2
P_1, n_1	P_2

Given the following information and using the ideal gas law, what equation would you use to solve the problem?

Given	Solve for
P_1, P_2, T_1	T_2
V_1, n_1, n_2	V_2
T_1, T_2, V_1, V_2, n_2	n_1

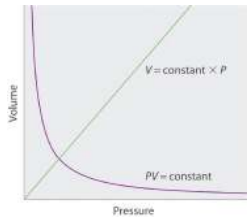
Using the ideal gas law as a starting point, derive the relationship between the density of a gas and its molar mass. Which would you expect to be denser—nitrogen or oxygen? Why does radon gas accumulate in basements and mine shafts?

Use the ideal gas law to derive an equation that relates the remaining variables for a sample of an ideal gas if the following are held constant.

1. amount and volume
2. pressure and amount
3. temperature and volume
4. temperature and amount
5. pressure and temperature

Tennis balls that are made for Denver, Colorado, feel soft and do not bounce well at lower altitudes. Use the ideal gas law to explain this observation. Will a tennis ball designed to be used at sea level be harder or softer and bounce better or worse at higher altitudes?

Answer

1. 

2.
3.

Numerical Problems

1. A 1.00 mol sample of gas at 25°C and 1.0 atm has an initial volume of 22.4 L. Calculate the results of each change, assuming all the other conditions remain constant.

    1. The pressure is changed to 85.7 Torr. How many milliliters does the gas occupy?
    2. The volume is reduced to 275 mL. What is the pressure in millimeters of mercury?
    3. The pressure is increased to 25.3 atm. What is the temperature in degrees Celsius?
    4. The sample is heated to 30°C. What is the volume in liters?
    5. The sample is compressed to 1255 mL, and the pressure is increased to 2555 torr. What is the temperature of the gas in kelvins?

2. A 1.00 mol sample of gas is at 300 K and 4.11 atm. What is the volume of the gas under these conditions? The sample is compressed to 6.0 atm at constant temperature, giving a volume of 3.99 L. Is this result consistent with Boyle's law?

    1. m

    A 8.60 L tank of nitrogen gas at a pressure of 455 Torr is connected to an empty tank with a volume of 5.35 L. What is the final pressure in the system after the valve connecting the two tanks is opened? Assume that the temperature is constant.

    At constant temperature, what pressure in atmospheres is needed to compress 14.2 L of gas initially at 25.2 atm to a volume of 12.4 L? What pressure is needed to compress 27.8 L of gas to 20.6 L under similar conditions?

One method for preparing hydrogen gas is to pass HCl gas over hot aluminum; the other product of the reaction is AlCl3. If you wanted to use this reaction to fill a balloon with a volume of 28,500 L at sea level and a temperature of 78°F, what mass of aluminum would you need? What volume of HCl at STP would you need?

An 3.50 g sample of acetylene is burned in excess oxygen according to the following reaction:

$2\ C2H2(g) + 5\ O2(g) \rightarrow 4\ CO2(g) + 2\ H2O(l)$

At STP, what volume of CO2(g) is produced?

Calculate the density of ethylene (C2H4) under each set of conditions.

1. 7.8 g at 0.89 atm and 26°C
2. 6.3 mol at 102.6 kPa and 38°C
3. 9.8 g at 3.1 atm and −45°C

Determine the density of O2 under each set of conditions.

1. 42 g at 1.1 atm and 25°C
2. 0.87 mol at 820 Torr and 45°C
3. 16.7 g at 2.4 atm and 67°C

At 140°C, the pressure of a diatomic gas in a 3.0 L flask is 635 kPa. The mass of the gas is 88.7 g. What is the most likely identity of the gas?

What volume must a balloon have to hold 6.20 kg of H2 for an ascent from sea level to an elevation of 20,320 ft, where the temperature is −37°C and the pressure is 369 Torr?

What must be the volume of a balloon that can hold 313.0 g of helium gas and ascend from sea level to an elevation of 1.5 km, where the temperature is 10.0°C and the pressure is 635.4 Torr?

A typical automobile tire is inflated to a pressure of 28.0 lb/in. Assume that the tire is inflated when the air temperature is 20°C; the car is then driven at high speeds, which increases the temperature of the tire to 43°C. What is the pressure in the tire? If the volume of the tire had increased by 8% at the higher temperature, what would the pressure be?

The average respiratory rate for adult humans is 20 breaths per minute. If each breath has a volume of 310 mL of air at 20°C and 0.997 atm, how many moles of air does a person inhale each day? If the density of air is 1.19 kg/m^3, what is the average molecular mass of air?

Kerosene has a self-ignition temperature of 255°C. It is a common accelerant used by arsonists, but its presence is easily detected in fire debris by a variety of methods. If a 1.0 L glass bottle containing a mixture of air and kerosene vapor at an initial pressure of 1 atm and an initial temperature of 23°C is pressurized, at what pressure would the kerosene vapor ignite?

Answer

1. 1. 1.99×10^5 mL
   2. 6.19×10^4 Torr
   3. 7270°C
   4. 22.8 L
   5. 51.4 K
2.

Contributors

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Chapter 6.5: Gas Mixtures

Learning Objective

- To determine the contribution of each component gas to the total pressure of a mixture of gases.

In our use of the ideal gas law thus far, we have focused entirely on the properties of pure gases with only a single chemical species. But what happens when two or more gases are mixed? In this section, we describe how to determine the contribution of each gas present to the total pressure of the mixture.

Partial Pressures

The ideal gas law *assumes* that all gases behave identically and that their behavior is independent of attractive and repulsive forces. If volume and temperature are held constant, the ideal gas equation can be rearranged to show that the pressure of a sample of gas is directly proportional to the number of moles of gas present:

$$P = n\left(\frac{RT}{V}\right) = n \times \text{const.} \tag{6.5.1}$$

Nothing in the equation depends on the *nature* of the gas—only the amount.

With this assumption, let's suppose we have a mixture of two ideal gases that are present in equal amounts. What is the total pressure of the mixture? Because the pressure depends on only the total number of particles of gas present, the total pressure of the mixture will simply be twice the pressure of either component. More generally, the total pressure exerted by a mixture of gases at a given temperature and volume is the sum of the pressures exerted by each gas alone. Furthermore, if we know the volume, the temperature, and the number of moles of each gas in a mixture, then we can calculate the pressure exerted by each gas individually, which is its partial pressureThe pressure a gas in a mixture would exert if it were the only one present (at the same temperature and volume)., the pressure the gas would exert if it were the only one present (at the same temperature and volume).

To summarize, *the total pressure exerted by a mixture of gases is the sum of the partial pressures of component gases*. This law was first discovered by John Dalton, the father of the atomic theory of matter. It is now known as Dalton's law of partial pressuresA law that states that the total pressure exerted by a mixture of gases is the sum of the partial pressures of component gases.. We can write it mathematically as

$$P_{tot} = P_1 + P_2 + P_3 + P_4 \ldots = \sum_{i=1}^{n} P_i \tag{6.5.2}$$

where P_t is the total pressure and the other terms are the partial pressures of the individual gases (Figure 6.5.1).

Figure 6.5.1 Dalton's Law. The total pressure of a mixture of gases is the sum of the partial pressures of the individual gases.

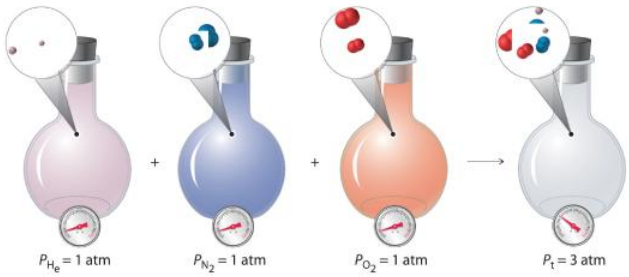


Figure 6.5.1 Dalton's Law. *The total pressure of a mixture of gases is the sum of the partial pressures of the individual gases.*

For a mixture of two ideal gases, A and B, we can write an expression for the total pressure:

$$P_{tot} = P_A + P_B = n_A\left(\frac{RT}{V}\right) + n_B\left(\frac{RT}{V}\right) = (n_A + n_B)\left(\frac{RT}{V}\right) \tag{6.5.3}$$

More generally, for a mixture of *i* components, the total pressure is given by

$$P_{tot} = (P_1 + P_2 + P_3 + \cdots + P_n)\left(\frac{RT}{V}\right) \tag{6.5.4a}$$

$$P_{tot} = \sum_{i=1}^{n} n_i \left(\frac{RT}{V}\right) \tag{6.5.4b}$$

Equation 6.5.4. restates Equation 6.5.3 in a more general form and makes it explicitly clear that, at constant temperature and volume, the pressure exerted by a gas depends on *only* the total number of moles of gas present, whether the gas is a single chemical species or a mixture of dozens or even hundreds of gaseous species. For Equation 6.5.4 to be valid, the identity of the particles present cannot have an effect. Thus an ideal gas must be one whose properties are not affected by either the size of the particles or their intermolecular interactions because both will vary from one gas to another. The calculation of total and partial pressures for mixtures of gases is illustrated in Example 11.

Example 6.5.1

Deep-sea divers must use special gas mixtures in their tanks, rather than compressed air, to avoid serious problems, most notably a condition called “the bends.” At depths of about 350 ft, divers are subject to a pressure of approximately 10 atm. A typical gas cylinder used for such depths contains 51.2 g of O_2 and 326.4 g of He and has a volume of 10.0 L. What is the partial pressure of each gas at 20.00°C, and what is the total pressure in the cylinder at this temperature?

Given: masses of components, total volume, and temperature

Asked for: partial pressures and total pressure

Strategy:

A Calculate the number of moles of He and O_2 present.

B Use the ideal gas law to calculate the partial pressure of each gas. Then add together the partial pressures to obtain the total pressure of the gaseous mixture.

Solution:

A The number of moles of He is

$$n_{\text{He}} = \frac{326.4\ \text{g}}{4.003\ \text{g/mol}} = 81.54\ \text{mol} \tag{Chapter 6.5.1}$$

The number of moles of O_2 is

$$n_{\text{O}_2} = \frac{51.2\ \text{g}}{32.00\ \text{g/mol}} = 1.60\ \text{mol} \tag{Chapter 6.5.2}$$

B We can now use the ideal gas law to calculate the partial pressure of each:

$$P_{\text{He}} = \frac{n_{\text{He}}RT}{V} \tag{Chapter 6.5.3}$$

$$= \frac{81.54\ \text{mol} \times 0.08206\ \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 293.15\ \text{K}}{10.0\ \text{L}} = 196.2\ \text{atm}$$

$$P_{\text{O}_2} = \frac{n_{\text{O}_2}RT}{V} \tag{Chapter 6.5.4}$$

$$= \frac{1.60\ \text{mol} \times 0.08206\ \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 293.15\ \text{K}}{10.0\ \text{L}} = 3.85\ \text{atm}$$

The total pressure is the sum of the two partial pressures:

$$P_{\text{tot}} = P_{\text{He}} + P_{\text{O}_2} = (196.2 + 3.85)\ \text{atm} = 200.1\ \text{atm} \tag{Chapter 6.5.5}$$

Exercise

A cylinder of compressed natural gas has a volume of 20.0 L and contains 1813 g of methane and 336 g of ethane. Calculate the partial pressure of each gas at 22.0°C and the total pressure in the cylinder.

Answer: P(CH_4) = 137 atm; P(C_2H_6) = 13.4 atm; P_t = 151 atm.

Mole Fractions of Gas Mixtures

The composition of a gas mixture can be described by the mole fractions of the gases present. The mole fraction (X)The ratio of the number of moles of any component of a mixture to the total number of moles of all species present in the mixture. of any component of a mixture is the ratio of the number of moles of that component to the total number of moles of all the species present in the mixture (n_t):

$$x_A = \frac{\text{moles of A}}{\text{total moles}} = \frac{n_A}{n_{tot}} = \frac{n_A}{n_A + n_B + \cdots} \tag{6.5.6}$$

The mole fraction is a dimensionless quantity between 0 and 1. If X_A = 1.0, then the sample is pure A, not a mixture. If X_A = 0, then no A is present in the mixture. The sum of the mole fractions of all the components present must equal 1.

To see how mole fractions can help us understand the properties of gas mixtures, let's evaluate the ratio of the pressure of a gas A to the total pressure of a gas mixture that contains A. We can use the ideal gas law to describe the pressures of both gas A and the mixture: $P_A = n_ART/V$ and $P_t = n_tRT/V$. The ratio of the two is thus

$$\frac{P_A}{P_{tot}} = \frac{n_ART/V}{n_{tot}RT/V} = \frac{n_A}{n_{tot}} = x_A \tag{6.5.7}$$

Rearranging this equation gives

$$P_A = x_AP_{tot} \tag{6.5.8}$$

That is, the partial pressure of any gas in a mixture is the total pressure multiplied by the mole fraction of that gas. This conclusion is a direct result of the ideal gas law, which assumes that all gas particles behave ideally. Consequently, the pressure of a gas in a mixture depends on only the percentage of particles in the mixture that are of that type, not their specific physical or chemical properties. By volume, Earth's atmosphere is about 78% N_2, 21% O_2, and 0.9% Ar, with trace amounts of gases such as CO_2, H_2O, and others. This means that 78% of the particles present in the atmosphere are N_2; hence the mole fraction of N_2 is 78%/100% = 0.78. Similarly, the mole fractions of O_2 and Ar are 0.21 and 0.009, respectively. Using Equation 6.5.8, we therefore know that the partial pressure of N_2 is 0.78 atm (assuming an atmospheric pressure of exactly 760 mmHg) and, similarly, the partial pressures of O_2 and Ar are 0.21 and 0.009 atm, respectively.

Example 6.5.2

We have just calculated the partial pressures of the major gases in the air we inhale. Experiments that measure the composition of the air we *exhale* yield different results, however. The following table gives the measured pressures of the major gases in both inhaled and exhaled air. Calculate the mole fractions of the gases in exhaled air.

	Inhaled Air (mmHg)	Exhaled Air (mmHg)
P_{N_2}	597	568
P_{O_2}	158	116
P_{H_2O}	0.3	28
P_{CO_2}	5	48
P_{Ar}	8	8
P_t	767	767

Given: pressures of gases in inhaled and exhaled air

Asked for: mole fractions of gases in exhaled air

Strategy:

Calculate the mole fraction of each gas using Equation 6.5.8.

Solution:

The mole fraction of any gas A is given by

$$x_A = \frac{P_A}{P_{tot}} \tag{Chapter 6.5.6}$$

where P_A is the partial pressure of A and P_t is the total pressure. In this case,

$$x_{CO_2} = \frac{48\ \text{mmHg}}{767\ \text{mmHg}} = 0.063 \tag{Chapter 6.5.7}$$

The following table gives the values of P_A and X_A for exhaled air.

P_A		X_A
N_2	$(568\ \cancel{mmHg})\frac{1\ atm}{760\ \cancel{mmHg}} = 0.747\ atm$	$\frac{0.747\ \cancel{atm}}{1.01\ \cancel{atm}} = 0.740$
O_2	$(116\ \cancel{mmHg})\frac{1\ atm}{760\ \cancel{mmHg}} = 0.153\ atm$	$\frac{0.153\ \cancel{atm}}{1.01\ \cancel{atm}} = 0.151$
H_2O	$(28\ \cancel{mmHg})\frac{1\ atm}{760\ \cancel{mmHg}} = 0.037\ atm$	$\frac{0.031\ \cancel{atm}}{1.01\ \cancel{atm}} = 0.031$
CO_2	$(48\ \cancel{mmHg})\frac{1\ atm}{760\ \cancel{mmHg}} = 0.063\ atm$	$\frac{0.063\ \cancel{atm}}{1.01\ \cancel{atm}} = 0.061$
Ar	$(8\ \cancel{mmHg})\frac{1\ atm}{760\ \cancel{mmHg}} = 0.011\ atm$	$\frac{0.011\ \cancel{atm}}{1.01\ \cancel{atm}} = 0.011$

Exercise

We saw in Example 10 that Venus is an inhospitable place, with a surface temperature of 560°C and a surface pressure of 90 atm. The atmosphere consists of about 96% CO_2 and 3% N_2, with trace amounts of other gases, including water, sulfur dioxide, and sulfuric acid. Calculate the partial pressures of CO_2 and N_2.

Answer: $P_{CO_2} = 86\ \text{atm}$, $P_{N_2} = 2.7\ \text{atm}$

Summary

The pressure exerted by each gas in a gas mixture (its **partial pressure**) is independent of the pressure exerted by all other gases present. Consequently, the total pressure exerted by a mixture of gases is the sum of the partial pressures of the components (**Dalton's law of partial pressures**). The amount of gas present in a mixture may be described by its partial pressure or its mole fraction. The **mole fraction** of any component of a mixture is the ratio of the number of moles of that substance to the total number of moles of all substances present. In a mixture of gases, the partial pressure of each gas is the product of the total pressure and the mole fraction of that gas.

Key Takeaway

- The partial pressure of each gas in a mixture is proportional to its mole fraction.

Key Equations

Mole fraction

Equation 6.5.6: $X_A = \frac{moles A}{total moles} = \frac{n_A}{n_t}$

Relationship between partial pressure and mole fraction

Equation 6.5.8: $P_A = X_A P_t$

Conceptual Problems

1. Dalton's law of partial pressures makes one key assumption about the nature of the intermolecular interactions in a mixture of gases. What is it?
2. What is the relationship between the partial pressure of a gas and its mole fraction in a mixture?

Numerical Problems

1. What is the partial pressure of each gas if the following amounts of substances are placed in a 25.0 L container at 25°C? What is the total pressure of each mixture?
    1. 1.570 mol of CH_4 and 0.870 mol of CO_2
    2. 2.63 g of CO and 1.24 g of NO_2
    3. 1.78 kg of CH_3Cl and 0.92 kg of SO_2
2. What is the partial pressure of each gas in the following 3.0 L mixtures at 37°C as well as the total pressure?
    1. 0.128 mol of SO_2 and 0.098 mol of methane (CH_4)
    2. 3.40 g of acetylene (C_2H_2) and 1.54 g of He
    3. 0.267 g of NO, 4.3 g of Ar, and 0.872 g of SO_2
3. In a mixture of helium, oxygen, and methane in a 2.00 L container, the partial pressures of He and O_2 are 13.6 kPa and 29.2 kPa, respectively, and the total pressure inside the container is 95.4 kPa. What is the partial pressure of methane? If the methane is ignited to initiate its combustion with oxygen and the system is then cooled to the original temperature of 30°C, what is the final pressure inside the container (in kilopascals)?
4. A 2.00 L flask originally contains 1.00 g of ethane (C_2H_6) and 32.0 g of oxygen at 21°C. During ignition, the ethane reacts completely with oxygen to produce CO_2 and water vapor, and the temperature of the flask increases to 200°C. Determine the total pressure and the partial pressure of each gas before and after the reaction.
5. If a 20.0 L cylinder at 19°C is charged with 5.0 g each of sulfur dioxide and oxygen, what is the partial pressure of each gas? The sulfur dioxide is ignited in the oxygen to produce sulfur trioxide gas, and the mixture is allowed to cool to 19°C at constant pressure. What is the final volume of the cylinder? What is the partial pressure of each gas in the piston?
6. The highest point on the continent of Europe is Mt. Elbrus in Russia, with an elevation of 18,476 ft. The highest point on the continent of South America is Mt. Aconcagua in Argentina, with an elevation of 22,841 ft.
    1. The following table shows the variation of atmospheric pressure with elevation. Use the data in the table to construct a plot of pressure versus elevation.

Elevation (km)	Pressure in Summer (mmHg)	Pressure in Winter (mmHg)
0.0	760.0	760.0
1.0	674.8	670.6
1.5	635.4	629.6
2.0	598.0	590.8
3.0	528.9	519.7
5.0	410.6	398.7
7.0	314.9	301.6
9.0	237.8	224.1

2. Use your graph to estimate the pressures in millimeters of mercury during the summer and the winter at the top of both mountains in both atmospheres and kilopascals.
3. Given that air is 20.95% O_2 by volume, what is the partial pressure of oxygen in atmospheres during the summer at each location?

Answers

1. 1. P(CH_4) = 1.54 atm, P(CO_2) = 0.851 atm, P_T = 2.39 atm
   2. *P(CO)* = 0.0918 atm, P(NO_2) = 0.0264 atm, P_T = 0.1182 atm
   3. P(CH3Cl) = 34.5 atm, P(SO_2) = 14 atm, P_T = 49 atm
2.
3. 52.6 kPa, 66.2 kPa
4.
5.
6.

Contributors

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Chapter 6.6: The Kinetic Theory of Gases

Learning Objective

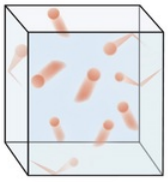
- To understand the significance of the kinetic molecular theory of gases.

The laws that describe the behavior of gases were well established long before anyone had developed a coherent model of the properties of gases. In this section, we introduce a theory that describes why gases behave the way they do. The theory we introduce can also be used to derive laws such as the ideal gas law from fundamental principles and the properties of individual particles.

A Molecular Description

The kinetic molecular theory of gasesA theory that describes, on the molecular level, why ideal gases behave the way they do. explains the laws that describe the behavior of gases. Developed during the mid-19th century by several physicists, including the Austrian Ludwig Boltzmann (1844–1906), the German Rudolf Clausius (1822–1888), and the Englishman James Clerk Maxwell (1831–1879), who is also known for his contributions to electricity and magnetism, this theory is based on the properties of individual particles as defined for an ideal gas and the fundamental concepts of physics. Thus the kinetic molecular theory of gases provides a molecular explanation for observations that led to the development of the ideal gas law. The kinetic molecular theory of gases is based on the following five postulates:

1. A gas is composed of a large number of particles called molecules (whether monatomic or polyatomic) that are in constant random motion.
2. Because the distance between gas molecules is much greater than the size of the molecules, the volume of the molecules is negligible.
3. Intermolecular interactions, whether repulsive or attractive, are so weak that they are also negligible.
4. Gas molecules collide with one another and with the walls of the container, but these collisions are perfectly elastic; that is, they do not change the average kinetic energy of the molecules.
5. The average kinetic energy of the molecules of any gas depends on only the temperature, and at a given temperature, all gaseous molecules have exactly the same average kinetic energy.



Although the molecules of real gases have nonzero volumes and exert both attractive and repulsive forces on one another, for the moment we will focus on how the kinetic molecular theory of gases relates to the properties of ideal gases.

Postulates 1 and 4 state that gas molecules are in constant motion and collide frequently with the walls of their containers. The collision of molecules with their container walls results in a **momentum transfer** (impulse) from molecules to the walls (Figure 6.6.1).

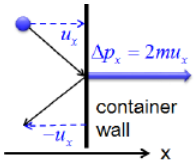


Figure 6.6.1 Momentum transfer (Impulse) from a molecule to the container wall as it bounces off the wall. u_x *and* Δp_x *are the* x *component of the molecular velocity and the momentum transfered to the wall, respectively. The wall is perpendicular to* x *axis. Since the collisions are elastic, the molecule bounces back with the same velocity in the opposite direction.*

The **momentum transfer** to the wall perpendicular to x axis as a molecule with an initial velocity u_x in x direction hits is expressed as:

$$\Delta p_x = 2mu_x \tag{6.6.1}$$

The **collision frequency**, a number of collisions of the molecules to the wall per unit area and per second, increases with the molecular speed and the number of molecules per unit volume.

$$f \propto (u_x) \times \left(\frac{N}{V}\right) \tag{6.6.2}$$

The pressure the gas exerts on the wall is expressed as the product of impulse and the collision frequency.

$$P \propto (2mu_x) \times (u_x) \times \left(\frac{N}{V}\right) \propto \left(\frac{N}{V}\right) mu_x^2 \tag{6.6.3}$$

At any instant, however, the molecules in a gas sample are traveling at different speed. Therefore, we must replace u_x^2 in the expression above with the average value of u_x^2, which is denoted by $\overline{u_x^2}$. The overbar designates the average value over all molecules.

The exact expression for pressure is given as :

$$P = \frac{N}{V} m\overline{u_x^2} \tag{6.6.4}$$

Finally, we must consider that there is nothing special about x direction. We should expect that $\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2} = \frac{1}{3}\overline{u^2}$. Here the quantity $\overline{u^2}$ is called the **mean-square speed** defined as the average value of square-speed (u^2) over all molecules. Since $u^2 = u_x^2 + u_y^2 + u_z^2$ for each molecule, $\overline{u^2} = \overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2}$. By substituting $\frac{1}{3}\overline{u^2}$ for $\overline{u_x^2}$ in the expression above, we can get the final expression for the pressure:

$$P = \frac{1}{3}\frac{N}{V} m\overline{u^2} \tag{6.6.5}$$

Anything that increases the frequency with which the molecules strike the walls or increases the momentum of the gas molecules (i.e., how hard they hit the walls) increases the pressure; anything that decreases that frequency or the momentum of the molecules decreases the pressure.

Because volumes and intermolecular interactions are negligible, postulates 2 and 3 state that all gaseous particles behave identically, regardless of the chemical nature of their component molecules. This is the essence of the ideal gas law, which treats all gases as collections of particles that are identical in all respects except mass. Postulate 2 also explains why it is relatively easy to compress a gas; you simply decrease the distance between the gas molecules.

Postulate 5 provides a molecular explanation for the temperature of a gas. It refers to the *average translational* kinetic energy of the molecules of a gas which can be represented as ($\overline{e_K}$), *and states that at a given Kelvin temperature* (T), *all gases have the same value of*

$$\overline{e_K} = \frac{1}{2} m\overline{u^2} = \frac{3}{2}\frac{R}{N_A}T \tag{6.6.6}$$

where N_A is the Avogadro's constant. The total translational kinetic energy of 1 mole of molecules can be obtained by multiplying the equation by N_A:

$$N_A\overline{e_K} = \frac{1}{2} M\overline{u^2} = \frac{3}{2}RT \tag{6.6.7}$$

where M is the molar mass of the gas molecules and is related to the molecular mass by $M = N_A m$.

By rearranging the equation, we can get the relationship between the root-mean square speed (u_{rms}) and the temperature.

The rms speed (u_{rms}) is the square root of the sum of the squared speeds divided by the number of particles:

$$u_{\text{rms}} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots u_N^2}{N}} \tag{6.6.8}$$

where N is the number of particles and u_i is the speed of particle i.

The relationship between u_{rms} and the temperature is given by:

$$u_{rms} = \sqrt{\frac{3RT}{M}} \tag{6.6.9}$$

In this equation, u_{rms} has units of meters per second; consequently, the units of molar mass M are kilograms per mole, temperature T is expressed in kelvins, and the ideal gas constant R has the value 8.3145 J/(K·mol).

The equation shows that u_{rms} of a gas is proportional to the square root of its Kelvin temperature and inversely proportional to the square root of its molar mass. The root mean-square speed of a gas increase with increasing temperature. At a given temperature, heavier gas molecules have slower speeds than do lighter ones.

The rms speed and the average speed do not differ greatly (typically by less than 10%). The distinction is important, however, because the rms speed is the speed of a gas particle that has average kinetic energy. Particles of different gases at the same temperature have the same average kinetic energy, not the same average speed. In contrast, the most probable speed (v_p) is the speed at which the greatest number of particles is moving. If the average kinetic energy of the particles of a gas increases linearly with increasing temperature, then Equation 6.6.9 tells us that the rms speed must also increase with temperature because the mass of the particles is constant. At higher temperatures, therefore, the molecules of a gas move more rapidly than at lower temperatures, and v_p increases.

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Note the Pattern

At a given temperature, all gaseous particles have the same average kinetic energy but not the same average speed.

Example 6.6.1

The speeds of eight particles were found to be 1.0, 4.0, 4.0, 6.0, 6.0, 6.0, 8.0, and 10.0 m/s. Calculate their average speed (v_{av}) root mean square speed (v_{rms}), and most probable speed (v_p).

Given: particle speeds

Asked for: average speed (v_{av}) root mean square speed (v_{rms}), and most probable speed (v_p)

Strategy:

Use Equation 6.6.9 to calculate the average speed and Equation 6.6.8 to calculate the rms speed. Find the most probable speed by determining the speed at which the greatest number of particles is moving.

Solution:

The average speed is the sum of the speeds divided by the number of particles:

$$v_{av} = \frac{(1.0 + 4.0 + 4.0 + 6.0 + 6.0 + 6.0 + 8.0 + 10.0)\ \text{m/s}}{8} = 5.6\ \text{m/s} \tag{Chapter 6.6.1}$$

The rms speed is the square root of the sum of the squared speeds divided by the number of particles:

$$v_{rms} = \sqrt{\frac{(1.0^2 + 4.0^2 + 4.0^2 + 6.0^2 + 6.0^2 + 6.0^2 + 8.0^2 + 10.0^2)\ \mathrm{m^2/s^2}}{8}} = 6.2\ \mathrm{m/s} \quad \text{(Chapter 6.6.2)}$$

The most probable speed is the speed at which the greatest number of particles is moving. Of the eight particles, three have speeds of 6.0 m/s, two have speeds of 4.0 m/s, and the other three particles have different speeds. Hence v_p = 6.0 m/s. The v_{rms} of the particles, which is related to the average kinetic energy, is greater than their average speed.

Exercise

Ten particles were found to have speeds of 0.1, 1.0, 2.0, 3.0, 3.0, 3.0, 4.0, 4.0, 5.0, and 6.0 m/s. Calculate their average speed (v_{av}) root mean square speed (v_{rms}), and most probable speed (v_p).

Answer:

$$\bar{v} = 3.1\ m/s;\ v_{rms} = 3.5\ m/s; v_p = 3.0 m/s \quad \text{(Chapter 6.6.3)}$$

Boltzmann Distributions

At any given time, what fraction of the molecules in a particular sample has a given speed? Some of the molecules will be moving more slowly than average, and some will be moving faster than average, but how many in each situation? Answers to questions such as these can have a substantial effect on the amount of product formed during a chemical reaction, as you will learn in Chapter 15. This problem was solved mathematically by Maxwell in 1866; he used statistical analysis to obtain an equation that describes the distribution of molecular speeds at a given temperature.

The kinetic molecular theory is used to determine the motion of a molecule of an ideal gas under a certain set of conditions. However, when looking at a mole of ideal gas, it is impossible to measure the velocity of each molecule at every instant of time. Therefore, the Maxwell-Boltzmann distribution is used to determine how many molecules are moving between velocities v and $v + dv$. Assuming that the one-dimensional distributions are independent of one another, that the velocity in the y and z directions does not affect the x velocity, for example, the Maxwell-Boltzmann distribution is given by

$$\frac{dN}{N} = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{\frac{-mv^2}{2k_B T}} dv \quad (6.6.10)$$

where

- dN/N is the fraction of molecules moving at velocity v to $v + dv$,
- m is the mass of the molecule,
- k_b is the Boltzmann constant, and
- T is the absolute temperature.[1]

Additionally, the function can be written in terms of the scalar quantity speed c instead of the vector quantity velocity. This form of the function defines the distribution of the gas molecules moving at different speeds, between c_1 and c_2, thus

$$f(c) = 4\pi c^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{\frac{-mc^2}{2k_B T}} \quad (6.6.11)$$

Finally, the Maxwell-Boltzmann distribution can be used to determine the distribution of the kinetic energy of for a set of molecules. The distribution of the kinetic energy is identical to the distribution of the speeds for a certain gas at any temperature.[2]

Figure 6.6.2 shows the Maxwell-Boltzmann distribution of speeds for a certain gas at a certain temperature, such as nitrogen at 298 K. The speed at the top of the curve is called the most probable speed because the largest number of molecules have that speed.

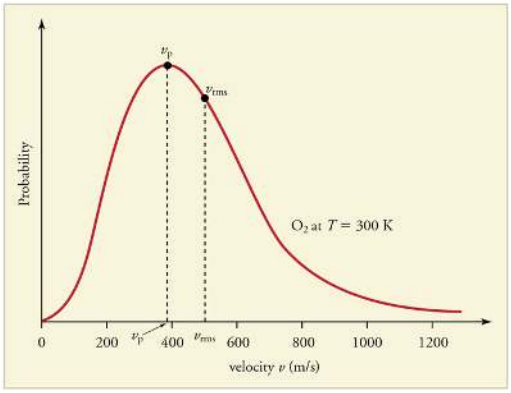


Figure 6.6.2: *The Maxwell-Boltzmann distribution is shifted to higher speeds and is broadened at higher temperatures.Image used with permission from OpenStax.*

Typical curves showing the distributions of speeds of molecules at several temperatures are displayed in Figure 6.6.3 . Increasing the temperature has two effects. First, the peak of the curve moves to the right because the most probable speed increases. Second, the curve becomes broader because of the increased spread of the speeds. Thus increased temperature increases the *value* of the most probable speed but decreases the relative number of molecules that have that speed. Because the molecules have greater energy at higher temperature, the molecules are moving faster on average. Although the mathematics behind curves such as those in Figure 6.6.3 were first worked out by Maxwell, the curves are almost universally referred to as Boltzmann distributionsA curve that shows the distribution of molecular speeds at a given temperature., after one of the other major figures responsible for the kinetic molecular theory of gases.

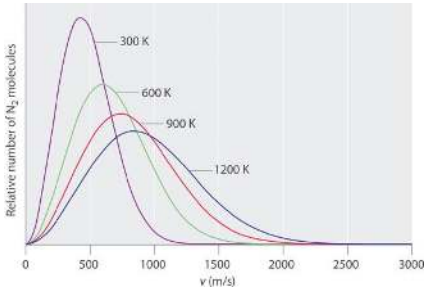


Figure 6.6.3 The Distributions of Molecular Speeds for a Sample of Nitrogen Gas at Various Temperature. *Increasing the temperature increases both the most probable speed (given at the peak of the curve) and the width of the curve.*

Figure 6.6.4 shows the dependence of the Maxwell-Boltzmann distribution on molecule mass. On average, heavier molecules move more slowly than lighter molecules. Therefore, heavier molecules will have a smaller speed distribution, while lighter molecules will have a speed distribution that is more spread out.

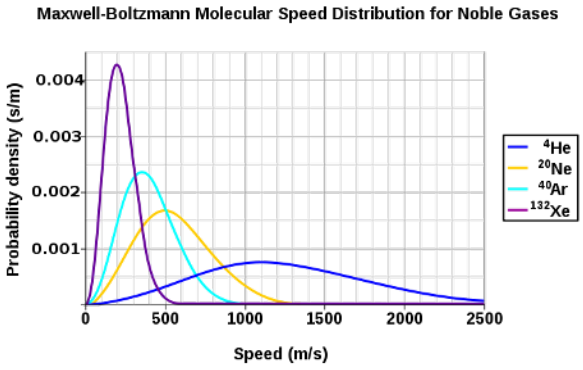


Figure 6.6.4*: The speed probability density functions of the speeds of a few noble gases at a temperature of 298.15 K (25 °C). The y-axis is in s/m so that the area under any section of the curve (which represents the probability of the speed being in that range) is dimensionless. Figure is used with permission from Wikipedia.*

The Relationships among Pressure, Volume, and Temperature

We now describe how the kinetic molecular theory of gases explains some of the important relationships we have discussed previously.

Pressure versus Volume

At constant temperature, the kinetic energy of the molecules of a gas and hence the rms speed remain unchanged. If a given gas sample is allowed to occupy a larger volume, then the speed of the molecules does not change, but the density of the gas (number of particles per unit volume) decreases, and the average distance between the molecules increases. Hence the molecules must, on average, travel farther between collisions. They therefore collide with one another and with the walls of their containers less often, leading to a decrease in pressure. Conversely, increasing the pressure forces the molecules closer together and increases the density, until the collective impact of the collisions of the molecules with the container walls just balances the applied pressure.

Volume versus Temperature

Raising the temperature of a gas increases the average kinetic energy and therefore the rms speed (and the average speed) of the gas molecules. Hence as the temperature increases, the molecules collide with the walls of their containers more frequently and with greater force. This increases the pressure, *unless* the volume increases to reduce the pressure, as we have just seen. Thus an increase in temperature must be offset by an increase in volume for the net impact (pressure) of the gas molecules on the container walls to remain unchanged.

Pressure of Gas Mixtures

Postulate 3 of the kinetic molecular theory of gases states that gas molecules exert no attractive or repulsive forces on one another. If the gaseous molecules do not interact, then the presence of one gas in a gas mixture will have no effect on the pressure exerted by another, and Dalton's law of partial pressures holds.

Example 6.6.2

The temperature of a 4.75 L container of N_2 gas is increased from 0°C to 117°C. What is the qualitative effect of this change on the

1. average kinetic energy of the N_2 molecules?
2. rms speed of the N_2 molecules?
3. average speed of the N_2 molecules?
4. impact of each N_2 molecule on the wall of the container during a collision with the wall?
5. total number of collisions per second of N_2 molecules with the walls of the entire container?
6. number of collisions per second of N_2 molecules with each square centimeter of the container wall?
7. pressure of the N_2 gas?

Given: temperatures and volume

Asked for: effect of increase in temperature

Strategy:

Use the relationships among pressure, volume, and temperature to predict the qualitative effect of an increase in the temperature of the gas.

Solution:

1. Increasing the temperature increases the average kinetic energy of the N_2 molecules.
2. An increase in average kinetic energy can be due only to an increase in the rms speed of the gas particles.
3. If the rms speed of the N_2 molecules increases, the average speed also increases.
4. If, on average, the particles are moving faster, then they strike the container walls with more energy.
5. Because the particles are moving faster, they collide with the walls of the container more often per unit time.
6. The number of collisions per second of N_2 molecules with each square centimeter of container wall increases because the total number of collisions has increased, but the volume occupied by the gas and hence the total area of the walls are unchanged.

7. The pressure exerted by the N_2 gas increases when the temperature is increased at constant volume, as predicted by the ideal gas law.

Exercise

A sample of helium gas is confined in a cylinder with a gas-tight sliding piston. The initial volume is 1.34 L, and the temperature is 22°C. The piston is moved to allow the gas to expand to 2.12 L at constant temperature. What is the qualitative effect of this change on the

1. average kinetic energy of the He atoms?
2. rms speed of the He atoms?
3. average speed of the He atoms?
4. impact of each He atom on the wall of the container during a collision with the wall?
5. total number of collisions per second of He atoms with the walls of the entire container?
6. number of collisions per second of He atoms with each square centimeter of the container wall?
7. pressure of the He gas?

Answer: a. no change; b. no change; c. no change; d. no change; e. decreases; f. decreases; g. decreases

Diffusion and Effusion

As you have learned, the molecules of a gas are *not* stationary but in constant motion. If someone opens a bottle of perfume in the next room, for example, you are likely to be aware of it soon. Your sense of smell relies on molecules of the aromatic substance coming into contact with specialized olfactory cells in your nasal passages, which contain specific receptors (protein molecules) that recognize the substance. How do the molecules responsible for the aroma get from the perfume bottle to your nose? You might think that they are blown by drafts, but, in fact, molecules can move from one place to another even in a draft-free environment. Figure 6.6.5 shows white fumes of solid ammonium chloride (NH_4Cl) forming when containers of aqueous ammonia and HCl are placed near each other, even with no draft to stir the air. This phenomenon suggests that NH_3 and HCl molecules (as well as the more complex organic molecules responsible for the aromas of pizza and perfumes) move without assistance.





Figure 6.6.5 The Diffusion of Gaseous Molecules. *When open containers of aqueous NH_3 and HCl are placed near each other in a draft-free environment, molecules of the two substances diffuse, collide, and react to produce white fumes of solid ammonium chloride (NH_4Cl). (From the Backyard Scientist)*

DiffusionThe gradual mixing of gases due to the motion of their component particles even in the absence of mechanical agitation such as stirring. The result is a gas mixture with a uniform composition. is the gradual mixing of gases due to the motion of their component particles even in the absence of mechanical agitation such as stirring. The result is a gas mixture with uniform composition. As we shall see in Chapter 7 , Chapter 8 , and Chapter 9 , diffusion is also a property of the particles in liquids and liquid solutions and, to a lesser extent, of solids and solid solutions. We can describe the phenomenon shown in Figure 6.6.5 by saying that the molecules of HCl and NH_3 are able to diffuse away from their containers, and that NH_4Cl is formed where the two gases come into contact. Similarly, we say that a perfume or an aroma diffuses throughout a room or a house. The related process, effusionThe escape of a gas through a small (usually microscopic) opening into an evacuated space., is the escape of gaseous molecules through a small (usually microscopic) hole, such as a hole in a balloon, into an evacuated space.

The phenomenon of effusion had been known for thousands of years, but it was not until the early 19th century that quantitative experiments related the rate of effusion to molecular properties. The rate of effusion of a gaseous substance is inversely proportional to the square root of its molar mass. This relationship,

$$rate \propto \frac{1}{\sqrt{M}} \tag{Chapter 6.6.4}$$

is referred to as Graham's lawA law that states that the rate of effusion of a gaseous substance is inversely proportional to the square root of its molar mass., after the Scottish chemist Thomas Graham (1805–1869). The ratio of the effusion rates of two gases is the square root of the inverse ratio of their molar masses. If r is the effusion rate and M is the molar mass, then

$$\frac{r_1}{r_2} = \frac{\sqrt{M_2}}{\sqrt{M_1}} \tag{6.6.12}$$

Although diffusion and effusion are different phenomena, the rate of diffusion is closely approximated using Equation 6.6.12 that is, if $M_1 < M_2$, then gas #1 will diffuse more rapidly than gas #2. This point is illustrated by the experiment shown in Figure 6.6.6 , which is a more quantitative version of the case shown in Figure 6.6.5 . The reaction is the same [$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(g)$], but in this experiment, two cotton balls containing aqueous ammonia and HCl are placed along a meter stick in a draft-free environment, and the position at which the initial NH_4Cl fumes appear is noted. The white cloud forms much nearer the HCl-containing ball than the NH_3-containing ball. Because ammonia (M = 17.0 g/mol) diffuses much faster than HCl (M = 36.5 g/mol), the NH_4Cl fumes form closer to HCl because the HCl molecules travel a shorter distance. The ratio of the distances traveled by NH_3 and HCl in is about 1.7, in reasonable agreement with the ratio of 1.47 predicted by their molar masses [$(36.5/17.0)^{1/2} = 1.47$].



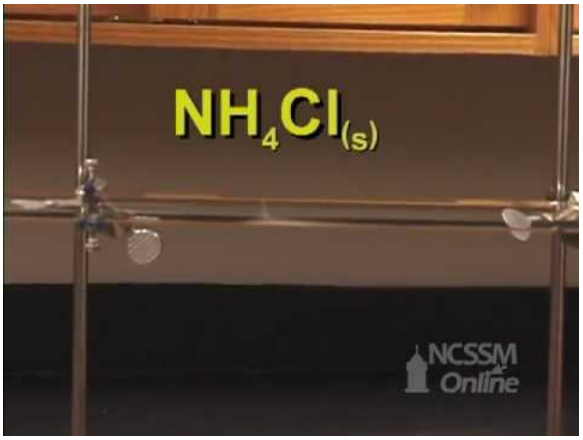
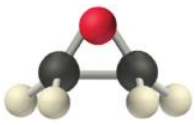


Figure 6.6.6 A Simple Experiment to Measure the Relative Rates of the Diffusion of Two Gases *Cotton balls containing aqueous NH_3 (left) and HCl (right) are placed a measured distance apart in a draft-free environment, and the position at which white fumes of NH_4Cl first appear is noted. The puff of white NH_4Cl forms much closer to the HCl-containing ball than to the NH_3-containing ball. The left edge of the white puff marks where the reaction was first observed. The position of the white puff (18.8 − 3.3 = 15.5 cm from the NH_3, 28.0 − 18.8 = 9.2 cm from the HCl, giving a ratio of distances of 15.5/9.2 = 1.7) is approximately the location predicted by Graham's law based on the square root of the inverse ratio of the molar masses of the reactants (1.47).*



Ethylene oxide

Heavy molecules effuse through a porous material more slowly than light molecules, as illustrated schematically in Figure 6.6.5 for ethylene oxide and helium. Helium (M = 4.00 g/mol) effuses much more rapidly than ethylene oxide (M = 44.0 g/mol). Because helium is less dense than air, helium-filled balloons "float" at the end of a tethering string. Unfortunately, rubber balloons filled with helium soon lose their buoyancy along with much of their volume. In contrast, rubber balloons filled with air tend to retain

their shape and volume for a much longer time. Because helium has a molar mass of 4.00 g/mol, whereas air has an average molar mass of about 29 g/mol, pure helium effuses through the microscopic pores in the rubber balloon

$$\sqrt{\frac{29}{4.00}} = 2.7 \qquad \text{(Chapter 6.6.5)}$$

times faster than air. For this reason, high-quality helium-filled balloons are usually made of Mylar, a dense, strong, opaque material with a high molecular mass that forms films that have many fewer pores than rubber. Mylar balloons can retain their helium for days.

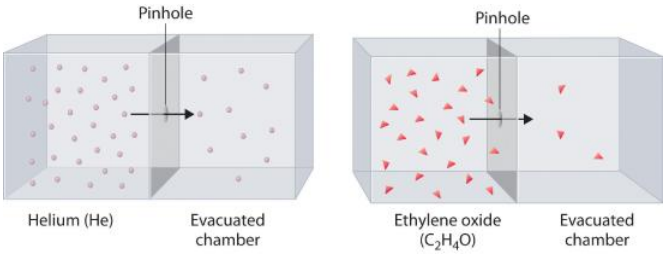


Figure 6.6.7 The Relative Rates of Effusion of Two Gases with Different Masses *The lighter He atoms (M = 4.00 g/mol) effuse through the small hole more rapidly than the heavier ethylene oxide (C_2H_4O) molecules (M = 44.0 g/mol), as predicted by Graham's law.*

Note the Pattern

At a given temperature, heavier molecules move more slowly than lighter molecules.

Example 6.6.3

During World War II, scientists working on the first atomic bomb were faced with the challenge of finding a way to obtain large amounts of ^{235}U. Naturally occurring uranium is only 0.720% ^{235}U, whereas most of the rest (99.275%) is ^{238}U, which is not fissionable (i.e., it will not break apart to release nuclear energy) and also actually poisons the fission process. Because both isotopes of uranium have the same reactivity, they cannot be separated chemically. Instead, a process of gaseous effusion was developed using the volatile compound UF_6 (boiling point = 56°C).

1. Calculate the ratio of the rates of effusion of $^{235}UF_6$ and $^{238}UF_6$ for a single step in which UF_6 is allowed to pass through a porous barrier. (The atomic mass of ^{235}U is 235.04, and the atomic mass of ^{238}U is 238.05.)
2. If *n* identical successive separation steps are used, the overall separation is given by the separation in a single step (in this case, the ratio of effusion rates) raised to the *n*th power. How many effusion steps are needed to obtain 99.0% pure $^{235}UF_6$?

Given: isotopic content of naturally occurring uranium and atomic masses of ^{235}U and ^{238}U

Asked for: ratio of rates of effusion and number of effusion steps needed to obtain 99.0% pure $^{235}UF_6$

Strategy:

A Calculate the molar masses of $^{235}UF_6$ and $^{238}UF_6$, and then use Graham's law to determine the ratio of the effusion rates. Use this value to determine the isotopic content of $^{235}UF_6$ after a single effusion step.

B Divide the final purity by the initial purity to obtain a value for the number of separation steps needed to achieve the desired purity. Use a logarithmic expression to compute the number of separation steps required.

Solution:

1. **A** The first step is to calculate the molar mass of UF_6 containing ^{235}U and ^{238}U. Luckily for the success of the separation method, fluorine consists of a single isotope of atomic mass 18.998. The molar mass of $^{235}UF_6$ is

$$234.04 + (6)(18.998) = 349.03\ g/mol \qquad \text{(Chapter 6.6.6)}$$

The molar mass of $^{238}UF_6$ is

$$238.05 + (6)(18.998) = 352.04\ g/mol \qquad \text{(Chapter 6.6.7)}$$

The difference is only 3.01 g/mol (less than 1%). The ratio of the effusion rates can be calculated from Graham's law using Equation 6.6.10:

$$\frac{rate\ ^{235}UF_6}{rate\ ^{238}UF_6} = \sqrt{\frac{352.04}{349.03}} = 1.0043 \qquad \text{(Chapter 6.6.8)}$$

Thus passing UF_6 containing a mixture of the two isotopes through a single porous barrier gives an enrichment of 1.0043, so after one step the isotopic content is (0.720%)(1.0043) = 0.723% $^{235}UF_6$.

2. **B** To obtain 99.0% pure $^{235}UF_6$ requires many steps. We can set up an equation that relates the initial and final purity to the number of times the separation process is repeated:

$$finalpurity = (initialpurity)(separation)^n \qquad \text{(Chapter 6.6.9)}$$

In this case, 0.990 = (0.00720)(1.0043)^n, which can be rearranged to give

$$\frac{0.990}{0.00720} = 1.38 = (1.0043)^n \qquad \text{(Chapter 6.6.10)}$$

Taking the logarithm of both sides gives

$$log\,(138) = nlog\,(1.0043) \qquad \text{(Chapter 6.6.11)}$$

$$n = \frac{log\,(138)}{log\,(1.0043)} = 1150 = 1.15 \times 10^3 \qquad \text{(Chapter 6.6.12)}$$

Thus at least a thousand effusion steps are necessary to obtain highly enriched ^{235}U. Figure 6.6.6 shows a small part of a system that is used to prepare enriched uranium on a large scale.

Exercise

Helium consists of two isotopes: ^3He (natural abundance = 0.000134%) and ^4He (natural abundance = 99.999866%). Their atomic masses are 3.01603 and 4.00260, respectively. Helium-3 has unique physical properties and is used in the study of ultralow temperatures. It is separated from the more abundant ^4He by a process of gaseous effusion.

1. Calculate the ratio of the effusion rates of ^3He and ^4He and thus the enrichment possible in a single effusion step.
2. How many effusion steps are necessary to yield 99.0% pure ^3He?

Answer: a. ratio of effusion rates = 1.15200; one step gives 0.000154% ^3He; b. 96 steps



Figure 6.6.6 A Portion of a Plant for Separating Uranium Isotopes by Effusion of UF_6 *The large cylindrical objects (note the human for scale) are so-called diffuser (actually effuser) units, in which gaseous UF_6 is pumped through a porous barrier to partially separate the isotopes. The UF_6 must be passed through multiple units to become substantially enriched in ^{235}U. While gaseous diffusion was the original method of uranium isotope separation today, this process is done using centrifuges*

Rates of Diffusion or Effusion

Graham's law is an empirical relationship that states that the ratio of the rates of diffusion or effusion of two gases is the square root of the inverse ratio of their molar masses. The relationship is based on the postulate that all gases at the same temperature have the same average kinetic energy. We can write the expression for the average kinetic energy of two gases with different molar masses:

$$\overline{KE} = \frac{1}{2}M_1 v_{rms_1}^2 = \frac{1}{2}M_2 v_{rms_2}^2 \tag{6.6.13}$$

Multiplying both sides by 2 and rearranging give

$$\frac{v_{rms_2}^2}{v_{rms_1}^2} = \frac{M_1}{M_2} \tag{6.6.14}$$

Taking the square root of both sides gives

$$\frac{v_{rms_2}}{v_{rms_1}} = \sqrt{\frac{M_1}{M_2}} \tag{6.6.15}$$

Thus the rate at which a molecule, or a mole of molecules, diffuses or effuses is directly related to the speed at which it moves. Equation 6.6.15 shows that Graham's law is a direct consequence of the fact that gaseous molecules at the same temperature have the same average kinetic energy.

Typically, gaseous molecules have a speed of hundreds of meters per second (hundreds of miles per hour). The effect of molar mass on these speeds is dramatic, as illustrated in Figure 6.6.9 for some common gases. Because all gases have the same average kinetic energy, according to the Boltzmann distribution, molecules with lower masses, such as hydrogen and helium, have a wider distribution of speeds. The postulates of the kinetic molecular theory of gases lead to the following equation, which directly relates molar mass, temperature, and rms speed:

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} \tag{6.6.16}$$

In this equation, v_{rms} has units of meters per second; consequently, the units of molar mass M are kilograms per mole, temperature T is expressed in kelvins, and the ideal gas constant R has the value 8.3145 J/(K·mol).

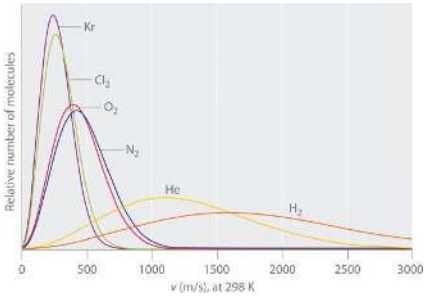


Figure 6.6.9 The Wide Variation in Molecular Speeds Observed at 298 K for Gases with Different Molar Masses *The lightest gases have a wider distribution of speeds and the highest average speeds.*

Note the Pattern

Molecules with lower masses have a wider distribution of speeds and a higher average speed.

Note the Pattern

The denser the gas, the shorter the mean free path.

Example 6.6.4

Calculate the rms speed of a sample of *cis*-2-butene (C_4H_8) at 20°C.

Given: compound and temperature

Asked for: rms speed

Strategy:

Calculate the molar mass of *cis*-2-butene. Be certain that all quantities are expressed in the appropriate units and then use Equation 10.39 to calculate the rms speed of the gas.

Solution:

To use Equation 6.6.14, we need to calculate the molar mass of *cis*-2-butene and make sure that each quantity is expressed in the appropriate units. Butene is C_4H_8, so its molar mass is 56.11 g/mol. Thus

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

Exercise

Calculate the rms speed of a sample of radon gas at 23°C

$$M = 56.11\ g/mol = 56.11 \times 10^{-3}\ kg/mol \qquad \text{(Chapter 6.6.13)}$$

$$T = 20 + 273 = 293\ K \qquad \text{(Chapter 6.6.14)}$$

$$R = 8.3145\ J/(K \cdot mol) = 8.3145\ \left(kg \cdot m^2\right) / \left(s^2 \cdot K \cdot mol\right) \qquad \text{(Chapter 6.6.15)}$$

$$v_{rms} = \sqrt{\frac{3RT}{M}} \qquad \text{(Chapter 6.6.16)}$$

$$= \sqrt{\frac{3 \cdot 8.3145\ \left(\cancel{kg} \cdot m^2\right) / \left(s^2 \cdot \cancel{K \cdot mol}\right) \cdot 293\ K}{56.11 \times 10^{-3}\ \cancel{kg} / \cancel{mol}}}$$

$$= 3.61 \times 10^2\ m/s$$

.

Answer: 1.82×10^2 m/s (about 410 mi/h)

The kinetic molecular theory of gases demonstrates how a successful theory can explain previously observed empirical relationships (laws) in an intuitively satisfying way. Unfortunately, the actual gases that we encounter are not "ideal," although their behavior usually approximates that of an ideal gas. In Chapter 10 we explore how the behavior of real gases differs from that of ideal gases.

Summary

The behavior of ideal gases is explained by the **kinetic molecular theory of gases**. Molecular motion, which leads to collisions between molecules and the container walls, explains pressure, and the large intermolecular distances in gases explain their high compressibility. Although all gases have the same average kinetic energy at a given temperature, they do not all possess the same **root mean square (rms) speed (v_{rms})**. The actual values of speed and kinetic energy are not the same for all particles of a gas but are given by a **Boltzmann distribution**, in which some molecules have higher or lower speeds (and kinetic energies) than average. **Diffusion** is the gradual mixing of gases to form a sample of uniform composition even in the absence of mechanical agitation. In contrast, **effusion** is the escape of a gas from a container through a tiny opening into an evacuated space. The rate of effusion of a gas is inversely proportional to the square root of its molar mass (**Graham's law**), a relationship that closely approximates the rate of diffusion. As a result, light gases tend to diffuse and effuse much more rapidly than heavier gases. The **mean free path** of a molecule is the average distance it travels between collisions.

Key Takeaway

- The kinetic molecular theory of gases provides a molecular explanation for the observations that led to the development of the ideal gas law.

Key Equations

Average kinetic energy

Equation 6.6.6:

$$\overline{e_K} = \frac{1}{2}m\overline{u^2} = \frac{3}{2}\frac{R}{N_A}T \tag{Chapter 6.6.17}$$

Root mean square speed

Equation 6.6.8 :

$$u_{\text{rms}} = \sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + \cdots u_N^2}{N}} \tag{Chapter 6.6.18}$$

Graham's law for diffusion and effusion

Equation 6..6.10

$$\frac{r_1}{r_2} = \frac{\sqrt{M_2}}{\sqrt{M_1}} \tag{Chapter 6.6.19}$$

Kinetic molecular theory of gases

Equation 6.6.14:

$$v_{rms} = \sqrt{\frac{3RT}{M}} \tag{Chapter 6.6.20}$$

Conceptual Problems

1. Which of the following processes represents effusion, and which represents diffusion?
    1. helium escaping from a hole in a balloon
    2. vapor escaping from the surface of a liquid
    3. gas escaping through a membrane
2. Which postulate of the kinetic molecular theory of gases most readily explains the observation that a helium-filled balloon is round?
3. Why is it relatively easy to compress a gas? How does the compressibility of a gas compare with that of a liquid? A solid? Why? Which of the postulates of the kinetic molecular theory of gases most readily explains these observations?
4. What happens to the average kinetic energy of a gas if the rms speed of its particles increases by a factor of 2? How is the rms speed different from the average speed?
5. Which gas—radon or helium—has a higher average kinetic energy at 100°C? Which has a higher average speed? Why? Which postulate of the kinetic molecular theory of gases most readily supports your answer?
6. What is the relationship between the average speed of a gas particle and the temperature of the gas? What happens to the distribution of molecular speeds if the temperature of a gas is increased? Decreased?
7. Qualitatively explain the relationship between the number of collisions of gas particles with the walls of a container and the pressure of a gas. How does increasing the temperature affect the number of collisions?
8. What happens to the average kinetic energy of a gas at constant temperature if the
    1. volume of the gas is increased?
    2. pressure of the gas is increased?
9. What happens to the density of a gas at constant temperature if the
    1. volume of the gas is increased?
    2. pressure of the gas is increased?

10. Use the kinetic molecular theory of gases to describe how a decrease in volume produces an increase in pressure at constant temperature. Similarly, explain how a decrease in temperature leads to a decrease in volume at constant pressure.
11. Graham's law is valid only if the two gases are at the same temperature. Why?
12. If we lived in a helium atmosphere rather than in air, would we detect odors more or less rapidly than we do now? Explain your reasoning. Would we detect odors more or less rapidly at sea level or at high altitude? Why?

Numerical Problems

1. At a given temperature, what is the ratio of the rms speed of the atoms of Ar gas to the rms speed of molecules of H_2 gas?
2. At a given temperature, what is the ratio of the rms speed of molecules of CO gas to the rms speed of molecules of H_2S gas?
3. What is the ratio of the rms speeds of argon and oxygen at any temperature? Which diffuses more rapidly?
4. What is the ratio of the rms speeds of Kr and NO at any temperature? Which diffuses more rapidly?
5. Deuterium (D) and tritium (T) are heavy isotopes of hydrogen. Tritium has an atomic mass of 3.016 amu and has a natural abundance of 0.000138%. The effusion of hydrogen gas (containing a mixture of H_2, HD, and HT molecules) through a porous membrane can be used to obtain samples of hydrogen that are enriched in tritium. How many membrane passes are necessary to give a sample of hydrogen gas in which 1% of the hydrogen molecules are HT?
6. Samples of HBr gas and NH_3 gas are placed at opposite ends of a 1 m tube. If the two gases are allowed to diffuse through the tube toward one another, at what distance from each end of the tube will the gases meet and form solid NH_4Br?

Answer

1. At any temperature, the rms speed of hydrogen is 4.45 times that of argon.
2.
3.
4.
5.
6.

Contributors

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Chapter 6.7: Mean Free Path

Learning Objective

- The mean free path is the average distance traveled by a moving molecule between collisions.

Introduction

Imagine gas leaking out of a pipe. It would take a while for the gas to diffuse and spread into the environment. This is because gas molecules collide with each other, causing them to change in speed and direction. Therefore, they can never move in a straight path without interruptions. Between every two consecutive collisions, a gas molecule travels a straight path. The average distance of all the paths of a molecule is the mean free path.

Gas molecules do not diffuse nearly as rapidly as their very high speeds might suggest. If molecules actually moved through a room at hundreds of miles per hour, we would detect odors faster than we hear sound. Instead, it can take several minutes for us to detect an aroma because molecules are traveling in a medium with other gas molecules. Because gas molecules collide as often as 10^{10} times per second, changing direction and speed with each collision, they do not diffuse across a room in a straight line, as illustrated schematically in Figure 6.7.1 The average distance traveled by a molecule between collisions is the mean free pathThe average distance traveled by a molecule between collisions.. The denser the gas, the shorter the mean free path; conversely, as density decreases, the mean free path becomes longer because collisions occur less frequently. At 1 atm pressure and 25°C, for example, an oxygen or nitrogen molecule in the atmosphere travels only about 6.0×10^{-8} m (60 nm) between collisions. In the upper atmosphere at about 100 km altitude, where gas density is much lower, the mean free path is about 10 cm; in space between galaxies, it can be as long as 1×10^{10} m (about 6 million miles).

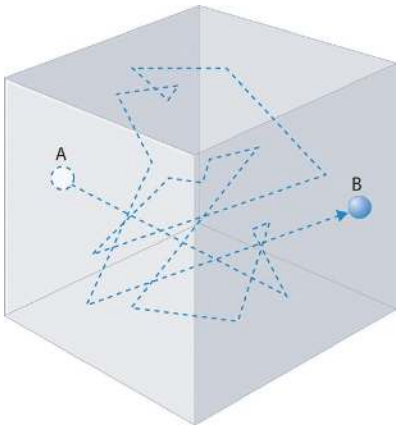


Figure 6.7.1 The Path of a Single Particle in a Gas Sample *The frequent changes in direction are the result of collisions with other gas molecules and with the walls of the container.*

Calculations

In reality, the mean free path cannot be calculated by taking the average of all the paths because it is impossible to know the distance of each path traveled by a molecule. However, we can calculate it from the average speed ($\langle c \rangle$) of the molecule divided by the collision frequency (Z). The formula for this is:

$$\lambda = \frac{\langle c \rangle}{Z} \tag{6.7.1}$$

Because Z is equal to $1/t$, where t is the average time between collisions, the formula can also be:

$$\lambda = \frac{\langle c \rangle}{\frac{1}{t}} \tag{Chapter 6.7.1}$$

$$= \langle c \rangle \times t \tag{Chapter 6.7.2}$$

In addition, because

$$\lambda = \sqrt{2}\pi d^2 \langle c \rangle (N/V) \tag{6.7.3}$$

where

- d is the diameter of the molecule and
- (N/V) is the density,

The formula can be further modified to:

$$l = \frac{\langle c \rangle}{\sqrt{2}\pi d^2 \langle c \rangle \frac{N}{V}} \tag{Chapter 6.7.3}$$

$$= \frac{1}{\sqrt{2}\pi d^2 \frac{N}{V}} \tag{Chapter 6.7.4}$$

Factors affecting mean free path

- Density: As gas density increases, the molecules become closer to each other. Therefore, they are more likely to run into each other, so the mean free path decreases.
  - Increasing the number of molecules or decreasing the volume causes density to increase. This decreases the mean free path.
- Radius of molecule: Increasing the radii of the molecules decreases the space between them, causing them to run into each other more often. Therefore, the mean free path decreases.
- Pressure, temperature, and other factors that affect density can indirectly affect mean free path.

Practice Problems

1. A gas has an average speed of 10 m/s and a collision frequency of 10 s^{-1}. What is its mean free path?
2. A gas has an average speed of 10 m/s and an average time of 0.1 s between collisions. What is its mean free path?
3. A gas has a density of 10 particles m^{-3} and a molecular diameter of 0.1 m. What is its mean free path?
4. A gas in a 1 m^3 container has a molecular diameter of 0.1 m. There are 10 molecules. What is its mean free path?
5. A gas has a molecular diameter of 0.1 m. It also has a mean free path of 2.25 m. What is its density?

Answers

1. l = <c> / = 10 m/s / 10 s^(-1) = 1 m
2. l = <c> X (average time between collisions) = 10 m/s X 0.1 s = 1 m
3. l = 1 / [√2 (pi) d^2 (N/v)] = 1 / [√2 (pi)(0.1 m)^2 (10 m^(-3))] = 2.25 m
4. l = 1 / [√2 (pi) d^2 (N/v)] = 1 / [√2 (pi)(0.1 m)^2 (10 / 1 m^3)] = 2.25 m
5. l = 1 / [√2 (pi) d^2 (N/v)]
   2.25 m = 1 / [√2 (pi)(0.1 m)^2 (N/v)]
   N/v = 10 m^(-3)

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CHAPTER OVERVIEW

Chapter 7: Fluids

- Chapter 7.0: Introduction
- Chapter 7.1: Real Gases
- Chapter 7.2: Intermolecular forces
- Chapter 7.3: Unique Properties of Liquids
- Chapter 7.4: Vapor Pressure
- Chapter 7.5: Changes of State
- Chapter 7.6: Critical Temperature and Pressure
- Chapter 7.7: Phase Diagrams
- Chapter 7.8: Liquid Crystals
- Chapter 7.9: End of Chapter Material

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Chapter 7.0: Introduction

Learning Objective

- To be familiar with the kinetic molecular description of liquids.

The kinetic molecular theory of gases described in Section 6.6 gives a reasonably accurate description of the behavior of gases. A similar model can be applied to liquids, but it must take into account the nonzero volumes of particles and the presence of strong intermolecular attractive forces.

In a gas, the distance between molecules, whether monatomic or polyatomic, is very large compared with the size of the molecules; thus gases have a low density and are highly compressible. In contrast, the molecules in liquids are very close together, with essentially no empty space between them. As in gases, however, the molecules in liquids are in constant motion, and their kinetic energy (and hence their speed) depends on their temperature. We begin our discussion by examining some of the characteristic properties of liquids to see how each is consistent with a modified kinetic molecular description.

Density

The molecules of a liquid are packed relatively close together. Consequently, liquids are much denser than gases. The density of a liquid is typically about the same as the density of the solid state of the substance. Densities of liquids are therefore more commonly measured in units of grams per cubic centimeter (g/cm^3) or grams per milliliter (g/mL) than in grams per liter (g/L), the unit commonly used for gases.

Molecular Order

Liquids exhibit short-range order because strong intermolecular attractive forces cause the molecules to pack together rather tightly. Because of their higher kinetic energy compared to the molecules in a solid, however, the molecules in a liquid move rapidly with respect to one another. Thus unlike the ions in the ionic solids discussed in Chapter 4 Section 4.1, the molecules in liquids are not arranged in a repeating three-dimensional array. Unlike the molecules in gases, however, the arrangement of the molecules in a liquid is not completely random.

Compressibility

Liquids have so little empty space between their component molecules that they cannot be readily compressed. Compression would force the atoms on adjacent molecules to occupy the same region of space.

Thermal Expansion

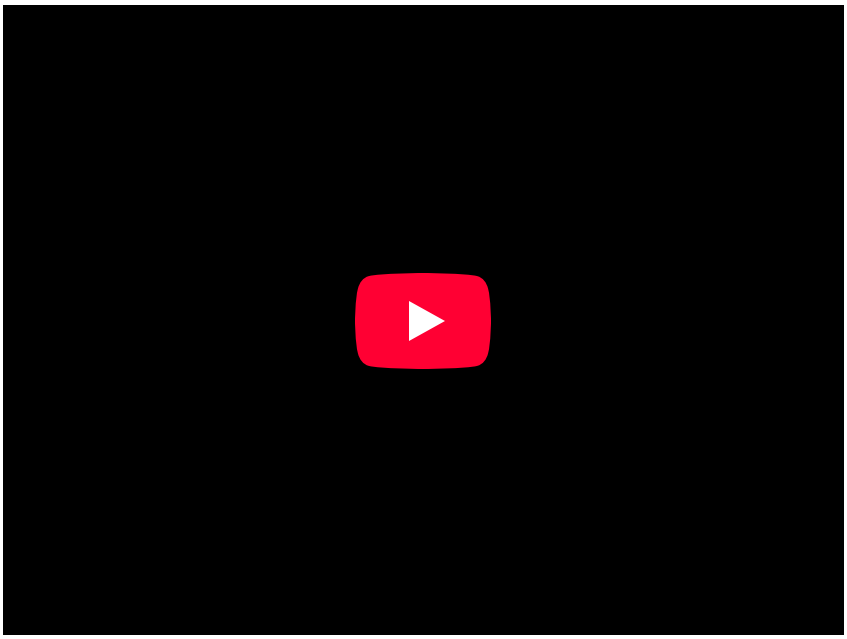
The intermolecular forces in liquids are strong enough to keep them from expanding significantly when heated (typically only a few percent over a 100°C temperature range). Thus the volumes of liquids are somewhat fixed. Notice from Table 7.0.1 that the density of water, for example, changes by only about 3% over a 90-degree temperature range.

Table 7.0.1 The Density of Water at Various Temperatures

T (°C)	Density (g/cm^3)
0	0.99984
30	0.99565
60	0.98320
90	0.96535

Diffusion

Molecules in liquids diffuse because they are in constant motion (Figure 7.0.1). A molecule in a liquid cannot move far before colliding with another molecule, however, so the mean free path in liquids is very short, and the rate of diffusion is much slower than in gases.



:ular Diffusion in a Liquid A drop of an aqueous solution containing a marker dye is added to a larger volume ses, the color of the dye becomes fainter at the edges.

Fluidity

Liquids can flow, adjusting to the shape of their containers, because their molecules are free to move. This freedom of motion and their close spacing allow the molecules in a liquid to move rapidly into the openings left by other molecules, in turn generating more openings, and so forth (Figure 7.0.2).

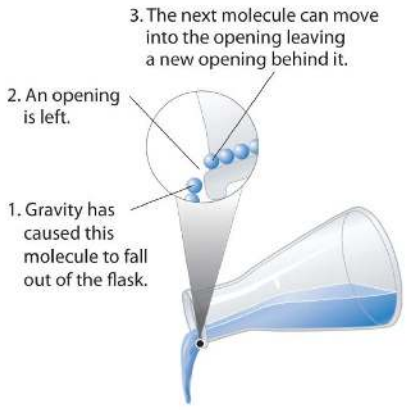


Figure 7.0.2 Why Liquids Flow *Molecules in a liquid are in constant motion. Consequently, when the flask is tilted, molecules move to the left and down due to the force of gravity, and the openings are occupied by other molecules. The result is a net flow of liquid out of the container.*

Summary

The properties of liquids can be explained using a modified version of the kinetic molecular theory of gases described in Chapter 10 . This model explains the higher density, greater order, and lower compressibility of liquids versus gases; the thermal expansion of liquids; why they diffuse; and why they adopt the shape (but not the volume) of their containers.

Key Takeaway

- The kinetic molecular description of liquids must take into account both the nonzero volumes of particles and the presence of strong intermolecular attractive forces.

Conceptual Problems

1. A liquid, unlike a gas, is virtually *incompressible*. Explain what this means using macroscopic and microscopic descriptions. What general physical properties do liquids share with solids? What properties do liquids share with gases?
2. Using a kinetic molecular approach, discuss the differences and similarities between liquids and gases with regard to
    1. thermal expansion.
    2. fluidity.
    3. diffusion.
3. How must the ideal gas law be altered to apply the kinetic molecular theory of gases to liquids? Explain.
4. Why are the root mean square speeds of molecules in liquids less than the root mean square speeds of molecules in gases?

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Chapter 7.1: Real Gases

Learning Objective

- To recognize the differences between the behavior of an ideal gas and a real gas.

The postulates of the kinetic molecular theory of gases ignore both the volume occupied by the molecules of a gas and all interactions between molecules, whether attractive or repulsive. In reality, however, all gases have nonzero molecular volumes. Furthermore, the molecules of real gases interact with one another in ways that depend on the structure of the molecules and therefore differ for each gaseous substance. In this section, we consider the properties of real gases and how and why they differ from the predictions of the ideal gas law. We also examine liquefaction, a key property of real gases that is not predicted by the kinetic molecular theory of gases.

Pressure, Volume, and Temperature Relationships in Real Gases

For an ideal gas, a plot of *PV*/*nRT* versus *P* gives a horizontal line with an intercept of 1 on the *PV*/*nRT* axis. Real gases, however, show significant deviations from the behavior expected for an ideal gas, particularly at high pressures (part (a) in Figure 7.1.1). Only at relatively low pressures (less than 1 atm) do real gases approximate ideal gas behavior (part (b) in Figure 7.1.1). Real gases also approach ideal gas behavior more closely at higher temperatures, as shown in Figure 7.1.2 for N_2. Why do real gases behave so differently from ideal gases at high pressures and low temperatures? Under these conditions, the two basic assumptions behind the ideal gas law—namely, that gas molecules have negligible volume and that intermolecular interactions are negligible—are no longer valid.

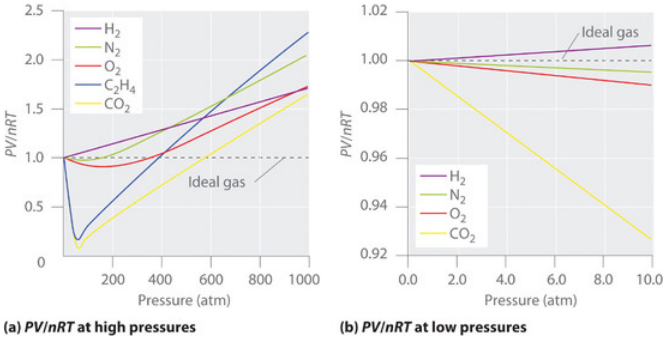


Figure 7.1.1 Real Gases Do Not Obey the Ideal Gas Law, Especially at High Pressures *(a) In these plots of PV/nRT versus P at 273 K for several common gases, there are large negative deviations observed for C_2H_4 and CO_2 because they liquefy at relatively low pressures. (b) These plots illustrate the relatively good agreement between experimental data for real gases and the ideal gas law at low pressures.*

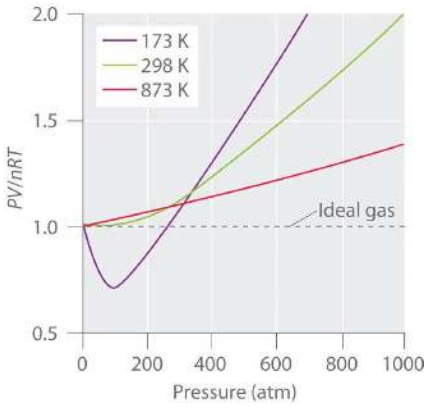


Figure 7.1.2 The Effect of Temperature on the Behavior of Real Gases *A plot of PV/nRT versus P for nitrogen gas at three temperatures shows that the approximation to ideal gas behavior becomes better as the temperature increases.*

Because the molecules of an ideal gas are assumed to have zero volume, the volume available to them for motion is always the same as the volume of the container. In contrast, the molecules of a real gas have small but measurable volumes. At low pressures, the gaseous molecules are relatively far apart, but as the pressure of the gas increases, the intermolecular distances become smaller and smaller (Figure 7.1.3). As a result, the volume occupied by the molecules becomes significant compared with the volume of the container. Consequently, the total volume occupied by the gas is greater than the volume predicted by the ideal gas law. Thus at very high pressures, the experimentally measured value of PV/nRT is greater than the value predicted by the ideal gas law.

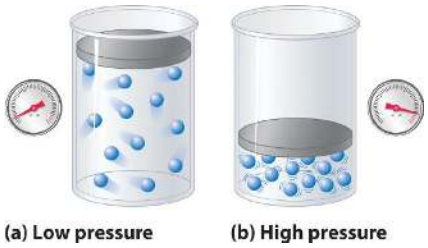


Figure 7.1.3 The Effect of Nonzero Volume of Gas Particles on the Behavior of Gases at Low and High Pressures *(a) At low pressures, the volume occupied by the molecules themselves is small compared with the volume of the container. (b) At high pressures, the molecules occupy a large portion of the volume of the container, resulting in significantly decreased space in which the molecules can move.*

Moreover, all molecules are attracted to one another by a combination of forces. These forces become particularly important for gases at low temperatures and high pressures, where intermolecular distances are shorter. Attractions between molecules reduce the number of collisions with the container wall, an effect that becomes more pronounced as the number of attractive interactions increases. Because the average distance between molecules decreases, the pressure exerted by the gas on the container wall decreases, and the observed pressure is *less* than expected (Figure 7.1.4). Thus as shown in Figure 7.1.2, at low temperatures, the ratio of PV/nRT is lower than predicted for an ideal gas, an effect that becomes particularly evident for complex gases and for simple gases at low temperatures. At very high pressures, the effect of nonzero molecular volume predominates. The competition between these effects is responsible for the minimum observed in the PV/nRT versus P plot for many gases.

Note the Pattern

Nonzero molecular volume makes the actual volume *greater* than predicted at high pressures; intermolecular attractions make the pressure *less* than predicted.

At high temperatures, the molecules have sufficient kinetic energy to overcome intermolecular attractive forces, and the effects of nonzero molecular volume predominate. Conversely, as the temperature is lowered, the kinetic energy of the gas molecules decreases. Eventually, a point is reached where the molecules can no longer overcome the intermolecular attractive forces, and the gas liquefies (condenses to a liquid).

The van der Waals Equation

The Dutch physicist Johannes van der Waals (1837–1923; Nobel Prize in Physics, 1910) modified the ideal gas law to describe the behavior of real gases by explicitly including the effects of molecular size and intermolecular forces. In his description of gas behavior, the so-called van der Waals equationA modification of the ideal gas law designed to describe the behavior of real gases by explicitly including the effects of molecular volume and intermolecular forces.,

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \tag{7.1.1}$$

a and b are empirical constants that are different for each gas. The values of a and b are listed in Table 7.1.1 for several common gases. The pressure term $P + (an^2/V^2)$ corrects for intermolecular attractive forces that tend to reduce the pressure from that predicted by the ideal gas law. Here, n^2/V^2 represents the concentration of the gas (n/V) squared because it takes two particles to engage in the pairwise intermolecular interactions of the type shown in Figure 7.1.4 . The volume term $V - nb$ corrects for the volume occupied by the gaseous molecules.

Table 7.1.1 van der Waals Constants for Some Common Gases

Gas	a ($L^2 \cdot atm/mol^2$)	b (L/mol)
He	0.03410	0.0238
Ne	0.205	0.0167
Ar	1.337	0.032
H_2	0.2420	0.0265
N_2	1.352	0.0387
O_2	1.364	0.0319
Cl_2	6.260	0.0542
NH_3	4.170	0.0371
CH_4	2.273	0.0430
CO_2	3.610	0.0429

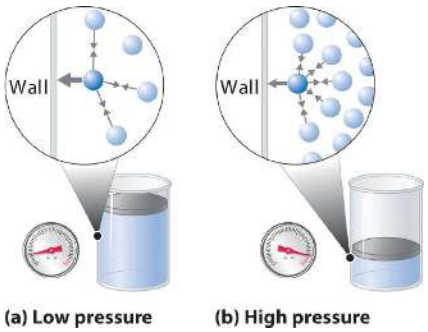


Figure 7.1.4 The Effect of Intermolecular Attractive Forces on the Pressure a Gas Exerts on the Container Walls *(a) At low pressures, there are relatively few attractive intermolecular interactions to lessen the impact of the molecule striking the wall of the container, and the pressure is close to that predicted by the ideal gas law. (b) At high pressures, with the average intermolecular distance relatively small, the effect of intermolecular interactions is to lessen the impact of a given molecule striking the container wall, resulting in a lower pressure than predicted by the ideal gas law.*

The correction for volume is negative, but the correction for pressure is positive to reflect the effect of each factor on V and P, respectively. Because nonzero molecular volumes produce a measured volume that is *larger* than that predicted by the ideal gas law, we must subtract the molecular volumes to obtain the actual volume available. Conversely, attractive intermolecular forces produce a pressure that is *less* than that expected based on the ideal gas law, so the an^2/V^2 term must be added to the measured pressure to correct for these effects.

Example 7.1.1

You are in charge of the manufacture of cylinders of compressed gas at a small company. Your company president would like to offer a 4.0 L cylinder containing 500 g of chlorine in the new catalog. The cylinders you have on hand have a rupture pressure of 40 atm. Use both the ideal gas law and the van der Waals equation to calculate the pressure in a cylinder at 25°C. Is this cylinder likely to be safe against sudden rupture (which would be disastrous and certainly result in lawsuits because chlorine gas is highly toxic)?

Given: volume of cylinder, mass of compound, pressure, and temperature

Asked for: safety

Strategy:

A Use the molar mass of chlorine to calculate the amount of chlorine in the cylinder. Then calculate the pressure of the gas using the ideal gas law.

B Obtain *a* and *b* values for Cl_2 from Table 7.1.1 . Use the van der Waals equation to solve for the pressure of the gas. Based on the value obtained, predict whether the cylinder is likely to be safe against sudden rupture.

Solution:

A We begin by calculating the amount of chlorine in the cylinder using the molar mass of chlorine (70.906 g/mol):

$$\left(500 \cancel{g}\right)\left(\frac{1\ mol}{70.906\ \cancel{g}} = 7.05 mol\ Cl_2\right)$$

Using the ideal gas law and the temperature in kelvins (298 K), we calculate the pressure:

$$P = \frac{nRT}{V} = \frac{\left(7.05\ \cancel{mol}\right)\left[0.08206\left(\cancel{L}\cdot atm\right)/\left(\cancel{K}\cdot\cancel{mol}\right)\right]\left(298\ \cancel{K}\right)}{4.0\ \cancel{L}} = 43\ atm$$

If chlorine behaves like an ideal gas, you have a real problem!

B Now let's use the van der Waals equation with the *a* and *b* values for Cl_2 from Table 7.1.1 . Solving for *P* gives

$$P = \frac{nRT}{V-nb} - \frac{an^2}{V^2}$$

$$= \frac{\left(7.05\ \cancel{mol}\right)\left[0.08206\left(\cancel{L}\cdot atm\right)/\left(\cancel{K}\cdot\cancel{mol}\right)\right]\left(298\ \cancel{K}\right)}{4.0\ \cancel{L} - 7.05\ \cancel{mol}\left(0.0542\ \cancel{L}/\cancel{mol}\right)} - \frac{6.260^2\ \cancel{L^2}\cdot atm/\cancel{mol^2}\left(7.05\ \cancel{mol^2}\right)}{4.0\ \cancel{L^2}}$$

$$= 47.7\ atm - 19.4\ atm = 28\ atm\ (2\ significant\ figures)$$

This pressure is well within the safety limits of the cylinder. The ideal gas law predicts a pressure 15 atm higher than that of the van der Waals equation.

Exercise

A 10.0 L cylinder contains 500 g of methane. Calculate its pressure to two significant figures at 27°C using the

1. ideal gas law.
2. van der Waals equation.

Answer: a. 77 atm; b. 67 atm

Liquefaction of Gases

LiquefactionThe condensation of gases into a liquid form. of gases is the condensation of gases into a liquid form, which is neither anticipated nor explained by the kinetic molecular theory of gases. Both the theory and the ideal gas law predict that gases compressed to very high pressures and cooled to very low temperatures should still behave like gases, albeit cold, dense ones. As gases are compressed and cooled, however, they invariably condense to form liquids, although very low temperatures are needed to liquefy light elements such as helium (for He, 4.2 K at 1 atm pressure).

Liquefaction can be viewed as an extreme deviation from ideal gas behavior. It occurs when the molecules of a gas are cooled to the point where they no longer possess sufficient kinetic energy to overcome intermolecular attractive forces. The precise combination of temperature and pressure needed to liquefy a gas depends strongly on its molar mass and structure, with heavier and more complex molecules usually liquefying at higher temperatures. In general, substances with large van der Waals *a* coefficients are relatively easy to liquefy because large *a* coefficients indicate relatively strong intermolecular attractive interactions. Conversely, small molecules with only light elements have small *a* coefficients, indicating weak intermolecular interactions, and they are relatively difficult to liquefy. Gas liquefaction is used on a massive scale to separate O_2, N_2, Ar, Ne, Kr, and Xe. After a sample of air is liquefied, the mixture is warmed, and the gases are separated according to their boiling points. In Section 7.2 , we will consider in more detail the nature of the intermolecular forces that allow gases to liquefy.

Note the Pattern

A large value of *a* indicates the presence of relatively strong intermolecular attractive interactions.

The ultracold liquids formed from the liquefaction of gases are called cryogenic liquids (an ultracold liquid formed from the liquefaction of gases., from the Greek *kryo*, meaning “cold,” and *genes*, meaning “producing”). They have applications as refrigerants in both industry and biology. For example, under carefully controlled conditions, the very cold temperatures afforded by liquefied gases such as nitrogen (boiling point = 77 K at 1 atm) can preserve biological materials, such as semen for the artificial insemination of cows and other farm animals. These liquids can also be used in a specialized type of surgery called *cryosurgery*, which selectively destroys tissues with a minimal loss of blood by the use of extreme cold.



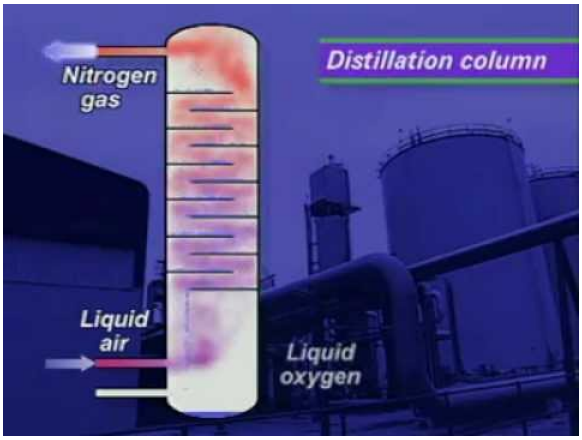


Figure 7.1.6 Compressing and Distilling Air: *this video from the Royal Society of Chemistry describes how air is liquefied by a combination of cooling and expansion and then distilled to yield liquid nitrogen, oxygen and argon*

Moreover, the liquefaction of gases is tremendously important in the storage and shipment of fossil fuels. Liquefied natural gas (LNG) and liquefied petroleum gas (LPG) are liquefied forms of hydrocarbons produced from natural gas or petroleum reserves. LNG consists mostly of methane, with small amounts of heavier hydrocarbons; it is prepared by cooling natural gas to below about −162°C. It can be stored in double-walled, vacuum-insulated containers at or slightly above atmospheric pressure. Because LNG occupies only about 1/600 the volume of natural gas, it is easier and more economical to transport. LPG is typically a mixture of

propane, propene, butane, and butenes and is primarily used as a fuel for home heating. It is also used as a feedstock for chemical plants and as an inexpensive and relatively nonpolluting fuel for some automobiles.



fying Natural Gas: *This video from Shell Oil describes the industrial process of liquefying natural gas*

Summary

No real gas exhibits ideal gas behavior, although many real gases approximate it over a range of conditions. Deviations from ideal gas behavior can be seen in plots of *PV*/*nRT* versus *P* at a given temperature; for an ideal gas, *PV*/*nRT* versus *P* = 1 under all conditions. At high pressures, most real gases exhibit larger *PV*/*nRT* values than predicted by the ideal gas law, whereas at low pressures, most real gases exhibit *PV*/*nRT* values close to those predicted by the ideal gas law. Gases most closely approximate ideal gas behavior at high temperatures and low pressures. Deviations from ideal gas law behavior can be described by the **van der Waals equation**, which includes empirical constants to correct for the actual volume of the gaseous molecules and quantify the reduction in pressure due to intermolecular attractive forces. If the temperature of a gas is decreased sufficiently, **liquefaction** occurs, in which the gas condenses into a liquid form. Liquefied gases have many commercial applications, including the transport of large amounts of gases in small volumes and the uses of ultracold **cryogenic liquids**.

Key Takeaway

- Molecular volumes and intermolecular attractions cause the properties of real gases to deviate from those predicted by the ideal gas law.

Key Equation

van der Waals equation

Equation 7.1.1: $\left(p + \frac{an^2}{V^2}\right)(V - b) = nRT$<mi/>

Conceptual Problems

1. What factors cause deviations from ideal gas behavior? Use a sketch to explain your answer based on interactions at the molecular level.
2. Explain the effect of nonzero atomic volume on the ideal gas law at high pressure. Draw a typical graph of volume versus $1/P$ for an ideal gas and a real gas.
3. For an ideal gas, the product of pressure and volume should be constant, regardless of the pressure. Experimental data for methane, however, show that the value of PV decreases significantly over the pressure range 0 to 120 atm at 0°C. The decrease in PV over the same pressure range is much smaller at 100°C. Explain why PV decreases with increasing temperature. Why is the decrease less significant at higher temperatures.
4. What is the effect of intermolecular forces on the liquefaction of a gas? At constant pressure and volume, does it become easier or harder to liquefy a gas as its temperature increases? Explain your reasoning. What is the effect of increasing the pressure on the liquefaction temperature?
5. Describe qualitatively what a and b, the two empirical constants in the van der Waals equation, represent.
6. In the van der Waals equation, why is the term that corrects for volume negative and the term that corrects for pressure positive? Why is n/V squared?
7. Liquefaction of a gas depends strongly on two factors. What are they? As temperature is decreased, which gas will liquefy first—ammonia, methane, or carbon monoxide? Why?
8. What is a cryogenic liquid? Describe three uses of cryogenic liquids.
9. Air consists primarily of O_2, N_2, Ar, Ne, Kr, and Xe. Use the concepts discussed in this chapter to propose two methods by which air can be separated into its components. Which component of air will be isolated first?
10. How can gas liquefaction facilitate the storage and transport of fossil fuels? What are potential drawbacks to these methods?

Numerical Problems

1. The van der Waals constants for xenon are $a = 4.19\ (L^2{\cdot}atm)/mol^2$ and $b = 0.0510$ L/mol. If a 0.250 mol sample of xenon in a container with a volume of 3.65 L is cooled to −90°C, what is the pressure of the sample assuming ideal gas behavior? What would be the *actual* pressure under these conditions?
2. The van der Waals constants for water vapor are $a = 5.46\ (L^2{\cdot}atm)/mol^2$ and $b = 0.0305$ L/mol. If a 20.0 g sample of water in a container with a volume of 5.0 L is heated to 120°C, what is the pressure of the sample assuming ideal gas behavior? What would be the *actual* pressure under these conditions?

Contributors

- Anonymous

Modified by Joshua Halpern, Scott Sinex and Scott Johnson

Video showing distillation of air from the Royal Society of Chemistry on YouTube

Video showing the purification of natural gas from Shell Oil on YouTube

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Chapter 7.2: Intermolecular forces

Learning Objective

- To describe the intermolecular forces in liquids.

The properties of liquids are intermediate between those of gases and solids but are more similar to solids. In contrast to *intra*molecular forces, such as the covalent bonds that hold atoms together in molecules and polyatomic ions, *inter*molecular forces hold molecules together in a liquid or solid. Intermolecular forces are generally much weaker than covalent bonds. For example, it requires 927 kJ to overcome the intramolecular forces and break both O–H bonds in 1 mol of water, but it takes only about 41 kJ to overcome the intermolecular attractions and convert 1 mol of liquid water to water vapor at 100°C. (Despite this seemingly low value, the intermolecular forces in liquid water are among the strongest such forces known!) Given the large difference in the strengths of intra- and intermolecular forces, changes between the solid, liquid, and gaseous states almost invariably occur for molecular substances *without breaking covalent bonds*.

Note the Pattern

The properties of liquids are intermediate between those of gases and solids but are more similar to solids.

Intermolecular forces determine bulk properties such as the melting points of solids and the boiling points of liquids. Liquids boil when the molecules have enough thermal energy to overcome the intermolecular attractive forces that hold them together, thereby forming bubbles of vapor within the liquid. Similarly, solids melt when the molecules acquire enough thermal energy to overcome the intermolecular forces that lock them into place in the solid.

Intermolecular forces are electrostatic in nature; that is, they arise from the interaction between positively and negatively charged species. Like covalent and ionic bonds, intermolecular interactions are the sum of both attractive and repulsive components. Because electrostatic interactions fall off rapidly with increasing distance between molecules, intermolecular interactions are most important for solids and liquids, where the molecules are close together. These interactions become important for gases only at very high pressures, where they are responsible for the observed deviations from the ideal gas law at high pressures. (For more information on the behavior of real gases and deviations from the ideal gas law, see Section 7.1.)

In this section, we explicitly consider three kinds of intermolecular interactions:There are two additional types of electrostatic interaction that you are already familiar with: the ion–ion interactions that are responsible for ionic bonding and the ion–dipole interactions that occur when ionic substances dissolve in a polar substance such as water. (For more information on ionic bonding, see Chapter 4. For more information on the dissolution of ionic substances, see Chapter 9) The intermolecular forces between neutral molecules are *dipole–dipole interactions*, *London dispersion forces*, and *hydrogen bonds*. The first two are often described collectively as van der Waals forcesThe intermolecular forces known as dipole–dipole interactions and London dispersion forces..

Dipole–Dipole Interactions

Recall from Chapter 4 that polar covalent bonds behave as if the bonded atoms have localized fractional charges that are equal but opposite (i.e., the two bonded atoms generate a *dipole*). If the structure of a molecule is such that the individual bond dipoles do not cancel one another, then the molecule has a net dipole moment. Molecules with net dipole moments tend to align themselves so that the positive end of one dipole is near the negative end of another and vice versa, as shown in part (a) in Figure 7.2.1 . These arrangements are more stable than arrangements in which two positive or two negative ends are adjacent (part (c) in Figure 7.2.1). Hence dipole–dipole interactionsA kind of intermolecular interaction (force) that results between molecules with net dipole moments., such as those in part (b) in Figure 7.2.1 , are *attractive intermolecular interactions*, whereas those in part (d) in Figure 7.2.1 are *repulsive intermolecular interactions*. Because molecules in a liquid move freely and continuously, molecules always experience both attractive and repulsive dipole–dipole interactions simultaneously, as shown in Figure 7.2.2 . On average, however, the attractive interactions dominate.

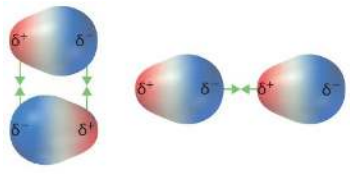


Figure 7.2.1 Attractive and Repulsive Dipole–Dipole Interactions *(a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions.*

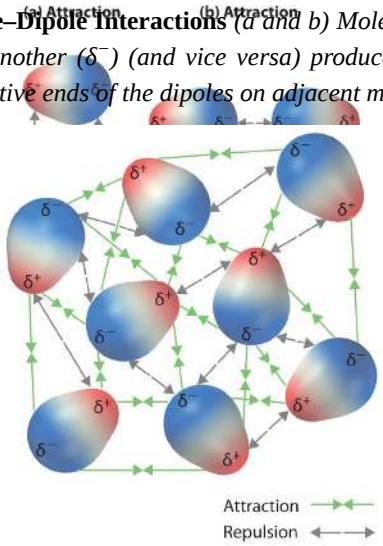


Figure 7.2.2 Both Attractive and Repulsive Dipole–Dipole Interactions Occur in a Liquid Sample with Many Molecules

Because each end of a dipole possesses only a fraction of the charge of an electron, dipole–dipole interactions are substantially weaker than the interactions between two ions, each of which has a charge of at least ±1, or between a dipole and an ion, in which one of the species has at least a full positive or negative charge. In addition, the attractive interaction between dipoles falls off much more rapidly with increasing distance than do the ion–ion interactions we considered in Chapter 4 . Recall that the attractive energy between two ions is proportional to $1/r$, where r is the distance between the ions. Doubling the distance ($r \rightarrow 2r$) decreases the attractive energy by one-half. In contrast, the energy of the interaction of two dipoles is proportional to $1/r^6$, so doubling the distance between the dipoles decreases the strength of the interaction by 2^6, or 64-fold. Thus a substance such as HCl, which is partially held together by dipole–dipole interactions, is a gas at room temperature and 1 atm pressure, whereas NaCl, which is held together by interionic interactions, is a high-melting-point solid. Within a series of compounds of similar molar mass, the strength of the intermolecular interactions increases as the dipole moment of the molecules increases, as shown in Table 7.2.1. Using what we learned in Chapter 4.7 about predicting relative bond polarities from the electronegativities of the bonded atoms, we can make educated guesses about the relative boiling points of similar molecules.

Table 7.2.1 Relationships between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass

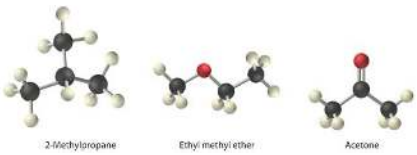
Compound	Molar Mass (g/mol)	Dipole Moment (D)	Boiling Point (K)
C_3H_6 (cyclopropane)	42	0	240
CH_3OCH_3 (dimethyl ether)	46	1.30	248
CH_3CN (acetonitrile)	41	3.9	355

Note the Pattern

The attractive energy between two ions is proportional to $1/r$, whereas the attractive energy between two dipoles is proportional to $1/r^6$.

Example 7.2.1

Arrange ethyl methyl ether ($CH_3OCH_2CH_3$), 2-methylpropane [isobutane, $(CH_3)_2CHCH_3$], and acetone (CH_3COCH_3) in order of increasing boiling points. Their structures are as follows:



Given: compounds

Asked for: order of increasing boiling points

Strategy:

Compare the molar masses and the polarities of the compounds. Compounds with higher molar masses and that are polar will have the highest boiling points.

Solution:

The three compounds have essentially the same molar mass (58–60 g/mol), so we must look at differences in polarity to predict the strength of the intermolecular dipole–dipole interactions and thus the boiling points of the compounds. The first compound, 2-methylpropane, contains only C–H bonds, which are not very polar because C and H have similar electronegativities. It should therefore have a very small (but nonzero) dipole moment and a very low boiling point. Ethyl methyl ether has a structure similar to H_2O; it contains two polar C–O single bonds oriented at about a 109° angle to each other, in addition to relatively nonpolar C–H bonds. As a result, the C–O bond dipoles partially reinforce one another and generate a significant dipole moment that should give a moderately high boiling point. Acetone contains a polar C=O double bond oriented at about 120° to two methyl groups with nonpolar C–H bonds. The C–O bond dipole therefore corresponds to the molecular dipole, which should result in both a rather large dipole moment and a high boiling point. Thus we predict the following order of boiling points: 2-methylpropane < ethyl methyl ether < acetone. This result is in good agreement with the actual data: 2-methylpropane, boiling point = −11.7°C, and the dipole moment (μ) = 0.13 D; methyl ethyl ether, boiling point = 7.4°C and μ = 1.17 D; acetone, boiling point = 56.1°C and μ = 2.88 D.

Exercise

Arrange carbon tetrafluoride (CF_4), ethyl methyl sulfide ($CH_3SC_2H_5$), dimethyl sulfoxide [$(CH_3)_2S{=}O$], and 2-methylbutane [isopentane, $(CH_3)_2CHCH_2CH_3$] in order of decreasing boiling points.

Answer: dimethyl sulfoxide (boiling point = 189.9°C) > ethyl methyl sulfide (boiling point = 67°C) > 2-methylbutane (boiling point = 27.8°C) > carbon tetrafluoride (boiling point = −128°C)

London Dispersion Forces

Thus far we have considered only interactions between polar molecules, but other factors must be considered to explain why many nonpolar molecules, such as bromine, benzene, and hexane, are liquids at room temperature, and others, such as iodine and naphthalene, are solids. Even the noble gases can be liquefied or solidified at low temperatures, high pressures, or both (Table 7.2.2)

What kind of attractive forces can exist between nonpolar molecules or atoms? This question was answered by Fritz London (1900–1954), a German physicist who later worked in the United States. In 1930, London proposed that temporary fluctuations in the electron distributions within atoms and nonpolar molecules could result in the formation of short-lived instantaneous dipole momentsThe short-lived dipole moment in atoms and nonpolar molecules caused by the constant motion of their electrons, which results in an asymmetrical distribution of charge at any given instant., which produce attractive forces called London dispersion forcesA kind of intermolecular interaction (force) that results from temporary fluctuations in the electron distribution within atoms and nonpolar molecules. between otherwise nonpolar substances.

Table 7.2.2 Normal Melting and Boiling Points of Some Elements and Nonpolar Compounds

Substance	Molar Mass (g/mol)	Melting Point (°C)	Boiling Point (°C)
Ar	40	−189.4	−185.9
Xe	131	−111.8	−108.1
N_2	28	−210	−195.8
O_2	32	−218.8	−183.0
F_2	38	−219.7	−188.1
I_2	254	113.7	184.4
CH_4	16	−182.5	−161.5

Consider a pair of adjacent He atoms, for example. On average, the two electrons in each He atom are uniformly distributed around the nucleus. Because the electrons are in constant motion, however, their distribution in one atom is likely to be asymmetrical at any given instant, resulting in an instantaneous dipole moment. As shown in part (a) in Figure 7.2.3, the instantaneous dipole moment on one atom can interact with the electrons in an adjacent atom, pulling them toward the positive end of the instantaneous dipole or repelling them from the negative end. The net effect is that the first atom causes the temporary formation of a dipole, called an induced dipoleA short-lived dipole moment that is created in atoms and nonpolar molecules adjacent to atoms or molecules with an instantaneous dipole moment., in the second. Interactions between these temporary dipoles cause atoms to be attracted to one another. These attractive interactions are weak and fall off rapidly with increasing distance. London was able to show with quantum mechanics that the attractive energy between molecules due to temporary dipole–induced dipole interactions falls off as $1/r^6$. Doubling the distance therefore decreases the attractive energy by 2^6, or 64-fold.

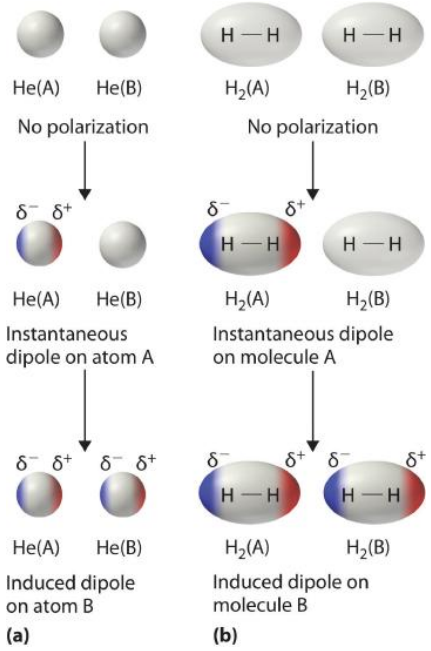


Figure 7.2.3 Instantaneous Dipole Moments *The formation of an instantaneous dipole moment on one He atom (a) or an H_2 molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.*

Instantaneous dipole–induced dipole interactions between nonpolar molecules can produce intermolecular attractions just as they produce interatomic attractions in monatomic substances like Xe. This effect, illustrated for two H_2 molecules in part (b) in Figure 7.2.3 tends to become more pronounced as atomic and molecular masses increase (Table 7.2.2). For example, Xe boils at −108.1°C, whereas He boils at −269°C. The reason for this trend is that the strength of London dispersion forces is related to the ease with which the electron distribution in a given atom can be perturbed. In small atoms such as He, the two 1*s* electrons are held close to the nucleus in a very small volume, and electron–electron repulsions are strong enough to prevent significant asymmetry in

their distribution. In larger atoms such as Xe, however, the outer electrons are much less strongly attracted to the nucleus because of filled intervening shells. (For more information on shielding, see Section 2.2) As a result, it is relatively easy to temporarily deform the electron distribution to generate an instantaneous or induced dipole. The ease of deformation of the electron distribution in an atom or molecule is called its polarizabilityThe ease of deformation of the electron distribution in an atom or molecule.. Because the electron distribution is more easily perturbed in large, heavy species than in small, light species, we say that heavier substances tend to be much more *polarizable* than lighter ones.

Note the Pattern

For similar substances, London dispersion forces get stronger with increasing molecular size.

The polarizability of a substance also determines how it interacts with ions and species that possess permanent dipoles, as we shall see when we discuss solutions in Chapter 9. Thus London dispersion forces are responsible for the general trend toward higher boiling points with increased molecular mass and greater surface area in a homologous series of compounds, such as the alkanes (part (a) in Figure 7.2.4). The strengths of London dispersion forces also depend significantly on molecular shape because shape determines how much of one molecule can interact with its neighboring molecules at any given time. For example, part (b) in Figure 7.2.4 shows 2,2-dimethylpropane (neopentane) and *n*-pentane, both of which have the empirical formula C_5H_{12}. Neopentane is almost spherical, with a small surface area for intermolecular interactions, whereas *n*-pentane has an extended conformation that enables it to come into close contact with other *n*-pentane molecules. As a result, the boiling point of neopentane (9.5°C) is more than 25°C lower than the boiling point of *n*-pentane (36.1°C).

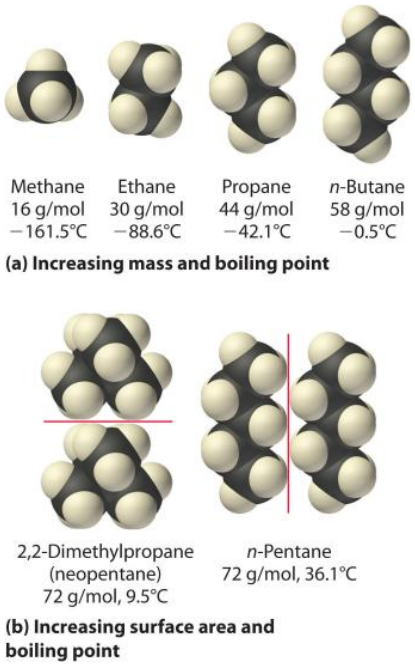


Figure 7.2.4 Mass and Surface Area Affect the Strength of London Dispersion Forces *(a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules and consequently higher boiling points. (b) Linear n-pentane molecules have a larger surface area and stronger intermolecular forces than spherical neopentane molecules. As a result, neopentane is a gas at room temperature, whereas n-pentane is a volatile liquid.*

All molecules, whether polar or nonpolar, are attracted to one another by London dispersion forces in addition to any other attractive forces that may be present. In general, however, dipole–dipole interactions in small polar molecules are significantly stronger than London dispersion forces, so the former predominate.

Example 7.2.2

Arrange *n*-butane, propane, 2-methylpropane [isobutene, $(CH_3)_2CHCH_3$], and *n*-pentane in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Determine the intermolecular forces in the compounds and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

The four compounds are alkanes and nonpolar, so London dispersion forces are the only important intermolecular forces. These forces are generally stronger with increasing molecular mass, so propane should have the lowest boiling point and *n*-pentane should have the highest, with the two butane isomers falling in between. Of the two butane isomers, 2-methylpropane is more compact, and *n*-butane has the more extended shape. Consequently, we expect intermolecular interactions for *n*-butane to be stronger due to its larger surface area, resulting in a higher boiling point. The overall order is thus as follows, with actual boiling points in parentheses: propane (−42.1°C) < 2-methylpropane (−11.7°C) < *n*-butane (−0.5°C) < *n*-pentane (36.1°C).

Exercise

Arrange GeH_4, $SiCl_4$, SiH_4, CH_4, and $GeCl_4$ in order of decreasing boiling points.

Answer: $GeCl_4$ (87°C) > $SiCl_4$ (57.6°C) > GeH_4 (−88.5°C) > SiH_4 (−111.8°C) > CH_4 (−161°C)

Hydrogen Bonds

Molecules with hydrogen atoms bonded to electronegative atoms such as O, N, and F (and to a much lesser extent Cl and S) tend to exhibit unusually strong intermolecular interactions. These result in much higher boiling points than are observed for substances in which London dispersion forces dominate, as illustrated for the covalent hydrides of elements of groups 14–17 in Figure 7.2.5 . Methane and its heavier congeners in group 14 form a series whose boiling points increase smoothly with increasing molar mass. This is the expected trend in nonpolar molecules, for which London dispersion forces are the exclusive intermolecular forces. In contrast, the hydrides of the lightest members of groups 15–17 have boiling points that are more than 100°C greater than predicted on the basis of their molar masses. The effect is most dramatic for water: if we extend the straight line connecting the points for H_2Te and H_2Se to the line for period 2, we obtain an estimated boiling point of −130°C for water! Imagine the implications for life on Earth if water boiled at −130°C rather than 100°C.

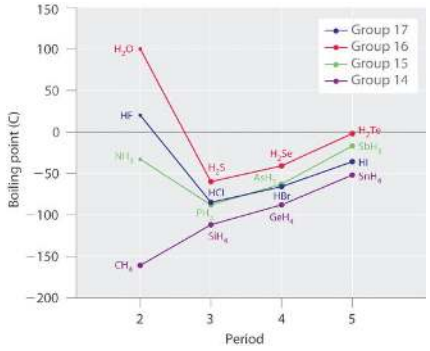


Figure 7.2.5 The Effects of Hydrogen Bonding on Boiling Points *These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously high for compounds with such low molecular masses.*

Why do strong intermolecular forces produce such anomalously high boiling points and other unusual properties, such as high enthalpies of vaporization and high melting points? The answer lies in the highly polar nature of the bonds between hydrogen and very electronegative elements such as O, N, and F. The large difference in electronegativity results in a large partial positive charge on hydrogen and a correspondingly large partial negative charge on the O, N, or F atom. Consequently, H–O, H–N, and H–F bonds have very large bond dipoles that can interact strongly with one another. Because a hydrogen atom is so small, these dipoles can also approach one another more closely than most other dipoles. The combination of large bond dipoles and short dipole–dipole distances results in very strong dipole–dipole interactions called hydrogen bondsAn unusually strong dipole-dipole interaction (intermolecular force) that results when hydrogen is bonded to very electronegative elements, such as O, N, and F., as shown for ice

in Figure 7.2.6 . A hydrogen bond is usually indicated by a dotted line between the hydrogen atom attached to O, N, or F (the *hydrogen bond donor*) and the atom that has the lone pair of electrons (the *hydrogen bond acceptor*). Because each water molecule contains two hydrogen atoms and two lone pairs, a tetrahedral arrangement maximizes the number of hydrogen bonds that can be formed. In the structure of ice, each oxygen atom is surrounded by a distorted tetrahedron of hydrogen atoms that form bridges to the oxygen atoms of adjacent water molecules. The bridging hydrogen atoms are *not* equidistant from the two oxygen atoms they connect, however. Instead, each hydrogen atom is 101 pm from one oxygen and 174 pm from the other. In contrast, each oxygen atom is bonded to two H atoms at the shorter distance and two at the longer distance, corresponding to two O–H covalent bonds and two O·H hydrogen bonds from adjacent water molecules, respectively. The resulting open, cagelike structure of ice means that the solid is actually slightly less dense than the liquid, which explains why ice floats on water rather than sinks. Remember that the hydrogens in one water molecule point towards one of the lone pairs of tetrahedal sp^3 orbitals of the oxygen atom on another water molecule.

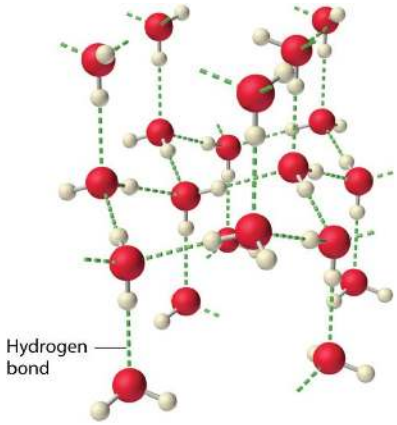


Figure 7.2.6 The Hydrogen-Bonded Structure of Ice *Each water molecule accepts two hydrogen bonds from two other water molecules and donates two hydrogen atoms to form hydrogen bonds with two more water molecules, producing an open, cagelike structure. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion.*

Note the Pattern

Hydrogen bond formation requires *both* a hydrogen bond donor *and* a hydrogen bond acceptor.

Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” (we will discuss how antifreeze works in Chapter 9) and why unprotected pipes in houses break if they are allowed to freeze.

Although hydrogen bonds are significantly weaker than covalent bonds, with typical dissociation energies of only 15–25 kJ/mol, they have a significant influence on the physical properties of a compound. Compounds such as HF can form only two hydrogen bonds at a time as can, on average, pure liquid NH_3. Consequently, even though their molecular masses are similar to that of water, their boiling points are significantly lower than the boiling point of water, which forms *four* hydrogen bonds at a time.

Example 7.2.3

Considering CH_3OH, C_2H_6, Xe, and $(CH_3)_3N$, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Given: compounds

Asked for: formation of hydrogen bonds and structure

Strategy:

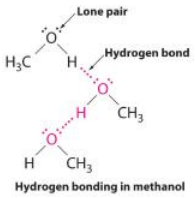
A Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.

B Of the compounds that can act as hydrogen bond donors, identify those that also contain lone pairs of electrons, which allow them to be hydrogen bond acceptors. If a substance is both a hydrogen donor and a hydrogen bond acceptor, draw a structure showing the hydrogen bonding.

Solution:

A Of the species listed, xenon (Xe), ethane (C_2H_6), and trimethylamine [$(CH_3)_3N$] do not contain a hydrogen atom attached to O, N, or F; hence they cannot act as hydrogen bond donors.

B The one compound that can act as a hydrogen bond donor, methanol (CH_3OH), contains both a hydrogen atom attached to O (making it a hydrogen bond donor) and two lone pairs of electrons on O (making it a hydrogen bond acceptor); methanol can thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor. The hydrogen-bonded structure of methanol is as follows:

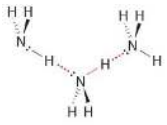


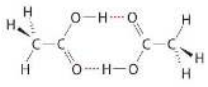
Hydrogen bonding in methanol

Exercise

Considering CH_3CO_2H, $(CH_3)_3N$, NH_3, and CH_3F, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Answer: CH_3CO_2H and NH_3;


Hydrogen bonding in ammonia


Hydrogen bonding in acetic acid

Example 7.2.4

Arrange C_{60} (buckminsterfullerene, which has a cage structure), NaCl, He, Ar, and N_2O in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Identify the intermolecular forces in each compound and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

Electrostatic interactions are strongest for an ionic compound, so we expect NaCl to have the highest boiling point. To predict the relative boiling points of the other compounds, we must consider their polarity (for dipole–dipole interactions), their ability to form hydrogen bonds, and their molar mass (for London dispersion forces). Helium is nonpolar and by far the lightest, so it should have the lowest boiling point. Argon and N_2O have very similar molar masses (40 and 44 g/mol, respectively), but N_2O is polar while Ar is not. Consequently, N_2O should have a higher boiling point. A C_{60} molecule is nonpolar, but its molar mass is 720 g/mol, much greater than that of Ar or N_2O. Because the boiling points of nonpolar substances increase rapidly with molecular mass, C_{60} should boil at a higher temperature than the other nonionic substances. The predicted order is thus as follows, with actual boiling points in parentheses: He (−269°C) < Ar (−185.7°C) < N_2O (−88.5°C) < C_{60} (>280°C) < NaCl (1465°C).

Exercise

Arrange 2,4-dimethylheptane, Ne, CS_2, Cl_2, and KBr in order of decreasing boiling points.

Answer: KBr (1435°C) > 2,4-dimethylheptane (132.9°C) > CS_2 (46.6°C) > Cl_2 (−34.6°C) > Ne (−246°C)

Summary

Molecules in liquids are held to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold the atoms together within molecules and polyatomic ions. Transitions between the solid and liquid or the liquid and gas phases are due to changes in intermolecular interactions but do not affect intramolecular interactions. The three major types of intermolecular interactions are dipole–dipole interactions, London dispersion forces (these two are often referred to collectively as **van der Waals forces**), and hydrogen bonds. **Dipole–dipole interactions** arise from the electrostatic interactions of the positive and negative ends of molecules with permanent dipole moments; their strength is proportional to the magnitude of the dipole moment and to $1/r^6$, where r is the distance between dipoles. **London dispersion forces** are due to the formation of **instantaneous dipole moments** in polar or nonpolar molecules as a result of short-lived fluctuations of electron charge distribution, which in turn cause the temporary formation of an **induced dipole** in adjacent molecules. Like dipole–dipole interactions, their energy falls off as $1/r^6$. Larger atoms tend to be more **polarizable** than smaller ones because their outer electrons are less tightly bound and are therefore more easily perturbed. **Hydrogen bonds** are especially strong dipole–dipole interactions between molecules that have hydrogen bonded to a highly electronegative atom, such as O, N, or F. The resulting partially positively charged H atom on one molecule (the *hydrogen bond donor*) can interact strongly with a lone pair of electrons of a partially negatively charged O, N, or F atom on adjacent molecules (the *hydrogen bond acceptor*). Because of strong O·H> hydrogen bonding between water molecules, water has an unusually high boiling point, and ice has an open, cagelike structure that is less dense than liquid water.

Key Takeaway

- Intermolecular forces are electrostatic in nature and include van der Waals forces and hydrogen bonds.

Conceptual Problems

1. What is the main difference between intramolecular interactions and intermolecular interactions? Which is typically stronger? How are changes of state affected by these different kinds of interactions?
2. Describe the three major kinds of intermolecular interactions discussed in this chapter and their major features. The hydrogen bond is actually an example of one of the other two types of interaction. Identify the kind of interaction that includes hydrogen bonds and explain why hydrogen bonds fall into this category.
3. Which are stronger—dipole–dipole interactions or London dispersion forces? Which are likely to be more important in a molecule with heavy atoms? Explain your answers.
4. Explain why hydrogen bonds are unusually strong compared to other dipole–dipole interactions. How does the strength of hydrogen bonds compare with the strength of covalent bonds?
5. Liquid water is essential for life as we know it, but based on its molecular mass, water should be a gas under standard conditions. Why is water a liquid rather than a gas under standard conditions?
6. Describe the effect of polarity, molecular mass, and hydrogen bonding on the melting point and boiling point of a substance.
7. Why are intermolecular interactions more important for liquids and solids than for gases? Under what conditions must these interactions be considered for gases?
8. Using acetic acid as an example, illustrate both attractive and repulsive intermolecular interactions. How does the boiling point of a substance depend on the magnitude of the repulsive intermolecular interactions?
9. In group 17, elemental fluorine and chlorine are gases, whereas bromine is a liquid and iodine is a solid. Why?
10. The boiling points of the anhydrous hydrogen halides are as follows: HF, 19°C; HCl, −85°C; HBr, −67°C; and HI, −34°C. Explain any trends in the data, as well as any deviations from that trend.
11. Identify the most important intermolecular interaction in each of the following.
    1. SO_2
    2. HF

3. CO_2
4. CCl_4
5. CH_2Cl_2

12. Identify the most important intermolecular interaction in each of the following.

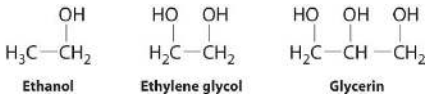
    1. LiF
    2. I_2
    3. ICl
    4. NH_3
    5. NH_2Cl

13. Would you expect London dispersion forces to be more important for Xe or Ne? Why? (The atomic radius of Ne is 38 pm, whereas that of Xe is 108 pm.)

14. Arrange Kr, Cl_2, H_2, N_2, Ne, and O_2 in order of increasing polarizability. Explain your reasoning.

15. Both water and methanol have anomalously high boiling points due to hydrogen bonding, but the boiling point of water is greater than that of methanol despite its lower molecular mass. Why? Draw the structures of these two compounds, including any lone pairs, and indicate potential hydrogen bonds.

16. The structures of ethanol, ethylene glycol, and glycerin are as follows:



    Arrange these compounds in order of increasing boiling point. Explain your rationale.

17. Do you expect the boiling point of H_2S to be higher or lower than that of H_2O? Justify your answer.

18. Ammonia (NH_3), methylamine (CH_3NH_2), and ethylamine ($CH_3CH_2NH_2$) are gases at room temperature, while propylamine ($CH_3CH_2CH_2NH_2$) is a liquid at room temperature. Explain these observations.

19. Why is it not advisable to freeze a sealed glass bottle that is completely filled with water? Use both macroscopic and microscopic models to explain your answer. Is a similar consideration required for a bottle containing pure ethanol? Why or why not?

20. Which compound in the following pairs will have the higher boiling point? Explain your reasoning.

    1. NH_3 or PH_3
    2. ethylene glycol ($HOCH_2CH_2OH$) or ethanol
    3. 2,2-dimethylpropanol [$CH_3C(CH_3)_2CH_2OH$] or *n*-butanol ($CH_3CH_2CH_2CH_2OH$)

21. Some recipes call for vigorous boiling, while others call for gentle simmering. What is the difference in the temperature of the cooking liquid between boiling and simmering? What is the difference in energy input?

22. Use the melting of a metal such as lead to explain the process of melting in terms of what is happening at the molecular level. As a piece of lead melts, the temperature of the metal remains constant, even though energy is being added continuously. Why?

23. How does the O–H distance in a hydrogen bond in liquid water compare with the O–H distance in the covalent O–H bond in the H_2O molecule? What effect does this have on the structure and density of ice?

24. 1. Explain why the hydrogen bonds in liquid HF are stronger than the corresponding intermolecular <math display="inline" xml:id="av_1.0-ch11_m003"><semantics><mrow><mtext>H</mtext><mo>·</mo><mo>·</mo><mo>·</mo><mtext>I</mtext></mrow></semantics></math> interactions in liquid HI.
    2. In which substance are the individual hydrogen bonds stronger: HF or H_2O? Explain your reasoning.
    3. For which substance will hydrogen bonding have the greater effect on the boiling point: HF or H_2O? Explain your reasoning.

5. Water is a liquid under standard conditions because of its unique ability to form four strong hydrogen bonds per molecule.

4.
6.
3.

Answers

7.
8.

9. As the atomic mass of the halogens increases, so does the number of electrons and the average distance of those electrons from the nucleus. Larger atoms with more electrons are more easily polarized than smaller atoms, and the increase in polarizability with atomic number increases the strength of London dispersion forces. These intermolecular interactions are strong enough to favor the condensed states for bromine and iodine under normal conditions of temperature and pressure.

10.

11.
    1. The V-shaped SO_2 molecule has a large dipole moment due to the polar S=O bonds, so dipole–dipole interactions will be most important.
    2. The H–F bond is highly polar, and the fluorine atom has three lone pairs of electrons to act as hydrogen bond acceptors; hydrogen bonding will be most important.
    3. Although the C=O bonds are polar, this linear molecule has no net dipole moment; hence, London dispersion forces are most important.
    4. This is a symmetrical molecule that has no net dipole moment, and the Cl atoms are relatively polarizable; thus, London dispersion forces will dominate.
    5. This molecule has a small dipole moment, as well as polarizable Cl atoms. In such a case, dipole–dipole interactions and London dispersion forces are often comparable in magnitude.

12.

13.

14.

15. Water has two polar O–H bonds with H atoms that can act as hydrogen bond donors, plus two lone pairs of electrons that can act as hydrogen bond acceptors, giving a net of *four* hydrogen bonds per H_2O molecule. Although methanol also has two lone pairs of electrons on oxygen that can act as hydrogen bond acceptors, it only has one O–H bond with an H atom that can act as a hydrogen bond donor. Consequently, methanol can only form *two* hydrogen bonds per molecule on average, versus four for water. Hydrogen bonding therefore has a much greater effect on the boiling point of water.

16.

17.

18.

19.

20.

21. Vigorous boiling causes more water molecule to escape into the vapor phase, but does not affect the temperature of the liquid. Vigorous boiling requires a higher energy input than does gentle simmering.

22.

23.

24.

Contributors

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Chapter 7.3: Unique Properties of Liquids

Learning Objective

- To describe the unique properties of liquids.

Although you have been introduced to some of the interactions that hold molecules together in a liquid, we have not yet discussed the consequences of those interactions for the bulk properties of liquids. We now turn our attention to three unique properties of liquids that intimately depend on the nature of intermolecular interactions: surface tension, capillary action, and viscosity.

Surface Tension

Liquids tend to adopt the shapes of their containers. Why, then, do small amounts of water on a freshly waxed car form raised droplets instead of a thin, continuous film? The answer lies in a property called *surface tension*, which depends on intermolecular forces.

Figure 7.3.1 presents a microscopic view of a liquid droplet. A typical molecule in the *interior* of the droplet is surrounded by other molecules that exert attractive forces from all directions. Consequently, there is no *net* force on the molecule that would cause it to move in a particular direction. In contrast, a molecule on the *surface* experiences a net attraction toward the drop because there are no molecules on the outside to balance the forces exerted by adjacent molecules in the interior. Because a sphere has the smallest possible surface area for a given volume, intermolecular attractive interactions between water molecules cause the droplet to adopt a spherical shape. This maximizes the number of attractive interactions and minimizes the number of water molecules at the surface. Hence raindrops are almost spherical, and drops of water on a waxed (nonpolar) surface, which does not interact strongly with water, form round beads (see the chapter opener photo). A dirty car is covered with a mixture of substances, some of which are polar. Attractive interactions between the polar substances and water cause the water to spread out into a thin film instead of forming beads.

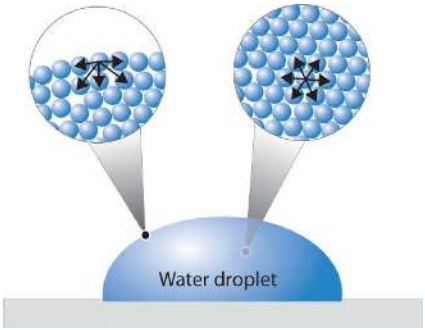


Figure 7.3.1 A Representation of Surface Tension in a Liquid *Molecules at the surface of water experience a net attraction to other molecules in the liquid, which holds the surface of the bulk sample together. In contrast, those in the interior experience uniform attractive forces.*.

The same phenomenon holds molecules together at the surface of a bulk sample of water, almost as if they formed a skin. When filling a glass with water, the glass can be overfilled so that the level of the liquid actually extends *above* the rim. Similarly, a sewing needle or a paper clip can be placed on the surface of a glass of water where it “floats,” even though steel is much denser than water (part (a) in Figure 7.3.2). Many insects take advantage of this property to walk on the surface of puddles or ponds without sinking (part (b) in Figure 7.3.2).





Figure 7.3.2 The Effects of the High Surface Tension of Liquid Water (a) *A paper clip can "float" on water because of surface tension (from Christopher Rozitis.*





(b) Surface tension also allows insects such as this water strider to "walk on water."

Such phenomena are manifestations of surface tensionThe energy required to increase the surface area of a liquid by a certain amount. Surface tension is measured in units of energy per area (e.g., J/m^2)., which is defined as the energy required to increase the surface area of a liquid by a specific amount. Surface tension is therefore measured as energy per unit area, such as joules per

square meter (J/m^2) or dyne per centimeter (dyn/cm), where 1 dyn = 1×10^{-5} N. The values of the surface tension of some representative liquids are listed in Table 7.3.1. Note the correlation between the surface tension of a liquid and the strength of the intermolecular forces: the stronger the intermolecular forces, the higher the surface tension. For example, water, with its strong intermolecular hydrogen bonding, has one of the highest surface tension values of any liquid, whereas low-boiling-point organic molecules, which have relatively weak intermolecular forces, have much lower surface tensions. Mercury is an apparent anomaly, but its very high surface tension is due to the presence of strong metallic bonding, which we discussed in Section 4.8.

Table 7.3.1 Surface Tension, Viscosity, Vapor Pressure (at 25°C Unless Otherwise Indicated), and Normal Boiling Points of Common Liquids

Substance	Surface Tension ($\times 10^{-3}$ J/m^2)	Viscosity (mPa·s)	Vapor Pressure (mmHg)	Normal Boiling Point (°C)
Organic Compounds				
diethyl ether	17	0.22	531	34.6
n-hexane	18	0.30	149	68.7
acetone	23	0.31	227	56.5
ethanol	22	1.07	59	78.3
ethylene glycol	48	16.1	~0.08	198.9
Liquid Elements				
bromine	41	0.94	218	58.8
mercury	486	1.53	0.0020	357
Water				
0°C	75.6	1.79	4.6	—
20°C	72.8	1.00	17.5	—
60°C	66.2	0.47	149	—
100°C	58.9	0.28	760	—

Adding soaps and detergents that disrupt the intermolecular attractions between adjacent water molecules can reduce the surface tension of water. Because they affect the surface properties of a liquid, soaps and detergents are called surface-active agents, or surfactantsSubstances (surface-active agents), such as soaps and detergents, that disrupt the attractive intermolecular interactions between molecules of a polar liquid, thereby reducing the surface tension of the liquid.. In the 1960s, US Navy researchers developed a method of fighting fires aboard aircraft carriers using “foams,” which are aqueous solutions of fluorinated surfactants. The surfactants reduce the surface tension of water below that of fuel, so the fluorinated solution is able to spread across the burning surface and extinguish the fire. Such foams are now used universally to fight large-scale fires of organic liquids.

Capillary Action

Intermolecular forces also cause a phenomenon called capillary actionThe tendency of a polar liquid to rise against gravity into a small-diameter glass tube., which is the tendency of a polar liquid to rise against gravity into a small-diameter tube (a *capillary*), as shown in Figure 7.3.3 . When a glass capillary is put into a dish of water, water is drawn up into the tube. The height to which the water rises depends on the diameter of the tube and the temperature of the water but *not* on the angle at which the tube enters the water. The smaller the diameter, the higher the liquid rises.





Figure 7.3.3 The Phenomenon of Capillary Action *When a capillary is placed in liquid ink the ink rises up into the capillary. The smaller the diameter of the capillary, the higher the water rises. The height of the water does not depend on the angle at which the capillary is tilted.*

Of course, you can see the same phenomina in anything with narrow channels, like bricks





Figure 7.3.4 The Phenomenon of Capillary Action: *Water rises through a brick in a time lapse video*

Capillary action is the net result of two opposing sets of forces: cohesive forcesThe intermolecular forces that hold a liquid together., which are the intermolecular forces that hold a liquid together, and adhesive forcesThe attractive intermolecular forces between a liquid and the substance comprising the surface of a capillary., which are the attractive forces between a liquid and the substance that composes the capillary. Water has both strong adhesion to glass, which contains polar SiOH groups, and strong intermolecular cohesion. When a glass capillary is put into water, the surface tension due to cohesive forces constricts the surface area of water within the tube, while adhesion between the water and the glass creates an upward force that maximizes the amount of glass surface in contact with the water. If the adhesive forces are stronger than the cohesive forces, as is the case for water, then the liquid in the capillary rises to the level where the downward force of gravity exactly balances this upward force. If, however, the cohesive forces are stronger than the adhesive forces, as is the case for mercury and glass, the liquid pulls itself down into the capillary below the surface of the bulk liquid to minimize contact with the glass (part (a) in Figure 7.3.5). The upper surface of a liquid in a tube is called the meniscusThe upper surface of the liquid in a tube., and the shape of the meniscus depends on the relative strengths of the cohesive and adhesive forces. In liquids such as water, the meniscus is concave; in liquids such as mercury, however, which have very strong cohesive forces and weak adhesion to glass, the meniscus is convex (part (b) in Figure 7.3.5).

Note the Pattern

Polar substances are drawn up a glass capillary and generally have a concave meniscus.

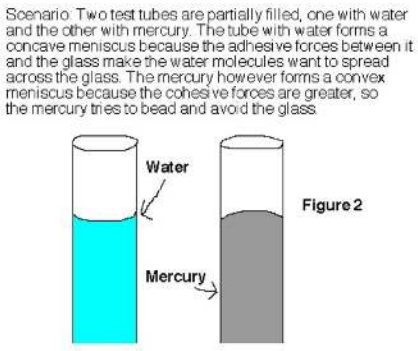
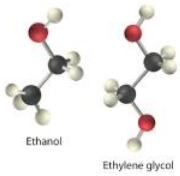


Figure 7.3.5 The Effects of Capillary Action *This drawing illustrates the shape of the meniscus and the relative height of a mercury column when a glass capillary is put into liquid mercury. The meniscus is convex and the surface of the liquid inside the tube is lower than the level of the liquid outside the tube. Because water adheres strongly to the polar surface of glass, it has a concave meniscus, whereas mercury, which does not adhere to the glass, has a convex meniscus.*

Fluids and nutrients are transported up the stems of plants or the trunks of trees by capillary action. Plants contain tiny rigid tubes composed of cellulose, to which water has strong adhesion. Because of the strong adhesive forces, nutrients can be transported from the roots to the tops of trees that are more than 50 m tall. Cotton towels are also made of cellulose; they absorb water because the tiny tubes act like capillaries and “wick” the water away from your skin. The moisture is absorbed by the entire fabric, not just the layer in contact with your body.

Viscosity



Viscosity (η)The resistance of a liquid to flow. is the resistance of a liquid to flow. Some liquids, such as gasoline, ethanol, and water, flow very readily and hence have a *low viscosity*. Others, such as motor oil, molasses, and maple syrup, flow very slowly and have a *high viscosity*. The two most common methods for evaluating the viscosity of a liquid are (1) to measure the time it takes for a quantity of liquid to flow through a narrow vertical tube and (2) to measure the time it takes steel balls to fall through a given volume of the liquid. The higher the viscosity, the slower the liquid flows through the tube and the steel balls fall. Viscosity is expressed in units of the poise (mPa·s); the higher the number, the higher the viscosity. The viscosities of some representative liquids are listed in Table 7.3.1 and show a correlation between viscosity and intermolecular forces. Because a liquid can flow only if the molecules can move past one another with minimal resistance, strong intermolecular attractive forces make it more difficult for molecules to move with respect to one another. The addition of a second hydroxyl group to ethanol, for example, which produces ethylene glycol ($HOCH_2CH_2OH$), increases the viscosity 15-fold. This effect is due to the increased number of hydrogen bonds that can form between hydroxyl groups in adjacent molecules, resulting in dramatically stronger intermolecular attractive forces.

There is also a correlation between viscosity and molecular shape. Liquids consisting of long, flexible molecules tend to have higher viscosities than those composed of more spherical or shorter-chain molecules. The longer the molecules, the easier it is for them to become “tangled” with one another, making it more difficult for them to move past one another. London dispersion forces also increase with chain length. Due to a combination of these two effects, long-chain hydrocarbons (such as motor oils) are highly viscous.

Note the Pattern

Viscosity increases as intermolecular interactions or molecular size increases.

Motor oils and other lubricants demonstrate the practical importance of controlling viscosity. The oil in an automobile engine must effectively lubricate under a wide range of conditions, from subzero starting temperatures to the 200°C that oil can reach in an

engine in the heat of the Mojave Desert in August. Viscosity decreases rapidly with increasing temperatures because the kinetic energy of the molecules increases, and higher kinetic energy enables the molecules to overcome the attractive forces that prevent the liquid from flowing. As a result, an oil that is thin enough to be a good lubricant in a cold engine will become too "thin" (have too low a viscosity) to be effective at high temperatures. The viscosity of motor oils is described by an SAE (Society of Automotive Engineers) rating ranging from SAE 5 to SAE 50 for engine oils: the lower the number, the lower the viscosity. So-called *single-grade oils* can cause major problems. If they are viscous enough to work at high operating temperatures (SAE 50, for example), then at low temperatures, they can be so viscous that a car is difficult to start or an engine is not properly lubricated. Consequently, most modern oils are *multigrade*, with designations such as SAE 20W/50 (a grade used in high-performance sports cars), in which case the oil has the viscosity of an SAE 20 oil at subzero temperatures (hence the W for winter) and the viscosity of an SAE 50 oil at high temperatures. These properties are achieved by a careful blend of additives that modulate the intermolecular interactions in the oil, thereby controlling the temperature dependence of the viscosity. Many of the commercially available oil additives "for improved engine performance" are highly viscous materials that increase the viscosity and effective SAE rating of the oil, but overusing these additives can cause the same problems experienced with highly viscous single-grade oils.

Example 7.3.1

Based on the nature and strength of the intermolecular cohesive forces and the probable nature of the liquid–glass adhesive forces, predict what will happen when a glass capillary is put into a beaker of SAE 20 motor oil. Will the oil be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)? (Hint: the surface of glass is lined with Si–OH groups.)

Given: substance and composition of the glass surface

Asked for: behavior of oil and the shape of meniscus

Strategy:

A Identify the cohesive forces in the motor oil.

B Determine whether the forces interact with the surface of glass. From the strength of this interaction, predict the behavior of the oil and the shape of the meniscus.

Solution:

A Motor oil is a nonpolar liquid consisting largely of hydrocarbon chains. The cohesive forces responsible for its high boiling point are almost solely London dispersion forces between the hydrocarbon chains. **B** Such a liquid cannot form strong interactions with the polar Si–OH groups of glass, so the surface of the oil inside the capillary will be lower than the level of the liquid in the beaker. The oil will have a convex meniscus similar to that of mercury.

Exercise

Predict what will happen when a glass capillary is put into a beaker of ethylene glycol. Will the ethylene glycol be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)?

Answer: Capillary action will pull the ethylene glycol up into the capillary. The meniscus will be concave.

Summary

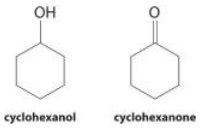
Surface tension is the energy required to increase the surface area of a liquid by a given amount. The stronger the intermolecular interactions, the greater the surface tension. **Surfactants** are molecules, such as soaps and detergents, that reduce the surface tension of polar liquids like water. **Capillary action** is the phenomenon in which liquids rise up into a narrow tube called a capillary. It results when **cohesive forces**, the intermolecular forces in the liquid, are weaker than **adhesive forces**, the attraction between a liquid and the surface of the capillary. The shape of the **meniscus**, the upper surface of a liquid in a tube, also reflects the balance between adhesive and cohesive forces. The **viscosity** of a liquid is its resistance to flow. Liquids that have strong intermolecular forces tend to have high viscosities.

Key Takeaway

- Surface tension, capillary action, and viscosity are unique properties of liquids that depend on the nature of intermolecular interactions.

Conceptual Problems

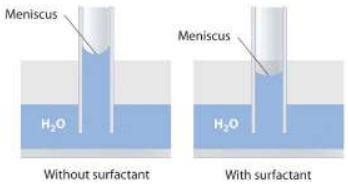
1. Why is a water droplet round?
2. How is the environment of molecules on the surface of a liquid droplet different from that of molecules in the interior of the droplet? How is this difference related to the concept of surface tension?
3. Explain the role of intermolecular and intramolecular forces in surface tension.
4. A mosquito is able to walk across water without sinking, but if a few drops of detergent are added to the water, the insect will sink. Why?
5. Explain how soaps or surfactants decrease the surface tension of a liquid. How does the meniscus of an aqueous solution in a capillary change if a surfactant is added? Illustrate your answer with a diagram.
6. Of CH_2Cl_2, hexane, and ethanol, which has the lowest viscosity? Which has the highest surface tension? Explain your reasoning in each case.
7. At 25°C, cyclohexanol has a surface tension of 32.92 mN/m^2, whereas the surface tension of cyclohexanone, which is very similar chemically is only 25.45 mN/m^2. Why is the surface tension of cyclohexanone so much less than that of cyclohexanol?



8. What is the relationship between
    1. surface tension and temperature?
    2. viscosity and temperature?

    Explain your answers in terms of a microscopic picture.
9. What two opposing forces are responsible for capillary action? How do these forces determine the shape of the meniscus?
10. Which of the following liquids will have a concave meniscus in a glass capillary? Explain your reasoning.
    1. pentane
    2. diethylene glycol ($HOCH_2CH_2OCH_2CH_2OH$)
    3. carbon tetrachloride
11. How does viscosity depend on molecular shape? What molecular features make liquids highly viscous?

Answers

1. 

2. Adding a soap or a surfactant to water disrupts the attractive intermolecular interactions between water molecules, thereby decreasing the surface tension. Because water is a polar molecule, one would expect that a soap or a surfactant would also disrupt the attractive interactions responsible for adhesion of water to the surface of a glass capillary. As shown in the sketch, this would decrease the height of the water column inside the capillary, as well as making the meniscus less concave.
6.
7. As the structures indicate, cyclohexanol is a polar substance that can engage in hydrogen bonding, much like methanol or ethanol; consequently, it is expected to have a higher surface tension due to stronger intermolecular interactions.
8.
9. Cohesive forces are the intermolecular forces that hold the molecules of the liquid together, while adhesive forces are the attractive forces between the molecules of the liquid and the walls of the capillary. If the adhesive forces are stronger than the

cohesive forces, the liquid is pulled up into the capillary and the meniscus is concave. Conversely, if the cohesive forces are stronger than the adhesive forces, the level of the liquid inside the capillary will be lower than the level outside the capillary, and the meniscus will be convex.

10.

11. Viscous substances often consist of molecules that are much longer than they are wide and whose structures are often rather flexible. As a result, the molecules tend to become tangled with one another (much like overcooked spaghetti), which decreases the rate at which they can move through the liquid.

Numerical Problems

1. The viscosities of five liquids at 25°C are given in the following table. Explain the observed trends in viscosity.

Compound	Molecular Formula	Viscosity (mPa·s)
benzene	C_6H_6	0.604
aniline	$C_6H_5NH_2$	3.847
1,2-dichloroethane	$C_2H_4Cl_2$	0.779
heptane	C_7H_{16}	0.357
1-heptanol	$C_7H_{15}OH$	5.810

2. The following table gives values for the viscosity, boiling point, and surface tension of four substances. Examine these data carefully to see whether the data for each compound are internally consistent and point out any obvious errors or inconsistencies. Explain your reasoning.

Compound	Viscosity (mPa·s at 20°C)	Boiling Point (°C)	Surface Tension (dyn/cm at 25°C)
A	0.41	61	27.16
B	0.55	65	22.55
C	0.92	105	36.76
D	0.59	110	28.53

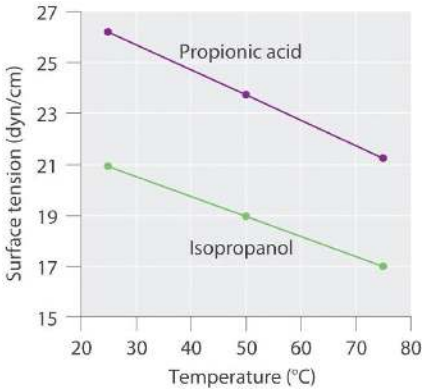
3. Surface tension data (in dyn/cm) for propanoic acid ($C_3H_6O_2$), and 2-propanol (C_3H_8O), as a function of temperature, are given in the following table. Plot the data for each compound and explain the differences between the two graphs. Based on these data, which molecule is more polar?

Compound	25°C	50°C	75°C
propanoic acid	26.20	23.72	21.23
2-propanol	20.93	18.96	16.98

Answer

2.

1.

3. 

The plots of surface tension versus temperature for propionic acid and isopropanol have essentially the same slope, but at all temperatures the surface tension of propionic acid is about 30% greater than for isopropanol. Because surface tension is a measure of the cohesive forces in a liquid, these data suggest that the cohesive forces for propionic acid are significantly greater than for isopropanol. Both substances consist of polar molecules with similar molecular masses, and the most important intermolecular interactions are likely to be dipole–dipole interactions. Consequently, these data suggest that propionic acid is more polar than isopropanol.

Contributors

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Video at 7.3.2a by Christopher Rozitis @ YouTube

Video at 7.3.2b by Cambridge University @ YouTube

Video at 7.3.3 by Fink Feed Systems @ YouTube

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Chapter 7.4: Vapor Pressure

Learning Objective

- To know how and why the vapor pressure of a liquid varies with temperature.

Nearly all of us have heated a pan of water with the lid in place and shortly thereafter heard the sounds of the lid rattling and hot water spilling onto the stovetop. When a liquid is heated, its molecules obtain sufficient kinetic energy to overcome the forces holding them in the liquid and they escape into the gaseous phase. By doing so, they generate a population of molecules in the vapor phase above the liquid that produces a pressure—the vapor pressureThe pressure created over a liquid by the molecules of a liquid substance that have enough kinetic energy to escape to the vapor phase. of the liquid. In the situation we described, enough pressure was generated to move the lid, which allowed the vapor to escape. If the vapor is contained in a sealed vessel, however, such as an unvented flask, and the vapor pressure becomes too high, the flask will explode (as many students have unfortunately discovered). In this section, we describe vapor pressure in more detail and explain how to quantitatively determine the vapor pressure of a liquid.

Evaporation and Condensation

Because the molecules of a liquid are in constant motion, we can plot the fraction of molecules with a given kinetic energy (*KE*) against their kinetic energy to obtain the kinetic energy distribution of the molecules in the liquid (Figure 7.4.1), just as we did for a gas. As for gases, increasing the temperature increases both the average kinetic energy of the particles in a liquid and the range of kinetic energy of the individual molecules. If we assume that a minimum amount of energy (E_0) is needed to overcome the intermolecular attractive forces that hold a liquid together, then some fraction of molecules in the liquid always has a kinetic energy greater than E_0. The fraction of molecules with a kinetic energy greater than this minimum value increases with increasing temperature. Any molecule with a kinetic energy greater than E_0 has enough energy to overcome the forces holding it in the liquid and escape into the vapor phase. Before it can do so, however, a molecule must also be at the surface of the liquid, where it is physically possible for it to leave the liquid surface; that is, only molecules at the surface can undergo evaporation (or vaporization)The physical process by which atoms or molecules in the liquid phase enter the gas or vapor phase., where molecules gain sufficient energy to enter a gaseous state above a liquid's surface, thereby creating a vapor pressure. Similarly, molecules in the gas phase can strike the surface and be absorbed. This process is called condensation.

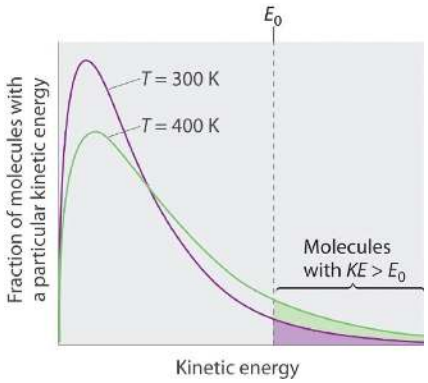


Figure 7.4.1 The Distribution of the Kinetic Energies of the Molecules of a Liquid at Two Temperatures *Just as with gases, increasing the temperature shifts the peak to a higher energy and broadens the curve. Only molecules with a kinetic energy greater than E_0 can escape from the liquid to enter the vapor phase, and the proportion of molecules with $KE > E_0$ is greater at the higher temperature.*

To understand the causes of vapor pressure, consider the apparatus shown in Figure 7.4.2 . When a liquid is introduced into an evacuated chamber (part (a) in Figure 7.4.2), the initial pressure above the liquid is approximately zero because there are as yet no molecules in the vapor phase. Some molecules at the surface, however, will have sufficient kinetic energy to escape from the liquid and form a vapor, thus increasing the pressure inside the container. As long as the temperature of the liquid is held constant, the fraction of molecules with $KE > E_0$ will not change, and the rate at which molecules escape from the liquid into the vapor phase will depend only on the surface area of the liquid phase. At equlibrium the rate of evaporation equals the rate of condensation.

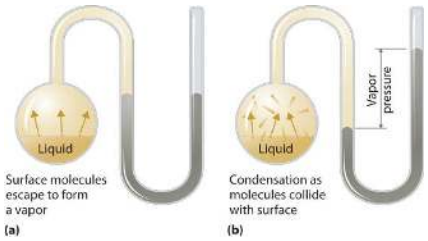


Figure 7.4.2 Vapor Pressure *(a) When a liquid is introduced into an evacuated chamber, molecules with sufficient kinetic energy escape from the surface and enter the vapor phase, causing the pressure in the chamber to increase. (b) When sufficient molecules are in the vapor phase for a given temperature, the rate of condensation equals the rate of evaporation (a steady state is reached), and the pressure in the container becomes constant.*

As soon as some vapor has formed, a fraction of the molecules in the vapor phase will collide with the surface of the liquid and reenter the liquid phase in a process known as condensationThe physical process by which atoms or molecules in the vapor phase enter the liquid phase. (part (b) in Figure 7.4.2). As the number of molecules in the vapor phase increases, the number of collisions between vapor-phase molecules and the surface will also increase. Eventually, a *steady state* will be reached in which exactly as many molecules per unit time leave the surface of the liquid (vaporize) as collide with it (condense). At this point, the pressure over the liquid stops increasing and remains constant at a particular value that is characteristic of the liquid at a given temperature. The rates of evaporation and condensation over time for a system such as this are shown graphically in Figure 7.4.3 .

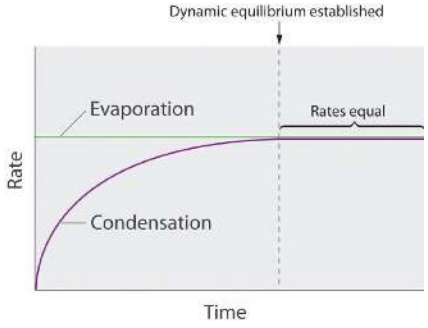


Figure 7.4.3 The Relative Rates of Evaporation and Condensation as a Function of Time after a Liquid Is Introduced into a Sealed Chamber *The rate of evaporation depends only on the surface area of the liquid and is essentially constant. The rate of condensation depends on the number of molecules in the vapor phase and increases steadily until it equals the rate of evaporation.*

Equilibrium Vapor Pressure

Two opposing processes (such as evaporation and condensation) that occur at the same rate and thus produce no *net* change in a system, constitute a dynamic equilibriumA state in which two opposing processes occur at the same rate, thus producing no net change in the system.. In the case of a liquid enclosed in a chamber, the molecules continuously evaporate and condense, but the amounts of liquid and vapor do not change with time. The pressure exerted by a vapor in dynamic equilibrium with a liquid is the equilibrium vapor pressureThe pressure exerted by a vapor in dynamic equilibrium with its liquid. of the liquid.

If a liquid is in an *open* container, however, most of the molecules that escape into the vapor phase will *not* collide with the surface of the liquid and return to the liquid phase. Instead, they will diffuse through the gas phase away from the container, and an equilibrium will never be established. Under these conditions, the liquid will continue to evaporate until it has “disappeared.” The speed with which this occurs depends on the vapor pressure of the liquid and the temperature. Volatile liquidsA liquid with a relatively high vapor pressure. have relatively high vapor pressures and tend to evaporate readily; nonvolatile liquidsA liquid with a relatively low vapor pressure. have low vapor pressures and evaporate more slowly. Although the dividing line between volatile and nonvolatile liquids is not clear-cut, as a general guideline, we can say that substances with vapor pressures greater than that of water (Table 7.3.1) are relatively volatile, whereas those with vapor pressures less than that of water are relatively nonvolatile. Thus diethyl ether (ethyl ether), acetone, and gasoline are volatile, but mercury, ethylene glycol, and motor oil are nonvolatile.

The equilibrium vapor pressure of a substance at a particular temperature is a characteristic of the material, like its molecular mass, melting point, and boiling point (Table 7.3.1). It does *not* depend on the amount of liquid as long as at least a tiny amount of liquid is present in equilibrium with the vapor. The equilibrium vapor pressure does, however, depend very strongly on the temperature and the intermolecular forces present, as shown for several substances in Figure 7.4.4 . Molecules that can hydrogen bond, such as ethylene glycol, have a much lower equilibrium vapor pressure than those that cannot, such as octane. The nonlinear increase in vapor pressure with increasing temperature is *much* steeper than the increase in pressure expected for an ideal gas over the corresponding temperature range. The temperature dependence is so strong because the vapor pressure depends on the fraction of molecules that have a kinetic energy greater than that needed to escape from the liquid, and this fraction increases exponentially with temperature. As a result, sealed containers of volatile liquids are potential bombs if subjected to large increases in temperature. The gas tanks on automobiles are vented, for example, so that a car won't explode when parked in the sun. Similarly, the small cans (1–5 gallons) used to transport gasoline are required by law to have a pop-off pressure release.

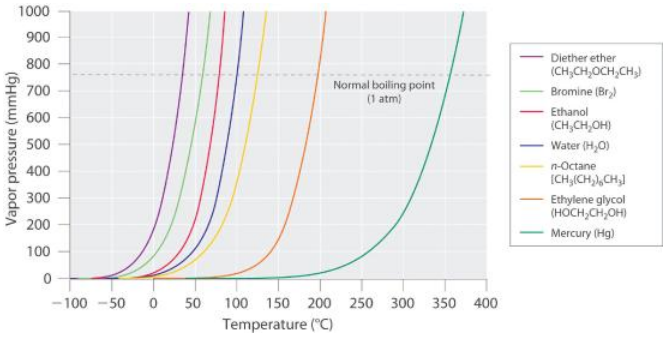


Figure 7.4.4 The Vapor Pressures of Several Liquids as a Function of Temperature *The point at which the vapor pressure curve crosses the P = 1 atm line (dashed) is the normal boiling point of the liquid.*

Note the Pattern

Volatile substances have low boiling points and relatively weak intermolecular interactions; nonvolatile substances have high boiling points and relatively strong intermolecular interactions.

The exponential rise in vapor pressure with increasing temperature in Figure 7.4.4 allows us to use natural logarithms to express the nonlinear relationship as a linear one.

$$ln\,(P) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + C \tag{7.4.1}$$

where ln P is the natural logarithm of the vapor pressure, ΔH_{vap} is the **molar enthalpy of vaporization** which is the amount of heat needed to vaporize one mole of a substance. R is the universal gas constant, just the same as the one in the ideal gas law, but in this case you must be sure to use 8.314 J/(mol·K) so that the units of energy in $\Delta H_{vap}/R$ cancel. T is the temperature in Kelvin, and C is the y-intercept, which is a constant for any given liquid. A plot of ln P versus the inverse of the absolute temperature ($1/T$) is a straight line with a slope of $-\Delta H_{vap}/R$. Equation 7.4.1, called the Clausius–Clapeyron equationA linear relationship that expresses the nonlinear relationship between the vapor pressure of a liquid and temperature: P is the pressure, ΔH_{vap}, R is the gas constant, T is the absolute temperature, and C is a constant. The Clausius–Clapeyron equation can be used to calculate the heat of vaporization of a liquid from its measured vapor pressure at two or more temperatures., can be used to calculate the ΔH_{vap} of a liquid from its measured vapor pressure at two or more temperatures. The simplest way to determine ΔH_{vap} is to measure the vapor pressure of a liquid at two temperatures and insert the values of P and T for these points into Equation 7.4.2, which is derived from the Clausius–Clapeyron equation:

$$ln\left(\frac{P_1}{P_2}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{7.4.2}$$

Conversely, if we know ΔH_{vap} and the vapor pressure P_1 at any temperature T_1, we can use Equation 7.4.2 to calculate the vapor pressure P_2 at any other temperature T_2, as shown in Example 6.

Example 7.4.1

The experimentally measured vapor pressures of liquid Hg at four temperatures are listed in the following table:

T (°C)	80.0	100	120	140
P (Torr)	0.0888	0.2729	0.7457	1.845

From these data, calculate the enthalpy of vaporization (ΔH_{vap}) of mercury and predict the vapor pressure of the liquid at 160°C. (Safety note: mercury is highly toxic; when it is spilled, its vapor pressure generates hazardous levels of mercury vapor.)

Given: vapor pressures at four temperatures

Asked for: ΔH_{vap} of mercury and vapor pressure at 160°C

Strategy:

A. Use Equation 7.4.2 to obtain ΔH_{vap} directly from two pairs of values in the table, making sure to convert all values to the appropriate units.
B. Substitute the calculated value of ΔH_{vap} into Equation 7.4.2 to obtain the unknown pressure (P_2).

Solution:

A The table gives the measured vapor pressures of liquid Hg for four temperatures. Although one way to proceed would be to plot the data using Equation 7.4.1 and find the value of ΔH_{vap} from the slope of the line, an alternative approach is to use Equation 7.4.2 to obtain ΔH_{vap} directly from two pairs of values listed in the table, assuming no errors in our measurement. We therefore select two sets of values from the table and convert the temperatures from degrees Celsius to kelvins because the equation requires absolute temperatures. Substituting the values measured at 80.0°C (T_1) and 120.0°C (T_2) into Equation 7.4.2 gives

$$ln\left(\frac{0.7457\ \cancel{Torr}}{0.0888\ \cancel{Torr}}\right) = \frac{-\Delta H_{vap}}{8.314\ J/mol \cdot K}\left(\frac{1}{(120+273)\,K} - \frac{1}{(80.0+273)\,K}\right) \quad \text{(Chapter 7.4.1)}$$

$$ln\,(8.398) = \frac{-\Delta H_{vap}}{8.314\ J/mol \cdot \cancel{K}}\left(-2.88 \times 10^{-4}\ \cancel{K^{-1}}\right) \quad \text{(Chapter 7.4.2)}$$

$$2.13 = -\Delta H_{vap}\left(-3.46 \times 10^{-4}\right) J^{-1} \cdot mol \quad \text{(Chapter 7.4.3)}$$

$$\Delta H_{vap} = 61,400\ J/mol = 61.4\ kJ/mol \quad \text{(Chapter 7.4.4)}$$

B We can now use this value of ΔH_{vap} to calculate the vapor pressure of the liquid (P_2) at 160.0°C (T_2):

$$ln\left(\frac{P_2}{0.0888\ Torr}\right) = \frac{-61,400\ \cancel{J/mol}}{8.314\ \cancel{J/mol}\ K^{-1}}\left(\frac{1}{(160+273)\,K} - \frac{1}{(80.0+273)\,K}\right) \quad \text{(Chapter 7.4.5)}$$

Using the relationship $e^{\ln x} = x$, we have

$$ln\left(\frac{P_2}{0.0888\ Torr}\right) = 3.86 \quad \text{(Chapter 7.4.6)}$$

$$\frac{P_2}{0.0888\ Torr} = e^{3.86} = 47.5 \quad \text{(Chapter 7.4.7)}$$

$$P_2 = 4.21 Torr \quad \text{(Chapter 7.4.8)}$$

At 160°C, liquid Hg has a vapor pressure of 4.21 Torr, substantially greater than the pressure at 80.0°C, as we would expect.

Exercise

The vapor pressure of liquid nickel at 1606°C is 0.100 Torr, whereas at 1805°C, its vapor pressure is 1.000 Torr. At what temperature does the liquid have a vapor pressure of 2.500 Torr?

Answer: 1896°C

Boiling Points

As the temperature of a liquid increases, the vapor pressure of the liquid increases until it equals the external pressure, or the atmospheric pressure in the case of an open container. Bubbles of vapor begin to form throughout the liquid, and the liquid begins to boil. The temperature at which a liquid boils at exactly 1 atm pressure is the normal boiling point. For water, the normal boiling point is exactly 100°C. The normal boiling points of the other liquids in Figure 7.4.4 are represented by the points at which the vapor pressure curves cross the line corresponding to a pressure of 1 atm. Although we usually cite the normal boiling point of a liquid, the *actual* boiling point depends on the pressure. At a pressure greater than 1 atm, water boils at a temperature greater than 100°C because the increased pressure forces vapor molecules above the surface to condense. Hence the molecules must have greater kinetic energy to escape from the surface. Conversely, at pressures less than 1 atm, water boils below 100°C.

Typical variations in atmospheric pressure at sea level are relatively small, causing only minor changes in the boiling point of water. For example, the highest recorded atmospheric pressure at sea level is 813 Torr, recorded during a Siberian winter; the lowest sea-level pressure ever measured was 658 Torr in a Pacific typhoon. At these pressures, the boiling point of water changes minimally, to 102°C and 96°C, respectively. At high altitudes, on the other hand, the dependence of the boiling point of water on pressure becomes significant. Table 7.4.1 lists the boiling points of water at several locations with different altitudes. At an elevation of only 5000 ft, for example, the boiling point of water is already lower than the lowest ever recorded at sea level. The lower boiling point of water has major consequences for cooking everything from soft-boiled eggs (a “three-minute egg” may well take four or more minutes in the Rockies and even longer in the Himalayas) to cakes (cake mixes are often sold with separate high-altitude instructions). Conversely, pressure cookers, which have a seal that allows the pressure inside them to exceed 1 atm, are used to cook food more rapidly by raising the boiling point of water and thus the temperature at which the food is being cooked.

Note the Pattern

As pressure increases, the boiling point of a liquid increases and vice versa.

Table 7.4.1 The Boiling Points of Water at Various Locations on Earth

Place	Altitude above Sea Level (ft)	Atmospheric Pressure (Torr)	Boiling Point of Water (°C)
Mt. Everest, Nepal/Tibet	29,028	240	70
Bogota, Colombia	11,490	495	88
Denver, Colorado	5280	633	95
Washington, DC	25	759	100
Dead Sea, Israel/Jordan	−1312	799	101.4

Example 7.4.2

Use Figure 7.4.4 to estimate the following.

1. the boiling point of water in a pressure cooker operating at 1000 Torr
2. the pressure required for mercury to boil at 250°C

Given: data in Figure 7.4.4 , pressure, and boiling point

Asked for: corresponding boiling point and pressure

Strategy:

A. To estimate the boiling point of water at 1000 Torr, refer to Figure 10.4.4 and find the point where the vapor pressure curve of water intersects the line corresponding to a pressure of 1000 mmHg.

B. To estimate the pressure required for mercury to boil at 250°C, find the point where the vapor pressure curve of mercury intersects the line corresponding to a temperature of 250°C.

Solution:

1. **A** The vapor pressure curve of water intersects the P = 1000 Torr line at about 110°C; this is therefore the boiling point of water at 1000 Torr.
2. **B** The vertical line corresponding to 250°C intersects the vapor pressure curve of mercury at $P \approx 75$ Torr. Hence this is the pressure required for mercury to boil at 250°C.

Exercise

Use the data in Figure 7.4.4 to estimate the following.

1. the normal boiling point of ethylene glycol
2. the pressure required for diethyl ether to boil at 20°C.

Answer:

1. 200°C
2. 450 mmHg

Summary

Because the molecules of a liquid are in constant motion and possess a wide range of kinetic energies, at any moment some fraction of them has enough energy to escape from the surface of the liquid to enter the gas or vapor phase. This process, called **vaporization** or **evaporation**, generates a **vapor pressure** above the liquid. Molecules in the gas phase can collide with the liquid surface and reenter the liquid via **condensation**. Eventually, a *steady state* is reached in which the number of molecules evaporating and condensing per unit time is the same, and the system is in a state of **dynamic equilibrium**. Under these conditions, a liquid exhibits a characteristic **equilibrium vapor pressure** that depends only on the temperature. We can express the nonlinear relationship between vapor pressure and temperature as a linear relationship using the **Clausius–Clapeyron equation**. This equation can be used to calculate the enthalpy of vaporization of a liquid from its measured vapor pressure at two or more temperatures. **Volatile liquids** are liquids with high vapor pressures, which tend to evaporate readily from an open container; **nonvolatile liquids** have low vapor pressures. When the vapor pressure equals the external pressure, bubbles of vapor form within the liquid, and it boils. The temperature at which a substance boils at a pressure of 1 atm is its **normal boiling point**.

Key Takeaways

- The equilibrium vapor pressure of a liquid depends on the temperature and the intermolecular forces present.
- The relationship between pressure, enthalpy of vaporization, and temperature is given by the Clausius-Clapeyron equation.

Key Equations

Clausius–Clapeyron equation

$$ln\,(P) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T}\right) + C \tag{7.4.1}$$

Use vapor pressure at two temperatures to calculate ΔH_{vap}

$$ln\left(\frac{P_1}{P_2}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{7.4.2}$$

Conceptual Problems

1. What is the relationship between the boiling point, vapor pressure, and temperature of a substance and atmospheric pressure?
2. What is the difference between a volatile liquid and a nonvolatile liquid? Suppose that two liquid substances have the same molecular mass, but one is volatile and the other is nonvolatile. What differences in the molecular structures of the two substances could account for the differences in volatility?

3. An “old wives’ tale” states that applying ethanol to the wrists of a child with a very high fever will help to reduce the fever because blood vessels in the wrists are close to the skin. Is there a scientific basis for this recommendation? Would water be as effective as ethanol?
4. Why is the air over a strip of grass significantly cooler than the air over a sandy beach only a few feet away?
5. If gasoline is allowed to sit in an open container, it often feels much colder than the surrounding air. Explain this observation. Describe the flow of heat into or out of the system, as well as any transfer of mass that occurs. Would the temperature of a sealed can of gasoline be higher, lower, or the same as that of the open can? Explain your answer.
6. What is the relationship between the vapor pressure of a liquid and
    1. its temperature?
    2. the surface area of the liquid?
    3. the pressure of other gases on the liquid?
    4. its viscosity?
7. At 25°C, benzene has a vapor pressure of 12.5 kPa, whereas the vapor pressure of acetic acid is 2.1 kPa. Which is more volatile? Based on the intermolecular interactions in the two liquids, explain why acetic acid has the lower vapor pressure.

Numerical Problems

1. Acetylene (C_2H_2), which is used for industrial welding, is transported in pressurized cylinders. Its vapor pressure at various temperatures is given in the following table. Plot the data and use your graph to estimate the vapor pressure of acetylene at 293 K. Then use your graph to determine the value of ΔH_{vap} for acetylene. How much energy is required to vaporize 2.00 g of acetylene at 250 K?

T (K)	145	155	175	200	225	250	300
P (Torr)	1.3	7.8	32.2	190	579	1370	5093

2. The following table gives the vapor pressure of water at various temperatures. Plot the data and use your graph to estimate the vapor pressure of water at 25°C and at 75°C. What is the vapor pressure of water at 110°C? Use these data to determine the value of ΔH_{vap} for water.

T (°C)	0	10	30	50	60	80	100
P (Torr)	4.6	9.2	31.8	92.6	150	355	760

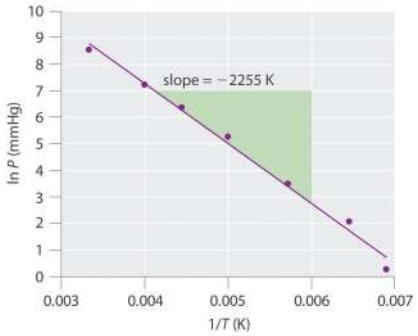
3. The ΔH_{vap} of carbon tetrachloride is 29.8 kJ/mol, and its normal boiling point is 76.8°C. What is its boiling point at 0.100 atm?
4. The normal boiling point of sodium is 883°C. If ΔH_{vap} is 97.4 kJ/mol, what is the vapor pressure (in Torr) of liquid sodium at 300°C?
5. An unknown liquid has a vapor pressure of 0.860 atm at 63.7°C and a vapor pressure of 0.330 atm at 35.1°C. Use the data in Table 11.5.1 in Section 11.5 to identify the liquid.
6. An unknown liquid has a boiling point of 75.8°C at 0.910 atm and a boiling point of 57.2°C at 0.430 atm. Use the data in Table 11.5.1 in Section 11.5 to identify the liquid.
7. If the vapor pressure of a liquid is 0.850 atm at 20°C and 0.897 atm at 25°C, what is the normal boiling point of the liquid?
8. If the vapor pressure of a liquid is 0.799 atm at 99.0°C and 0.842 atm at 111°C, what is the normal boiling point of the liquid?
9. The vapor pressure of liquid SO_2 is 33.4 torr at −63.4°C and 100.0 Torr at −47.7 K.
    1. What is the ΔH_{vap} of SO_2?
    2. What is its vapor pressure at −24.5 K?
    3. At what temperature is the vapor pressure equal to 220 torr?

10. The vapor pressure of CO_2 at various temperatures is given in the following table:

T (°C)	−120	−110	−100	−90
P (Torr)	9.81	34.63	104.81	279.5

1. What is ΔH_{vap} over this temperature range?
2. What is the vapor pressure of CO_2 at −70°C?
3. At what temperature does CO_2 have a vapor pressure of 310 torr?

Answers

1. 

   vapor pressure at 273 K is 3050 Torr; ΔH_{vap} = 18.7 kJ/mol, 1.44 kJ
2.
3. 12.5°C
4.
5. ΔH_{vap} = 28.9 kJ/mol, *n*-hexane
6.
7. ΔH_{vap} = 7.81 kJ/mol, 36°C
8.
9.
10.

Contributors

- Anonymous

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Chapter 7.5: Changes of State

Learning Objective

- To calculate the energy changes that accompany phase changes.

We take advantage of changes between the gas, liquid, and solid states to cool a drink with ice cubes (solid to liquid), cool our bodies by perspiration (liquid to gas), and cool food inside a refrigerator (gas to liquid and vice versa). We use dry ice, which is solid CO_2, as a refrigerant (solid to gas), and we make artificial snow for skiing and snowboarding by transforming a liquid to a solid. In this section, we examine what happens when any of the three forms of matter is converted to either of the other two. These changes of state are often called phase changesA change of state that occurs when any of the three forms of matter (solids, liquids, and gases) is converted to either of the other two.. The six most common phase changes are shown in Figure 7.5.1.

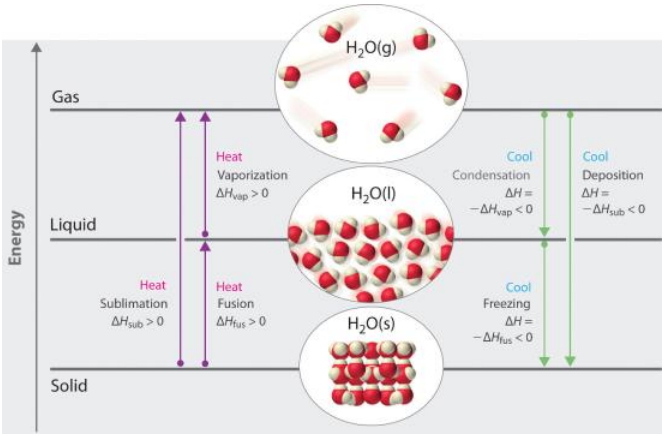


Figure 7.5.1 The Three Phases of Matter and the Processes That Interconvert Them When the Temperature Is Changed
Enthalpy changes that accompany phase transitions are indicated by purple and green arrows.

Energy Changes That Accompany Phase Changes

Phase changes are *always* accompanied by a change in the energy of a system. For example, converting a liquid, in which the molecules are close together, to a gas, in which the molecules are, on average, far apart, requires an input of energy (heat) to give the molecules enough kinetic energy to allow them to overcome the intermolecular attractive forces. The stronger the attractive forces, the more energy is needed to overcome them. Solids, which are highly ordered, have the strongest intermolecular interactions, whereas gases, which are very disordered, have the weakest. Thus any transition from a more ordered to a less ordered state (solid to liquid, liquid to gas, or solid to gas) requires an input of energy; it is **endothermic**. Conversely, any transition from a less ordered to a more ordered state (liquid to solid, gas to liquid, or gas to solid) releases energy; it is **exothermic**. The energy change associated with each common phase change is shown in Figure 7.5.1.

The melting points and molar **enthalpies of fusion (ΔH_{fus})**, the energy required to convert from a solid to a liquid, a process known as fusion (or melting)The conversion of a solid to a liquid., as well as the normal boiling points and enthalpies of vaporization (ΔH_{vap}) of selected compounds are listed in Table 7.5.1. The substances with the highest melting points usually have the highest enthalpies of fusion; they tend to be ionic compounds that are held together by very strong electrostatic interactions. Substances with high boiling points are those with strong intermolecular interactions that must be overcome to convert a liquid to a gas, resulting in high enthalpies of vaporization. The enthalpy of vaporization of a given substance is much greater than its enthalpy of fusion because it takes more energy to completely separate molecules (conversion from a liquid to a gas) than to enable them only to move past one another freely (conversion from a solid to a liquid).

Table 7.5.1 Melting and Boiling Points and Enthalpies of Fusion and Vaporization for Selected Substances

Substance	Melting Point (°C)	ΔH_{fus} (kJ/mol)	Boiling Point (°C)	ΔH_{vap} (kJ/mol)
N_2	−210.0	0.71	−195.8	5.6
HCl	−114.2	2.00	−85.1	16.2
Br_2	−7.2	10.6	58.8	30.0
CCl_4	−22.6	2.56	76.8	29.8
CH_3CH_2OH (ethanol)	−114.1	4.93	78.3	38.6
$CH_3(CH_2)_4CH_3$ (*n*-hexane)	−95.4	13.1	68.7	28.9
H_2O	0	6.01	100	40.7
Na	97.8	2.6	883	97.4
NaF	996	33.4	1704	176.1

Note the Pattern

ΔH is positive for any transition from a more ordered to a less ordered state and negative for a transition from a less ordered to a more ordered state.

The direct conversion of a solid to a gas, without an intervening liquid phase, is called sublimationThe conversion of a solid directly to a gas (without an intervening liquid phase).. The amount of energy required to sublime 1 mol of a pure solid is the enthalpy of sublimation (ΔH_{sub})The enthalpy change that accompanies the conversion of a solid directly to a gas.. Common substances that sublime at standard temperature and pressure (STP; 0°C, 1 atm) include CO_2 (dry ice); iodine (Figure 7.5.2); naphthalene, a substance used to protect woolen clothing against moths; and 1,4-dichlorobenzene. As shown in Figure 7.5.1 the enthalpy of sublimation of a substance is the sum of its enthalpies of fusion and vaporization provided all values are at the same *T*.

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap} \tag{7.5.1}$$





Figure 7.5.2 The Sublimation of Solid Iodine *When solid iodine is heated at ordinary atmospheric pressure, it sublimes. When the I_2 vapor comes in contact with a cold surface, it deposits I_2 crystals.*

Fusion, vaporization, and sublimation are endothermic processes; they occur only with the absorption of heat. Anyone who has ever stepped out of a swimming pool on a cool, breezy day has felt the heat loss that accompanies the evaporation of water from the skin. Our bodies use this same phenomenon to maintain a constant temperature: we perspire continuously, even when at rest, losing about 600 mL of water daily by evaporation from the skin. We also lose about 400 mL of water as water vapor in the air we exhale, which also contributes to cooling. Refrigerators and air-conditioners operate on a similar principle: heat is absorbed from the object or area to be cooled and used to vaporize a low-boiling-point liquid, such as ammonia or the chlorofluorocarbons (CFCs) and the hydrofluorocarbons (HCFCs). The vapor is then transported to a different location and compressed, thus releasing and dissipating the heat. Likewise, ice cubes efficiently cool a drink not because of their low temperature but because heat is required to convert ice at 0°C to liquid water at 0°C, as demonstrated later in Example 8.

Temperature Curves

The processes on the right side of Figure 7.5.1 —freezing, condensation, and deposition, which are the reverse of fusion, sublimation, and vaporization—are exothermic. Thus heat pumps that use refrigerants are essentially air-conditioners running in reverse. Heat from the environment is used to vaporize the refrigerant, which is then condensed to a liquid in coils within a house to provide heat. The energy changes that occur during phase changes can be quantified by using a heating or cooling curve.

Heating Curves

Figure 7.5.3 shows a heating curveA plot of the temperature of a substance versus the heat added or versus the heating time at a constant rate of heating., a plot of temperature versus heating time, for a 75 g sample of water. The sample is initially ice at 1 atm and −23°C; as heat is added, the temperature of the ice increases linearly with time. The slope of the line depends on both the mass of the ice and the specific heat (C_s)The number of joules required to raise the temperature of 1 g of a substance by 1°C. of ice, which is the number of joules required to raise the temperature of 1 g of ice by 1°C. As a general rule the specific heat over a very large range is a constant, so the heating is linear. Over large ranges or where high accuracy is required the specific heat can be a polynomial in temperature.

As the temperature of the ice increases, the water molecules in the ice crystal absorb more and more energy and vibrate more vigorously. At the melting point, they have enough kinetic energy to overcome attractive forces and move with respect to one another. As more heat is added, the temperature of the system does *not* increase further but remains constant at 0°C until all the ice has melted. Once all the ice has been converted to liquid water, the temperature of the water again begins to increase. Now, however, the temperature increases more slowly than before because the specific heat capacity of water is *greater* than that of ice. When the temperature of the water reaches 100°C, the water begins to boil. Here, too, the temperature remains constant at 100°C until all the water has been converted to steam. At this point, the temperature again begins to rise, but at a *faster* rate than seen in the other phases because the heat capacity of steam is *less* than that of ice or water.

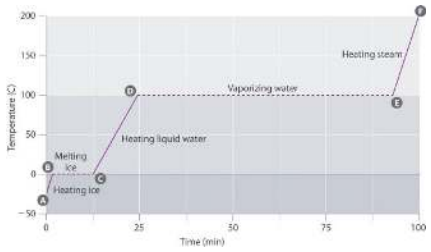


Figure 7.5.3 A Heating Curve for Water *This plot of temperature shows what happens to a 75 g sample of ice initially at 1 atm and −23°C as heat is added at a constant rate: A–B: heating solid ice; B–C: melting ice; C–D: heating liquid water; D–E: vaporizing water; E–F: heating steam.*

It is important to recognize that these heating curves assume that the amount of heat added or taken away is constant with time and that for a single phase, the change in temperature varies linearly with the amount of heat added and thus the heating curves are straight lines whose slopes are proportional to the amount of heat added per unit time divided by the specific heat. Since the specific heat for different phases will be different the slope of the heating lines will also be different.

The temperature of a system does not change during a phase change. In this example, as long as even a tiny amount of ice is present, the temperature of the system remains at 0°C during the melting process, and as long as even a small amount of liquid water is present, the temperature of the system remains at 100°C during the boiling process. The rate at which heat is added does *not* affect the temperature of the ice/water or water/steam mixture because the added heat is being used exclusively to overcome the attractive forces that hold the more condensed phase together. Many cooks think that food will cook faster if the heat is turned up higher so that the water boils more rapidly. Instead, the pot of water will boil to dryness sooner, but the temperature of the water does not depend on how vigorously it boils.

Note the Pattern

The temperature of a sample does not change during a phase change.

If heat is added at a constant rate, as in Figure 7.5.3, then the length of the horizontal lines, which represents the time during which the temperature does not change, is directly proportional to the magnitude of the enthalpies associated with the phase changes. In Figure 7.5.3, the horizontal line at 100°C is much longer than the line at 0°C because the enthalpy of vaporization of water is several times greater than the enthalpy of fusion.

A superheated liquidAn unstable liquid at a temperature and pressure at which it should be a gas. is a sample of a liquid at the temperature and pressure at which it should be a gas. Superheated liquids are not stable; the liquid will eventually boil, sometimes violently. The phenomenon of superheating causes “bumping” when a liquid is heated in the laboratory. When a test tube containing water is heated over a Bunsen burner, for example, one portion of the liquid can easily become too hot. When the superheated liquid converts to a gas, it can push or “bump” the rest of the liquid out of the test tube. Placing a stirring rod or a small piece of ceramic (a “boiling chip”) in the test tube allows bubbles of vapor to form on the surface of the object so the liquid boils instead of becoming superheated. Superheating is the reason a liquid heated in a smooth cup in a microwave oven may not boil until the cup is moved, when the motion of the cup allows bubbles to form.

Cooling Curves

The cooling curveA plot of the temperature of a substance versus the heat removed or versus the cooling time at a constant rate of cooling., a plot of temperature versus cooling time, in Figure 7.5.4 plots temperature versus time as a 75 g sample of steam, initially at 1 atm and 200°C, is cooled. Although we might expect the cooling curve to be the mirror image of the heating curve in Figure 7.5.3 , the cooling curve is *not* an identical mirror image. As heat is removed from the steam, the temperature falls until it reaches 100°C. At this temperature, the steam begins to condense to liquid water. No further temperature change occurs until all the steam is converted to the liquid; then the temperature again decreases as the water is cooled. We might expect to reach another plateau at 0°C, where the water is converted to ice; in reality, however, this does not always occur. Instead, the temperature often drops below the freezing point for some time, as shown by the little dip in the cooling curve below 0°C. This region corresponds to an unstable form of the liquid, a supercooled liquidA metastable liquid phase that exists below the normal melting point of a substance.. If the liquid is allowed to stand, if cooling is continued, or if a small crystal of the solid phase is added (a seed crystalA

solid sample of a substance that can be added to a supercooled liquid or a supersaturated solution to help induce crystallization.), the supercooled liquid will convert to a solid, sometimes quite suddenly. As the water freezes, the temperature increases slightly due to the heat evolved during the freezing process and then holds constant at the melting point as the rest of the water freezes. Subsequently, the temperature of the ice decreases again as more heat is removed from the system.

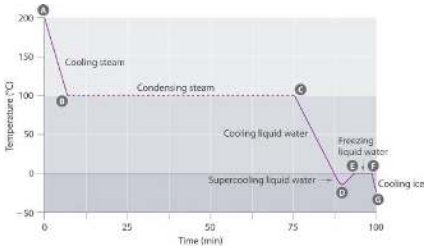
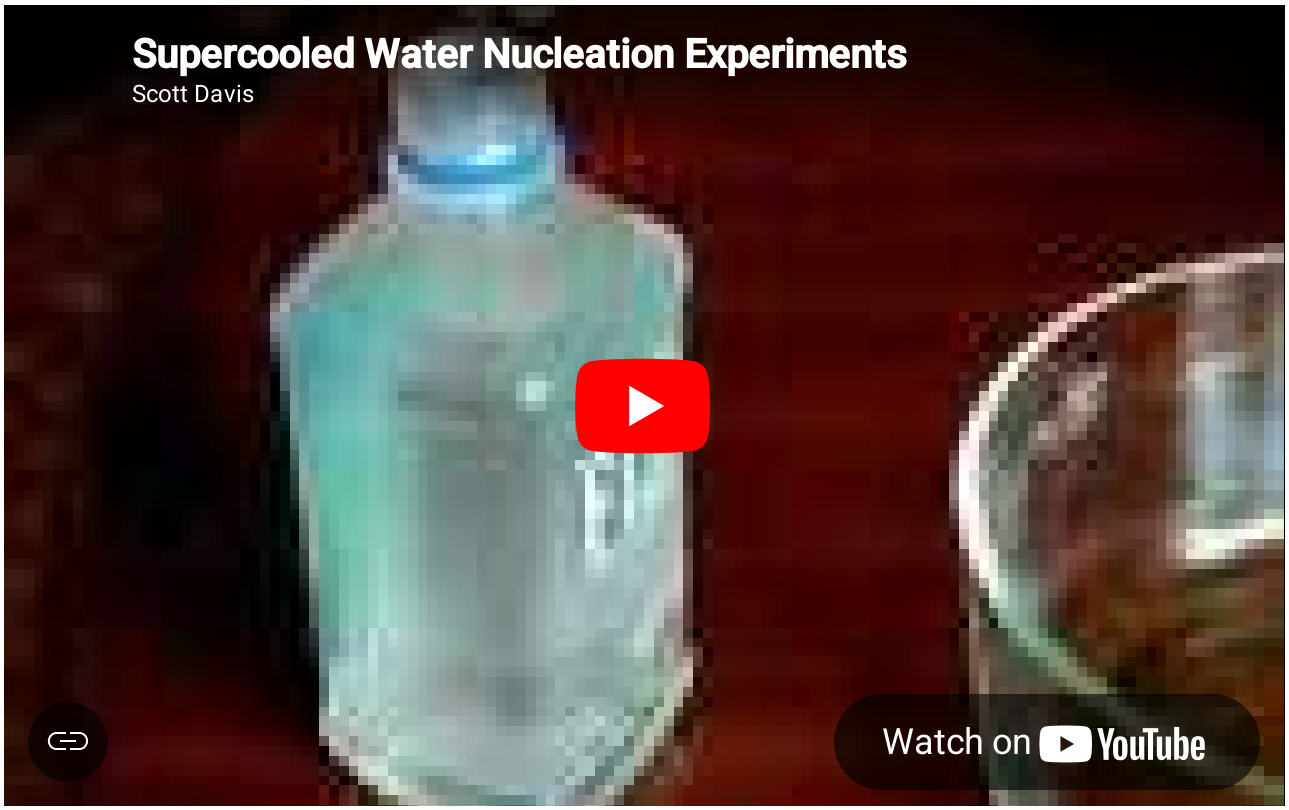


Figure 7.5.4 A Cooling Curve for Water *This plot of temperature shows what happens to a 75 g sample of steam initially at 1 atm and 200°C as heat is removed at a constant rate: A–B: cooling steam; B–C: condensing steam; C–D: cooling liquid water to give a supercooled liquid; D–E: warming the liquid as it begins to freeze; E–F: freezing liquid water; F–G: cooling ice.*





s have a huge impact on Earth's climate. For example, supercooling of water droplets in clouds can prevent the ng precipitation over regions that are persistently arid as a result. Clouds consist of tiny droplets of water, which in principle should be dense enough to fall as rain. In fact, however, the droplets must aggregate to reach a certain size before they can fall to the ground. Usually a small particle (a *nucleus*) is required for the droplets to aggregate; the nucleus can be a dust particle, an ice crystal, or a particle of silver iodide dispersed in a cloud during *seeding* (a method of inducing rain). Unfortunately, the small droplets of water generally remain as a supercooled liquid down to about −10°C, rather than freezing into ice crystals that are more suitable nuclei for raindrop formation. One approach to producing rainfall from an existing cloud is to cool the water droplets so that they crystallize to provide nuclei around which raindrops can grow. This is best done by dispersing small granules

of solid CO_2 (dry ice) into the cloud from an airplane. Solid CO_2 sublimes directly to the gas at pressures of 1 atm or lower, and the enthalpy of sublimation is substantial (25.3 kJ/mol). As the CO_2 sublimes, it absorbs heat from the cloud, often with the desired results.

Example 7.5.1

If a 50.0 g ice cube at 0.0°C is added to 500 mL of tea at 20.0°C, what is the temperature of the tea when the ice cube has just melted? Assume that no heat is transferred to or from the surroundings. The density of water (and iced tea) is 1.00 g/mL over the range 0°C–20°C, the specific heats of liquid water and ice are 4.184 J/(g·°C) and 2.062 J/(g·°C), respectively, and the enthalpy of fusion of ice is 6.01 kJ/mol.

Given: mass, volume, initial temperature, density, specific heats, and ΔH_{fus}

Asked for: final temperature

Strategy:

Substitute the values given into the general equation relating heat gained to heat lost to obtain the final temperature of the mixture.

Solution:

When two substances or objects at different temperatures are brought into contact, heat will flow from the warmer one to the cooler. The amount of heat that flows is given by

$$q = mC_s\Delta T$$

where q is heat, m is mass, C_s is the specific heat, and ΔT is the temperature change. Eventually, the temperatures of the two substances will become equal at a value somewhere between their initial temperatures. Calculating the temperature of iced tea after adding an ice cube is slightly more complicated. The general equation relating heat gained and heat lost is still valid, but in this case we also have to take into account the amount of heat required to melt the ice cube from ice at 0.0°C to liquid water at 0.0C:

$$q_{lost} = -q_{gained} \tag{Chapter 7.5.1}$$

$$\begin{aligned} &m_{iced\ tea}C_s\left(H_2O\right)\Delta T_{iced\ tea} \\ &= -\left[m_{ice}C_s\left(H_2O\right)\Delta T_{ice}\right] + mol_{ice}\Delta H_{fus}\left(H_2O\right) \end{aligned} \tag{Chapter 7.5.2}$$

$$\begin{aligned} &500\ \cancel{g}\left[4.184\ J/\left(\cancel{g}\cdot{}^{\circ}C\right)\right]\left(T_f - 20.0\ {}^{\circ}C\right) \\ &= -50\ \cancel{g}\left[4.184\ J/\left(\cancel{g}\cdot{}^{\circ}C\right)\right]\left(T_f - 0.0\ {}^{\circ}C\right) \\ &\quad - \frac{50.0\ \cancel{g}}{18.0\ \cancel{g}/\cancel{mol}} 6.01 \times 10^3\ J/\cancel{mol} \end{aligned} \tag{Chapter 7.5.3}$$

$$\left(2090\ J/{}^{\circ}C\right)\left(T_f - 20.0\ {}^{\circ}C\right) = -\left(209\ J/{}^{\circ}C\right)T_f - 1.67 \times 10^4 J \tag{Chapter 7.5.4}$$

$$2.53 \times 10^4 J = \left(2310\ J/{}^{\circ}C\right)T_f \tag{Chapter 7.5.5}$$

$$11.0\ {}^{\circ}C = T_f \tag{Chapter 7.5.6}$$

Exercise

Suppose you are overtaken by a blizzard while ski touring and you take refuge in a tent. You are thirsty, but you forgot to bring liquid water. You have a choice of eating a few handfuls of snow (say 400 g) at −5.0°C immediately to quench your thirst or setting up your propane stove, melting the snow, and heating the water to body temperature before drinking it. You recall that the survival guide you leafed through at the hotel said something about not eating snow, but you can't remember why—after all, it's just frozen water. To understand the guide's recommendation, calculate the amount of heat that your body will have to supply to bring 400 g of snow at −5.0°C to your body's internal temperature of 37°C. Use the data in Example 8

Answer: 200 kJ (4.1 kJ to bring the ice from −5.0°C to 0.0°C, 133.6 kJ to melt the ice at 0.0°C, and 61.9 kJ to bring the water from 0.0°C to 37°C), which is energy that would not have been expended had you first melted the snow.

Summary

Changes of state are examples of **phase changes**, or *phase transitions*. All phase changes are accompanied by changes in the energy of a system. Changes from a more-ordered state to a less-ordered state (such as a liquid to a gas) are *endothermic*. Changes from a less-ordered state to a more-ordered state (such as a liquid to a solid) are always *exothermic*. The conversion of a solid to a liquid is called **fusion (or melting)**. The energy required to melt 1 mol of a substance is its enthalpy of fusion (ΔH_{fus}). The energy change required to vaporize 1 mol of a substance is the enthalpy of vaporization (ΔH_{vap}). The direct conversion of a solid to a gas is **sublimation**. The amount of energy needed to sublime 1 mol of a substance is its **enthalpy of sublimation (ΔH_{sub})** and is the sum of the enthalpies of fusion and vaporization. Plots of the temperature of a substance versus heat added or versus heating time at a constant rate of heating are called **heating curves**. Heating curves relate temperature changes to phase transitions. A **superheated liquid**, a liquid at a temperature and pressure at which it should be a gas, is not stable. A **cooling curve** is not exactly the reverse of the heating curve because many liquids do not freeze at the expected temperature. Instead, they form a **supercooled liquid**, a metastable liquid phase that exists below the normal melting point. Supercooled liquids usually crystallize on standing, or adding a **seed crystal** of the same or another substance can induce crystallization.

Key Takeaway

- Fusion, vaporization, and sublimation are endothermic processes, whereas freezing, condensation, and deposition are exothermic processes.

Conceptual Problems

1. In extremely cold climates, snow can disappear with no evidence of its melting. How can this happen? What change(s) in state are taking place? Would you expect this phenomenon to be more common at high or low altitudes? Explain your answer.
2. Why do car manufacturers recommend that an automobile should not be left standing in subzero temperatures if its radiator contains only water? Car manufacturers also warn car owners that they should check the fluid level in a radiator only when the engine is cool. What is the basis for this warning? What is likely to happen if it is ignored?
3. Use Hess's law and a thermochemical cycle to show that, for any solid, the enthalpy of sublimation is equal to the sum of the enthalpy of fusion of the solid and the enthalpy of vaporization of the resulting liquid.
4. Three distinct processes occur when an ice cube at −10°C is used to cool a glass of water at 20°C. What are they? Which causes the greatest temperature change in the water?
5. When frost forms on a piece of glass, crystals of ice are deposited from water vapor in the air. How is this process related to sublimation? Describe the energy changes that take place as the water vapor is converted to frost.
6. What phase changes are involved in each process? Which processes are exothermic, and which are endothermic?
    1. ice melting
    2. distillation
    3. condensation forming on a window
    4. the use of dry ice to create a cloud for a theatrical production
7. What phase changes are involved in each process? Which processes are exothermic, and which are endothermic?
    1. evaporation of methanol
    2. crystallization
    3. liquefaction of natural gas
    4. the use of naphthalene crystals to repel moths
8. Why do substances with high enthalpies of fusion tend to have high melting points?
9. Why is the enthalpy of vaporization of a compound invariably much larger than its enthalpy of fusion?
10. What is the opposite of fusion, sublimation, and condensation? Describe the phase change in each pair of opposing processes and state whether each phase change is exothermic or endothermic.
11. Draw a typical heating curve (temperature versus amount of heat added at a constant rate) for conversion of a solid to a liquid and then to a gas. What causes some regions of the plot to have a positive slope? What is happening in the regions of the plot

where the curve is horizontal, meaning that the temperature does not change even though heat is being added?

12. If you know the mass of a sample of a substance, how could you use a heating curve to calculate the specific heat of the substance, as well as the change in enthalpy associated with a phase change?

13. Draw the heating curve for a liquid that has been superheated. How does this differ from a normal heating curve for a liquid? Draw the cooling curve for a liquid that has been supercooled. How does this differ from a normal cooling curve for a liquid?

Answers

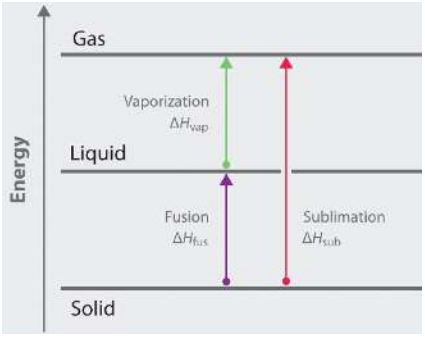
1. When snow disappears without melting, it must be subliming directly from the solid state to the vapor state. The rate at which this will occur depends solely on the partial pressure of water, not on the total pressure due to other gases. Consequently, altitude (and changes in atmospheric pressure) will not affect the rate of sublimation directly.

2.

3. The general equations and enthalpy changes for the changes of state involved in converting a solid to a gas are:

$$\begin{array}{ll} solid \rightarrow liquid & \Delta H_{fus} \\ liquid \rightarrow gas & \Delta H_{vap} \\ solid \rightarrow gas & \Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap} \end{array} \qquad \text{(Chapter 7.5.7)}$$

The relationship between these enthalpy changes is shown schematically in the thermochemical cycle below:



4.

5. The formation of frost on a surface is an example of deposition, which is the reverse of sublimation. The change in enthalpy for deposition is equal in magnitude, but opposite in sign, to ΔH_{sub}, which is a positive number: $\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$.

6.

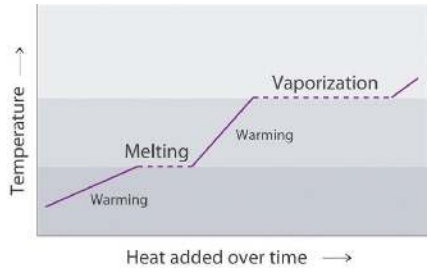
7. 1. liquid + heat → vapor: endothermic
   2. liquid → solid + heat: exothermic
   3. gas → liquid + heat: exothermic
   4. solid + heat → vapor: endothermic

8.

9. The enthalpy of vaporization is larger than the enthalpy of fusion because vaporization requires the addition of enough energy to disrupt all intermolecular interactions and create a gas in which the molecules move essentially independently. In contrast, fusion requires much less energy, because the intermolecular interactions in a liquid and a solid are similar in magnitude in all condensed phases. Fusion requires only enough energy to overcome the intermolecular interactions that lock molecules in place in a lattice, thereby allowing them to move more freely.

10.

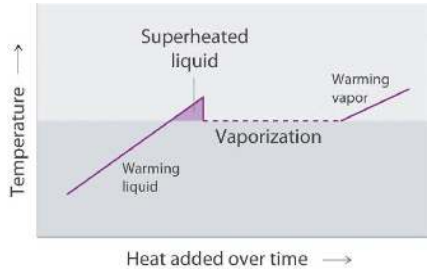
11.



The portions of the curve with a positive slope correspond to heating a single phase, while the horizontal portions of the curve correspond to phase changes. During a phase change, the temperature of the system does not change, because the added heat is melting the solid at its melting point or evaporating the liquid at its boiling point.

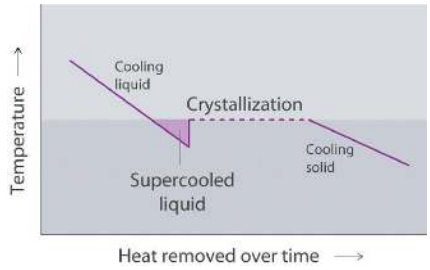
12.

13.



A superheated liquid exists temporarily as liquid with a temperature above the normal boiling point of the liquid. When a supercooled liquid boils, the temperature drops as the liquid is converted to vapor.

Conversely, a supercooled liquid exists temporarily as a liquid with a temperature lower than the normal melting point of the solid. As shown below, when a supercooled liquid crystallizes, the temperature increases as the liquid is converted to a solid.



Numerical Problems

1. The density of oxygen at 1 atm and various temperatures is given in the following table. Plot the data and use your graph to predict the normal boiling point of oxygen.

***T* (K)**	60	70	80	90	100	120	140
***d* (mol/L)**	40.1	38.6	37.2	35.6	0.123	0.102	0.087

2. The density of propane at 1 atm and various temperatures is given in the following table. Plot the data and use your graph to predict the normal boiling point of propane.

***T* (K)**	100	125	150	175	200	225	250	275
***d* (mol/L)**	16.3	15.7	15.0	14.4	13.8	13.2	0.049	0.044

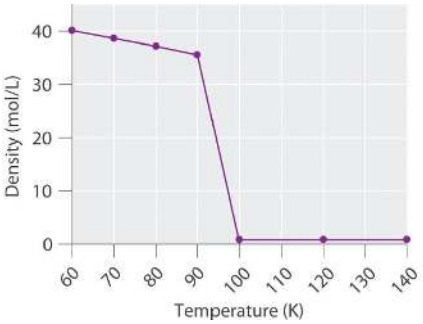
3. Draw the cooling curve for a sample of the vapor of a compound that has a melting point of 34°C and a boiling point of 77°C as it is cooled from 100°C to 0°C.

4. Propionic acid has a melting point of −20.8°C and a boiling point of 141°C. Draw a heating curve showing the temperature versus time as heat is added at a constant rate to show the behavior of a sample of propionic acid as it is heated from −50°C to its boiling point. What happens above 141°C?
5. A 0.542 g sample of I_2 requires 96.1 J of energy to be converted to vapor. What is the enthalpy of sublimation of I_2?
6. A 2.0 L sample of gas at 210°C and 0.762 atm condenses to give 1.20 mL of liquid, and 476 J of heat is released during the process. What is the enthalpy of vaporization of the compound?
7. One fuel used for jet engines and rockets is aluminum borohydride [$Al(BH_4)_3$], a liquid that readily reacts with water to produce hydrogen. The liquid has a boiling point of 44.5°C. How much energy is needed to vaporize 1.0 kg of aluminum borohydride at 20°C, given a ΔH_{vap} of 30 kJ/mol and a molar heat capacity (C_p) of 194.6 J/(mol·K)?
8. How much energy is released when freezing 100.0 g of dimethyl disulfide ($C_2H_6S_2$) initially at 20°C? Use the following information: melting point = −84.7°C, ΔH_{fus} = 9.19 kJ/mol, C_p = 118.1 J/(mol·K).

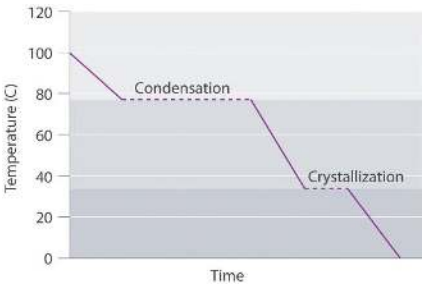
The following four problems use the following information (the subscript p indicates measurements taken at constant pressure): $\Delta H_{fus}(H_2O)$ = 6.01 kJ/mol, $\Delta H_{vap}(H_2O)$ = 40.66 kJ/mol, $C_{p(s)}$(crystalline H_2O) = 38.02 J/(mol·K), $C_{p(l)}$(liquid H_2O) = 75.35 J/(mol·K), and $C_{p(g)}$(H_2O gas) = 33.60 J/(mol·K).

9. How much heat is released in the conversion of 1.00 L of steam at 21.9 atm and 200°C to ice at −6.0°C and 1 atm?
10. How much heat must be applied to convert a 1.00 g piece of ice at −10°C to steam at 120°C?
11. How many grams of boiling water must be added to a glass with 25.0 g of ice at −3°C to obtain a liquid with a temperature of 45°C?
12. How many grams of ice at −5.0°C must be added to 150.0 g of water at 22°C to give a final temperature of 15°C?

Answers

1. 

   The transition from a liquid to a gaseous phase is accompanied by a drastic decrease in density. According to the data in the table and the plot, the boiling point of liquid oxygen is between 90 and 100 K (actually 90.2 K).

2.
3. 

4.
5. 45.0 kJ/mol
6.

7. 488 kJ
8.
9. 32.6 kJ
10.
11. 57 g
12.

Contributors

- Anonymous

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Chapter 7.6: Critical Temperature and Pressure

Learning Objective

- To know what is meant by the critical temperature and pressure of a liquid.

In Section 7.1, we saw that a combination of high pressure and low temperature allows gases to be liquefied. As we increase the temperature of a gas, liquefaction becomes more and more difficult because higher and higher pressures are required to overcome the increased kinetic energy of the molecules. In fact, for every substance, there is some temperature above which the gas can no longer be liquefied, regardless of pressure. This temperature is the critical temperature (T_c)The highest temperature at which a substance can exist as a liquid, regardless of the applied pressure., the highest temperature at which a substance can exist as a liquid. Above the critical temperature, the molecules have too much kinetic energy for the intermolecular attractive forces to hold them together in a separate liquid phase. Instead, the substance forms a single phase that completely occupies the volume of the container. Substances with strong intermolecular forces tend to form a liquid phase over a very large temperature range and therefore have high critical temperatures. Conversely, substances with weak intermolecular interactions have relatively low critical temperatures. Each substance also has a critical pressure (P_c)The minimum pressure needed to liquefy a substance at its critical temperature., the minimum pressure needed to liquefy it at the critical temperature. The combination of critical temperature and critical pressure is called the critical pointThe combination of the critical temperature and the critical pressure of a substance. of a substance. The critical temperatures and pressures of several common substances are listed in Table 7.6.1.

Note the Pattern

High-boiling-point, nonvolatile liquids have high critical temperatures and vice versa.

Table 7.6.1 Critical Temperatures and Pressures of Some Simple Substances

Substance	T_c (°C)	P_c (atm)
NH_3	132.4	113.5
CO_2	31.0	73.8
CH_3CH_2OH (ethanol)	240.9	61.4
He	−267.96	2.27
Hg	1477	1587
CH_4	−82.6	46.0
N_2	−146.9	33.9
H_2O	374.0	217.7

Supercritical Fluids

To understand what happens at the critical point, consider the effects of temperature and pressure on the densities of liquids and gases, respectively. As the temperature of a liquid increases, its density decreases. As the pressure of a gas increases, its density increases. At the critical point, the liquid and gas phases have exactly the same density, and only a single phase exists. This single phase is called a supercritical fluidThe single, dense fluid phase that exists above the critical temperature of a substance., which exhibits many of the properties of a gas but has a density more typical of a liquid. For example, the density of water at its critical point (T = 374°C, P = 217.7 atm) is 0.32 g/mL, about one-third that of liquid water at room temperature but much greater than that of water vapor under most conditions. The transition between a liquid/gas mixture and a supercritical phase is demonstrated for a sample of chlorine in Figure 7.6.1 . At the critical temperature, the meniscus separating the liquid and gas phases disappears.



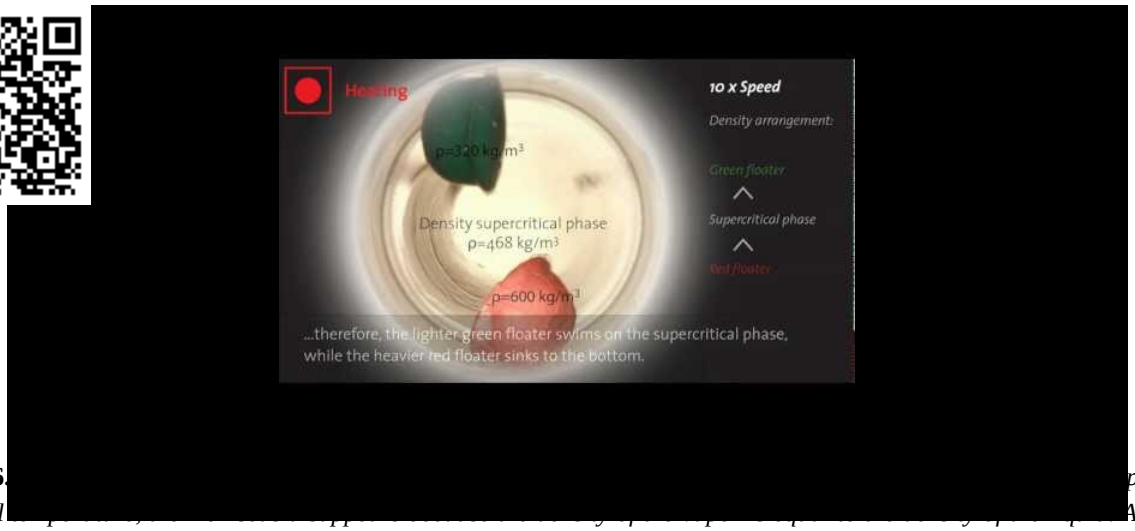


Figure 7.6. *pparent. At the critical Above T_c, a dense homogeneous fluid fills the tube. From the ETH Zurich*

In the last few years, supercritical fluids have evolved from laboratory curiosities to substances with important commercial applications. For example, carbon dioxide has a low critical temperature (31°C), a comparatively low critical pressure (73 atm), and low toxicity, making it easy to contain and relatively safe to manipulate. Because many substances are quite soluble in supercritical CO_2, commercial processes that use it as a solvent are now well established in the oil industry, the food industry, and others. Supercritical CO_2 is pumped into oil wells that are no longer producing much oil to dissolve the residual oil in the underground reservoirs. The less-viscous solution is then pumped to the surface, where the oil can be recovered by evaporation (and recycling) of the CO_2. In the food, flavor, and fragrance industry, supercritical CO_2 is used to extract components from natural substances for use in perfumes, remove objectionable organic acids from hops prior to making beer, and selectively extract caffeine from whole coffee beans without removing important flavor components. The latter process was patented in 1974, and now virtually all decaffeinated coffee is produced this way. The earlier method used volatile organic solvents such as methylene chloride (dichloromethane [CH_2Cl_2], boiling point = 40°C), which is difficult to remove completely from the beans and is known to cause cancer in laboratory animals at high doses.

Example 7.6.1

Arrange methanol, *n*-butane, *n*-pentane, and N_2O in order of increasing critical temperatures.

Given: compounds

Asked for: order of increasing critical temperatures

Strategy:

A Identify the intermolecular forces in each molecule and then assess the strengths of those forces.

B Arrange the compounds in order of increasing critical temperatures.

Solution:

A The critical temperature depends on the strength of the intermolecular interactions that hold a substance together as a liquid. In N_2O, a slightly polar substance, weak dipole–dipole interactions and London dispersion forces are important. Butane (C_4H_{10}) and pentane (C_5H_{12}) are larger, nonpolar molecules that exhibit only London dispersion forces. Methanol, in contrast, should have substantial intermolecular hydrogen bonding interactions. Because hydrogen bonds are stronger than the other intermolecular forces, methanol will have the highest T_c. London forces are more important for pentane than for butane because of its larger size, so *n*-pentane will have a higher T_c than *n*-butane. The only remaining question is whether N_2O is polar enough to have stronger intermolecular interactions than pentane or butane. Because the electronegativities of O and N are quite similar, the answer is probably no, so N_2O should have the lowest T_c. **B** We therefore predict the order of increasing critical temperatures as N_2O < *n*-butane < *n*-pentane < methanol. The actual values are N_2O (36.9°C) < *n*-butane (152.0°C) < *n*-pentane (196.9°C) < methanol (239.9°C). This is the same order as their normal boiling points—N_2O (−88.7°C) < *n*-butane (−0.2°C) < *n*-pentane (36.0°C) <

methanol (65°C)—because both critical temperature and boiling point depend on the relative strengths of the intermolecular interactions.

Exercise

Arrange ethanol, methanethiol (CH_3SH), ethane, and *n*-hexanol in order of increasing critical temperatures.

Answer: ethane (32.3°C) < methanethiol (196.9°C) < ethanol (240.9°C) < *n*-hexanol (336.9°C)

Molten Salts and Ionic Liquids

Heating a salt to its melting point produces a molten saltA salt that has been heated to its melting point.. If we heated a sample of solid NaCl to its melting point of 801°C, for example, it would melt to give a stable liquid that conducts electricity. The characteristics of molten salts other than electrical conductivity are their high heat capacity, ability to attain very high temperatures (over 700°C) as a liquid, and utility as solvents because of their relatively low toxicity.

Molten salts have many uses in industry and the laboratory. For example, in solar power towers in the desert of California, mirrors collect and focus sunlight to melt a mixture of sodium nitrite and sodium nitrate. The heat stored in the molten salt is used to produce steam that drives a steam turbine and a generator, thereby producing electricity from the sun for southern California.

Due to their low toxicity and high thermal efficiency, molten salts have also been used in nuclear reactors to enable operation at temperatures greater than 750°C. One prototype reactor tested in the 1950s used a fuel and a coolant consisting of molten fluoride salts, including NaF, ZrF_4, and UF_4. Molten salts are also useful in catalytic processes such as coal gasification, in which carbon and water react at high temperatures to form CO and H_2.

Note the Pattern

Molten salts are good electrical conductors, have a high heat capacity, can maintain a high temperature as a liquid, and are relatively nontoxic.

Although molten salts have proven highly useful, more recently chemists have been studying the characteristics of ionic liquidsIonic substances that are liquids at room temperature and pressure and that consist of small, symmetrical anions combined with larger, symmetrical organic cations that prevent the formation of a highly organized structure., ionic substances that are *liquid* at room temperature and pressure. These substances consist of small, symmetrical anions, such as PF_6^- and BF_4^-, combined with larger, asymmetrical organic cations that prevent the formation of a highly organized structure, resulting in a low melting point. By varying the cation and the anion, chemists can tailor the liquid to specific needs, such as using a solvent in a given reaction or extracting specific molecules from a solution. For example, an ionic liquid consisting of a bulky cation and anions that bind metal contaminants such as mercury and cadmium ions can remove those toxic metals from the environment. A similar approach has been applied to removing uranium and americium from water contaminated by nuclear waste.

Note the Pattern

Ionic liquids consist of small, symmetrical anions combined with larger asymmetrical cations, which produce a highly polar substance that is a liquid at room temperature and pressure.

The initial interest in ionic liquids centered on their use as a low-temperature alternative to molten salts in batteries for missiles, nuclear warheads, and space probes. Further research revealed that ionic liquids had other useful properties—for example, some could dissolve the black rubber of discarded tires, allowing it to be recovered for recycling. Others could be used to produce commercially important organic compounds with high molecular mass, such as Styrofoam and Plexiglas, at rates 10 times faster than traditional methods.

Summary

A substance cannot form a liquid above its **critical temperature**, regardless of the applied pressure. Above the critical temperature, the molecules have enough kinetic energy to overcome the intermolecular attractive forces. The minimum pressure needed to liquefy a substance at its critical temperature is its **critical pressure**. The combination of the critical temperature and critical pressure of a substance is its **critical point**. Above the critical temperature and pressure, a substance exists as a dense fluid called a **supercritical fluid**, which resembles a gas in that it completely fills its container but has a density comparable to that of a liquid. A

molten salt is a salt heated to its melting point, giving a stable liquid that conducts electricity. **Ionic liquids** are ionic substances that are liquids at room temperature. Their disorganized structure results in a low melting point.

Key Takeaway

- The critical temperature and critical pressure of a substance define its critical point, beyond which the substance forms a supercritical fluid.

Conceptual Problems

1. Describe the changes that take place when a liquid is heated above its critical temperature. How does this affect the physical properties?
2. What is meant by the term *critical pressure*? What is the effect of increasing the pressure on a gas to above its critical pressure? Would it make any difference if the temperature of the gas was greater than its critical temperature?
3. Do you expect the physical properties of a supercritical fluid to be more like those of the gas or the liquid phase? Explain. Can an ideal gas form a supercritical fluid? Why or why not?
4. What are the limitations in using supercritical fluids to extract organic materials? What are the advantages?
5. Describe the differences between a molten salt and an ionic liquid. Under what circumstances would an ionic liquid be preferred over a molten salt?

Contributors

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Chapter 7.7: Phase Diagrams

Learning Objective

- To understand the general features of a phase diagram.

The state exhibited by a given sample of matter depends on the identity, temperature, and pressure of the sample. A phase diagramA graphic summary of the physical state of a substance as a function of temperature and pressure in a closed system. is a graphic summary of the physical state of a substance as a function of temperature and pressure in a closed system.

A typical phase diagram consists of discrete regions that represent the different phases exhibited by a substance (Figure 7.7.1). Each region corresponds to the range of combinations of temperature and pressure over which that phase is stable. The combination of high pressure and low temperature (upper left of Figure 7.7.1) corresponds to the solid phase, whereas the gas phase is favored at high temperature and low pressure (lower right). The combination of high temperature and high pressure (upper right) corresponds to a supercritical fluid.

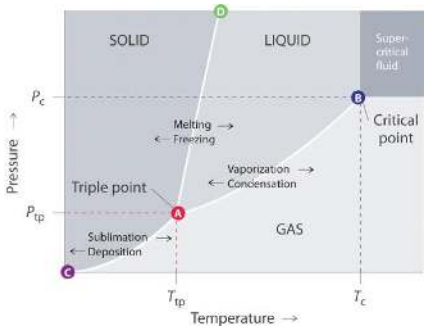


Figure 7.7.1 A Typical Phase Diagram for a Substance That Exhibits Three Phases—Solid, Liquid, and Gas—and a Supercritical Region

Note the Pattern

The solid phase is favored at low temperature and high pressure; the gas phase is favored at high temperature and low pressure.

General Features of a Phase Diagram

The lines in a phase diagram correspond to the combinations of temperature and pressure at which two phases can coexist in equilibrium. In Figure 7.7.1 the line that connects points A and D separates the solid and liquid phases and shows how the melting point of a solid varies with pressure. The solid and liquid phases are in equilibrium all along this line; crossing the line horizontally corresponds to melting or freezing. The line that connects points A and B is the vapor pressure curve of the liquid, which we discussed in Section 7.4 . It ends at the critical point, beyond which the substance exists as a supercritical fluid. The line that connects points A and C is the vapor pressure curve of the *solid* phase. Along this line, the solid is in equilibrium with the vapor phase through sublimation and deposition. Finally, point A, where the solid/liquid, liquid/gas, and solid/gas lines intersect, is the triple pointThe point in a phase diagram where the solid/liquid, liquid/gas, and solid/gas lines intersect; it represents the only combination of temperature and pressure at which all three phases are in equilibrium and can therefore exist simultaneously.; it is the *only* combination of temperature and pressure at which all three phases (solid, liquid, and gas) are in equilibrium and can therefore exist simultaneously. Because no more than three phases can ever coexist, a phase diagram can never have more than three lines intersecting at a single point.

Remember that a phase diagram, such as the one in Figure 7.7.1 , is for a single pure substance in a closed system, not for a liquid in an open beaker in contact with air at 1 atm pressure. In practice, however, the conclusions reached about the behavior of a substance in a closed system can usually be extrapolated to an open system without a great deal of error.

The Phase Diagram of Water

Figure 7.7.2 shows the phase diagram of water and illustrates that the triple point of water occurs at 0.01°C and 0.00604 atm (4.59 mmHg). Far more reproducible than the melting point of ice, which depends on the amount of dissolved air and the atmospheric

pressure, the triple point (273.16 K) is used to define the absolute (Kelvin) temperature scale. The triple point also represents the lowest pressure at which a liquid phase can exist in equilibrium with the solid or vapor. At pressures less than 0.00604 atm, therefore, ice does not melt to a liquid as the temperature increases; the solid sublimes directly to water vapor. Sublimation of water at low temperature and pressure can be used to "freeze-dry" foods and beverages. The food or beverage is first cooled to subzero temperatures and placed in a container in which the pressure is maintained below 0.00604 atm. Then, as the temperature is increased, the water sublimes, leaving the dehydrated food (such as that used by backpackers or astronauts) or the powdered beverage (as with freeze-dried coffee).

The phase diagram for water illustrated in part (b) in Figure 7.7.2 shows the boundary between ice and water on an expanded scale. The melting curve of ice slopes up and slightly to the left rather than up and to the right as in Figure 7.7.1 ; that is, the melting point of ice *decreases* with increasing pressure; at 100 MPa (987 atm), ice melts at −9°C. Water behaves this way because it is one of the few known substances for which the crystalline solid is *less dense* than the liquid (others include antimony and bismuth). Increasing the pressure of ice that is in equilibrium with water at 0°C and 1 atm tends to push some of the molecules closer together, thus decreasing the volume of the sample. The decrease in volume (and corresponding increase in density) is smaller for a solid or a liquid than for a gas, but it is sufficient to melt some of the ice.

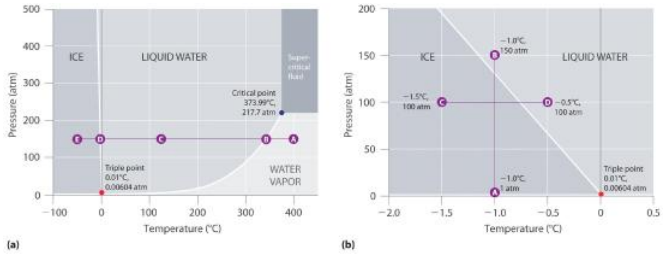


Figure 7.7.2 Two Versions of the Phase Diagram of Water *(a) In this graph with linear temperature and pressure axes, the boundary between ice and liquid water is almost vertical. (b) This graph with an expanded scale illustrates the decrease in melting point with increasing pressure. (The letters refer to points discussed in Example 10.)*

In part (b) in Figure 7.7.2 , point A is located at P = 1 atm and T = −1.0°C, within the solid (ice) region of the phase diagram. As the pressure increases to 150 atm while the temperature remains the same, the line from point A crosses the ice/water boundary to point B, which lies in the liquid water region. Consequently, applying a pressure of 150 atm will melt ice at −1.0°C. We have already indicated that the pressure dependence of the melting point of water is of vital importance. If the solid/liquid boundary in the phase diagram of water were to slant up and to the right rather than to the left, ice would be denser than water, ice cubes would sink, water pipes would not burst when they freeze, and antifreeze would be unnecessary in automobile engines.

Although at usual temperatures and pressures the phase diagram of water is simple, increasing the pressure above 1000 atm crushes the open solid structure of normal ice into increasingly compact structures as shown in Figure 7.73

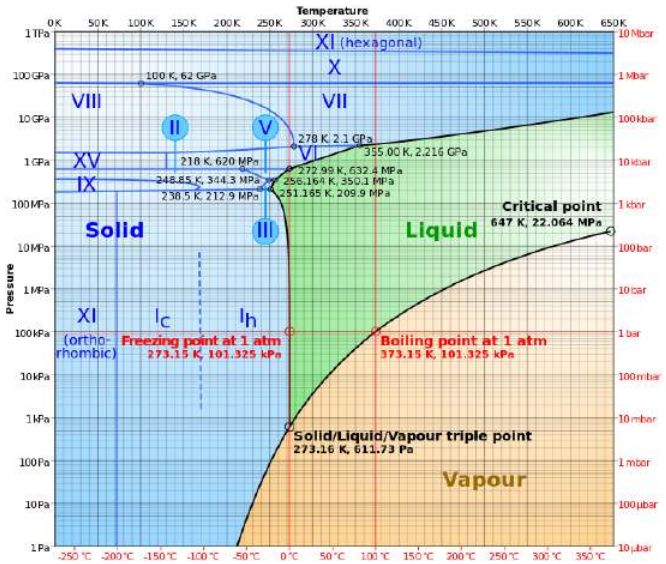


Figure 7.7.3 The Phase Diagram of Water: *At high pressures, new solid phases appear as the open structure of normal ice is crushed. This figure is from the Wikipedia.*

We will take up ice structures again in the next chapter when we discuss solids.

The Phase Diagram of Carbon Dioxide

In contrast to the phase diagram of water, the phase diagram of CO_2 (Figure 7.7.3) has a more typical melting curve, sloping up and to the right. The triple point is −56.6°C and 5.11 atm, which means that liquid CO_2 cannot exist at pressures lower than 5.11 atm. At 1 atm, therefore, solid CO_2 sublimes directly to the vapor while maintaining a temperature of −78.5°C, the normal sublimation temperature. Solid CO_2 is generally known as dry ice because it is a cold solid with no liquid phase observed when it is warmed. Also notice the critical point at 30.98°C and 72.79 atm. In addition to the uses discussed in Section 7.6 , supercritical carbon dioxide is emerging as a natural refrigerant, making it a low carbon (and thus a more environmentally friendly) solution for domestic heat pumps.

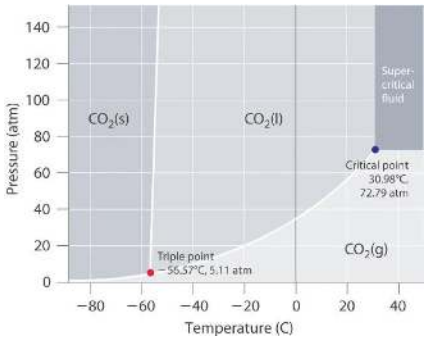


Figure 7.73 The Phase Diagram of Carbon Dioxide *Note the critical point, the triple point, and the normal sublimation temperature in this diagram.*

Example 7.71

Referring to the phase diagram of water in Figure 7.7.2 ,

1. predict the physical form of a sample of water at 400°C and 150 atm.
2. describe the changes that occur as the sample in part (a) is slowly allowed to cool to −50°C at a constant pressure of 150 atm.

Given: phase diagram, temperature, and pressure

Asked for: physical form and physical changes

Strategy:

A Identify the region of the phase diagram corresponding to the initial conditions and identify the phase that exists in this region.

B Draw a line corresponding to the given pressure. Move along that line in the appropriate direction (in this case cooling) and describe the phase changes.

Solution:

1. **A** Locate the starting point on the phase diagram in part (a) in Figure 7.7.2 . The initial conditions correspond to point A, which lies in the region of the phase diagram representing water vapor. Thus water at T = 400°C and P = 150 atm is a gas.
2. **B** Cooling the sample at constant pressure corresponds to moving left along the horizontal line in part (a) in Figure 7.72 . At about 340°C (point B), we cross the vapor pressure curve, at which point water vapor will begin to condense and the sample will consist of a mixture of vapor and liquid. When all of the vapor has condensed, the temperature drops further, and we enter the region corresponding to liquid water (indicated by point C). Further cooling brings us to the melting curve, the line that separates the liquid and solid phases at a little below 0°C (point D), at which point the sample will consist of a mixture of liquid and solid water (ice). When all of the water has frozen, cooling the sample to −50°C takes us along the horizontal line to point E, which lies within the region corresponding to solid water. At P = 150 atm and T = −50°C, therefore, the sample is solid ice.

Exercise

Referring to the phase diagram of water in Figure 7.7.2 , predict the physical form of a sample of water at −0.0050°C as the pressure is gradually increased from 1.0 mmHg to 218 atm.

Answer: The sample is initially a gas, condenses to a solid as the pressure increases, and then melts when the pressure is increased further to give a liquid.

Summary

The states of matter exhibited by a substance under different temperatures and pressures can be summarized graphically in a **phase diagram**, which is a plot of pressure versus temperature. Phase diagrams contain discrete regions corresponding to the solid, liquid, and gas phases. The solid and liquid regions are separated by the melting curve of the substance, and the liquid and gas regions are separated by its vapor pressure curve, which ends at the critical point. Within a given region, only a single phase is stable, but along the lines that separate the regions, two phases are in equilibrium at a given temperature and pressure. The lines separating the three phases intersect at a single point, the **triple point**, which is the only combination of temperature and pressure at which all three phases can coexist in equilibrium. Water has an unusual phase diagram: its melting point decreases with increasing pressure because ice is less dense than liquid water. The phase diagram of carbon dioxide shows that liquid carbon dioxide cannot exist at atmospheric pressure. Consequently, solid carbon dioxide sublimes directly to a gas.

Key Takeaway

- A phase diagram is a graphic summary of the physical state of a substance as a function of temperature and pressure in a closed system. It shows the triple point, the critical point, and four regions: solid, liquid, gas, and a supercritical region.

Conceptual Problems

1. A phase diagram is a graphic representation of the stable phase of a substance at any combination of temperature and pressure. What do the lines separating different regions in a phase diagram indicate? What information does the slope of a line in a phase diagram convey about the physical properties of the phases it separates? Can a phase diagram have more than one point where three lines intersect?

2. If the slope of the line corresponding to the solid/liquid boundary in the phase diagram of water were positive rather than negative, what would be the effect on aquatic life during periods of subzero temperatures? Explain your answer.

Answer

1. The lines in a phase diagram represent boundaries between different phases; at any combination of temperature and pressure that lies on a line, two phases are in equilibrium. It is physically impossible for more than three phases to coexist at any combination of temperature and pressure, but in principle there can be more than one triple point in a phase diagram. The slope

of the line separating two phases depends upon their relative densities. For example, if the solid–liquid line slopes up and to the *right*, the liquid is less dense than the solid, while if it slopes up and to the *left*, the liquid is denser than the solid.

2.

Numerical Problems

1. Naphthalene ($C_{10}H_8$) is the key ingredient in mothballs. It has normal melting and boiling points of 81°C and 218°C, respectively. The triple point of naphthalene is 80°C at 1000 Pa. Use these data to construct a phase diagram for naphthalene and label all the regions of your diagram.
2. Argon is an inert gas used in welding. It has normal boiling and freezing points of 87.3 K and 83.8 K, respectively. The triple point of argon is 83.8 K at 0.68 atm. Use these data to construct a phase diagram for argon and label all the regions of your diagram.

Contributors

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Chapter 7.8: Liquid Crystals

Learning Objective

- To describe the properties of liquid crystals.

When cooled, most liquids undergo a simple phase transitionAnother name for a phase change. to an ordered crystalline solid, a relatively rigid substance that has a fixed shape and volume. In the phase diagrams for these liquids, there are no regions between the liquid and solid phases. Thousands of substances are known, however, that exhibit one or more phases intermediate between the liquid state, in which the molecules are free to tumble and move past one another, and the solid state, in which the molecules or ions are rigidly locked into place. In these intermediate phases, the molecules have an ordered arrangement and yet can still flow like a liquid. Hence they are called liquid crystalsA substance that exhibits phases that have properties intermediate between those of a crystalline solid and a normal liquid and possess long-range molecular order but still flow., and their unusual properties have found a wide range of commercial applications. They are used, for example, in the liquid crystal displays (LCDs) in digital watches, calculators, and computer and video displays.

The first documented example of a liquid crystal was reported by the Austrian Frederick Reinitzer in 1888. Reinitzer was studying the properties of a cholesterol derivative, cholesteryl benzoate, and noticed that it behaved strangely as it melted. The white solid first formed a cloudy white liquid phase at 145°C, which reproducibly transformed into a clear liquid at 179°C. The transitions were completely reversible: cooling molten cholesteryl benzoate below 179°C caused the clear liquid to revert to a milky one, which then crystallized at the melting point of 145°C.

In a normal liquid, the molecules possess enough thermal energy to overcome the intermolecular attractive forces and tumble freely. This arrangement of the molecules is described as isotropicThe arrangement of molecules that is equally disordered in all directions., which means that it is equally disordered in all directions. Liquid crystals, in contrast, are anisotropicAn arrangement of molecules in which their properties depend on the direction they are measured.: their properties depend on the direction in which they are viewed. Hence liquid crystals are not as disordered as a liquid because the molecules have some degree of alignment.

Most substances that exhibit the properties of liquid crystals consist of long, rigid rod- or disk-shaped molecules that are easily polarizable and can orient themselves in one of three different ways, as shown in Figure 7.8.1. In the nematic phaseOne of three different ways that most liquid crystals can orient themselves. Only the long axes of the molecules are aligned, so they are free to rotate or to slide past one another., the molecules are not layered but are pointed in the same direction. As a result, the molecules are free to rotate or slide past one another. In the smectic phaseOne of three different ways that most liquid crystals can orient themselves. The long axes of the molecules are aligned (similar to the nematic phase), but the molecules are arranged in planes, too., the molecules maintain the general order of the nematic phase but are also aligned in layers. Several variants of the smectic phase are known, depending on the angle formed between the molecular axes and the planes of molecules. The simplest such structure is the so-called smectic A phase, in which the molecules can rotate about their long axes within a given plane, but they cannot readily slide past one another. In the cholesteric phaseOne of three different ways that most liquid crystals can orient themselves. The molecules are arranged in planes (similar to the smectic phase), but each layer is rotated by a certain amount with respect to those above and below it, giving it a helical structure., the molecules are directionally oriented and stacked in a helical pattern, with each layer rotated at a slight angle to the ones above and below it. As the degree of molecular ordering increases from the nematic phase to the cholesteric phase, the liquid becomes more opaque, although direct comparisons are somewhat difficult because most compounds form only one of these liquid crystal phases when the solid is melted or the liquid is cooled.

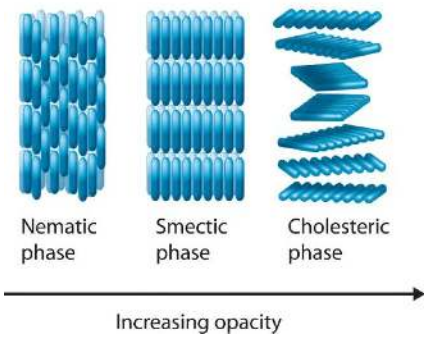


Figure 7.8.1 The Arrangement of Molecules in the Nematic, Smectic, and Cholesteric Liquid Crystal Phases *In the nematic phase, only the long axes of the molecules are parallel, and the ends are staggered at random intervals. In the smectic phase, the long axes of the molecules are parallel, and the molecules are also arranged in planes. Finally, in the cholesteric phase, the molecules are arranged in layers; each layer is rotated with respect to the ones above and below it to give a spiral structure. The molecular order increases from the nematic phase to the smectic phase to the cholesteric phase, and the phases become increasingly opaque.*

Molecules that form liquid crystals tend to be rigid molecules with polar groups that exhibit relatively strong dipole–dipole or dipole–induced dipole interactions, hydrogen bonds, or some combination of both. Some examples of substances that form liquid crystals are listed in Figure 7.8.2 along with their characteristic phase transition temperature ranges. In most cases, the intermolecular interactions are due to the presence of polar or polarizable groups. Aromatic rings and multiple bonds between carbon and nitrogen or oxygen are especially common. Moreover, many liquid crystals are composed of molecules with two similar halves connected by a unit having a multiple bond.

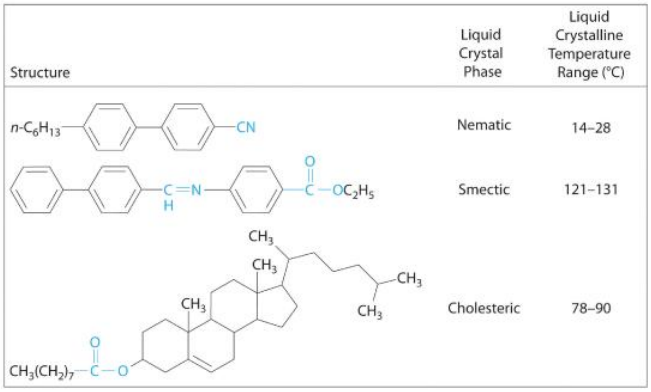


Figure 7.8.2 Structures of Typical Molecules That Form Liquid Crystals *Polar or polarizable groups are indicated in blue.*

Because of their anisotropic structures, liquid crystals exhibit unusual optical and electrical properties. The intermolecular forces are rather weak and can be perturbed by an applied electric field. Because the molecules are polar, they interact with an electric field, which causes them to change their orientation slightly. Nematic liquid crystals, for example, tend to be relatively translucent, but many of them become opaque when an electric field is applied and the molecular orientation changes. This behavior is ideal for producing dark images on a light or an opalescent background, and it is used in the LCDs in digital watches; handheld calculators; flat-screen monitors; and car, ship, and aircraft instrumentation. Although each application differs in the details of its construction and operation, the basic principles are similar, as illustrated in Figure 7.8.3.

Note the Pattern

Liquid crystals tend to form from long, rigid molecules with polar groups.

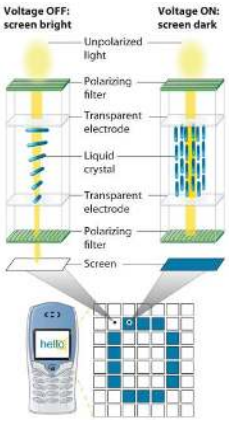
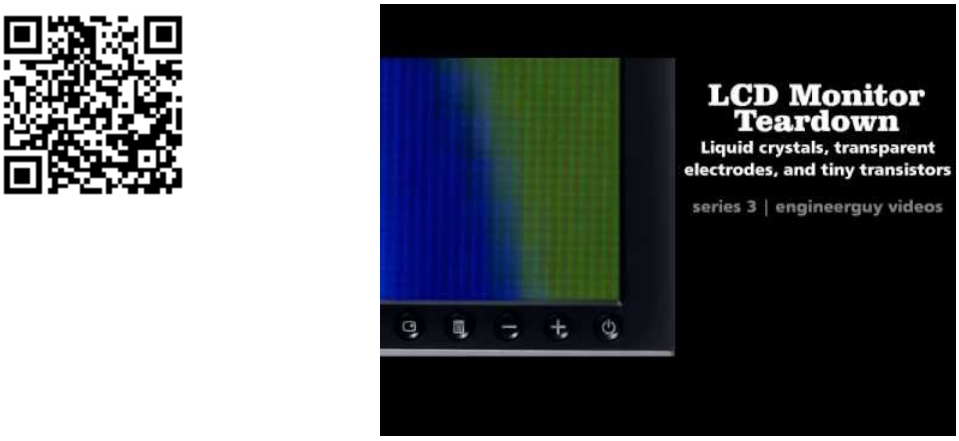


Figure 7.8.3 Schematic Drawing of an LCD Device, Showing the Various Layers *Applying a voltage to selected segments of the device will produce any of the numbers. The device is a sandwich that contains several very thin layers, consisting of (from top to bottom) a sheet of polarizer to produce polarized light, a transparent electrode, a thin layer of a liquid crystalline substance, a second transparent electrode, a second polarizer, and a screen. Applying an electrical voltage to the liquid crystal changes its orientation slightly, which rotates the plane of the polarized light and makes the area appear dark.*

Today we all use LCD monitors. How do they work? The video below shows.



Changes in molecular orientation that are dependent on temperature result in an alteration of the wavelength of reflected light. Changes in reflected light produce a change in color, which can be customized by using either a single type of liquid crystalline material or mixtures. It is therefore possible to build a liquid crystal thermometer that indicates temperature by color (Figure 7.8.4) and to use liquid crystals in heat-sensitive films to detect flaws in electronic board connections where overheating can occur.

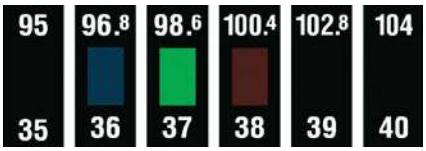


Figure 7.8.4 An Inexpensive Fever Thermometer That Uses Liquid Crystals *Each section contains a liquid crystal sample with a different liquid crystalline range. The section whose liquid crystalline range corresponds to the temperature of the body becomes translucent (here shown in green), indicating the temperature.*

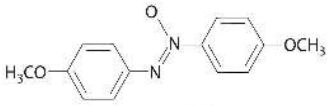
We also see the effect of liquid crystals in nature. Iridescent green beetles, known as jewel beetles, change color because of the light-reflecting properties of the cells that make up their external skeletons, not because of light absorption from their pigment. The cells form helices with a structure like those found in cholesteric liquid crystals. When the pitch of the helix is close to the wavelength of visible light, the cells reflect light with wavelengths that lead to brilliant metallic colors. Because a color change occurs depending on a person's angle of view, researchers in New Zealand are studying the beetles to develop a thin material that can be used as a currency security measure. The automobile industry is also interested in exploring such materials for use in paints that would change color at different viewing angles.

With only molecular structure as a guide, one cannot precisely predict which of the various liquid crystalline phases a given compound will actually form. One can, however, identify molecules containing the kinds of structural features that tend to result in liquid crystalline behavior, as demonstrated in Example 11.

Example 7.8.1

Which molecule is most likely to form a liquid crystalline phase as the isotropic liquid is cooled?

1. isooctane (2,2,4-trimethylpentane)
2. ammonium thiocyanate [$NH_4(SCN)$]
3. *p*-azoxyanisole



p-Azoxyanisole

4. sodium decanoate {$Na[CH_3(CH_2)_8CO_2]$}

Given: compounds

Asked for: liquid crystalline behavior

Strategy:

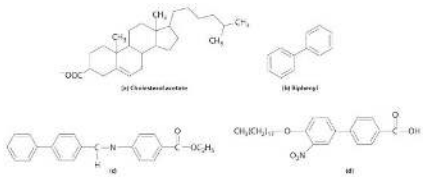
Determine which compounds have a rigid structure and contain polar groups. Those that do are likely to exhibit liquid crystal behavior.

Solution:

1. Isooctane is not long and rigid and contains no polar groups, so it is unlikely to exhibit liquid crystal behavior.
2. Ammonium thiocyanate is ionic, and ionic compounds tend to have high melting points, so it should not form a liquid crystalline phase. In fact, ionic compounds that form liquid crystals are very rare indeed.
3. *p*-Azoxyanisole combines two planar phenyl rings linked through a multiply bonded unit, and it contains polar groups. The combination of a long, rigid shape and polar groups makes it a reasonable candidate for a liquid crystal.
4. Sodium decanoate is the sodium salt of a straight-chain carboxylic acid. The *n*-alkyl chain is long, but it is flexible rather than rigid, so the compound is probably not a liquid crystal.

Exercise

Which compound is least likely to form a liquid crystal phase?



Answer: (b) Biphenyl; although it is rather long and rigid, it lacks any polar substituents.

Summary

Many substances exhibit phases that have properties intermediate between those of a crystalline solid and a normal liquid. These substances, which possess long-range molecular order but still flow like liquids, are called **liquid crystals**. Liquid crystals are typically long, rigid molecules that can interact strongly with one another; they do not have **isotropic** structures, which are completely disordered, but rather have **anisotropic** structures, which exhibit different properties when viewed from different directions. In the **nematic phase**, only the long axes of the molecules are aligned, whereas in the **smectic phase**, the long axes of the molecules are parallel and the molecules are arranged in planes. In the **cholesteric phase**, the molecules are arranged in planes, but each layer is rotated by a certain amount with respect to those above and below it, giving a helical structure.

Key Takeaway

- Liquid crystals tend to consist of rigid molecules with polar groups, and their anisotropic structures exhibit unusual optical and electrical properties.

Conceptual Problems

1. Describe the common structural features of molecules that form liquid crystals. What kind of intermolecular interactions are most likely to result in a long-chain molecule that exhibits liquid crystalline behavior? Does an electrical field affect these interactions?
2. What is the difference between an *isotropic* liquid and an *anisotropic* liquid? Which is more anisotropic—a cholesteric liquid crystal or a nematic liquid crystal?

Contributors

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LCD Monitor teardown by engineerguy on YouTube

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Chapter 7.9: End of Chapter Material

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Application Problems

Problems marked with a ♦ involve multiple concepts.

1. During cold periods, workers in the citrus industry often spray water on orange trees to prevent them from being damaged, even though ice forms on the fruit.
   a. Explain the scientific basis for this practice.
   b. To illustrate why the production of ice prevents damage to the fruit during cold weather, calculate the heat released by formation of ice from 1000 L of water at 10°C.
2. ♦ Relative humidity is the ratio of the actual partial pressure of water in the air to the vapor pressure of water at that temperature (i.e., if the air was completely saturated with water vapor), multiplied by 100 to give a percentage. On a summer day in the Chesapeake, when the temperature was recorded as 35°C, the partial pressure of water was reported to be 33.9 Torr.
   a. The following table gives the vapor pressure of water at various temperatures. Calculate the relative humidity.

T **(°C)**	0	10	30	50	60	80	100
P **(Torr)**	4.6	9.2	31.8	92.6	150	355	760

   b. Why does it seem “drier” in the winter, even though the relative humidity may be the same as in the summer?
3. ♦ Liquids are frequently classified according to their physical properties, such as surface tension, vapor pressure, and boiling point. Such classifications are useful when substitutes are needed for a liquid that might not be available.
   a. Draw the structure of methanol, benzene, pentane, toluene, cyclohexane, 1-butanol, trichloroethylene, acetic acid, acetone, and chloroform.
   b. Identify the most important kind of intermolecular interaction in each.
   c. Sort the compounds into three groups with similar characteristics.
   d. If you needed a substitute for trimethylpentane, from which group would you make your selection?
4. ♦ In the process of freeze drying, which is used as a preservation method and to aid in the shipping or storage of fruit and biological samples, a sample is cooled and then placed in a compartment in which a very low pressure is maintained, ≈0.01 atm.
   a. Explain how this process removes water and “dries” the sample.
   b. Identify the phase change that occurs during this process.
   c. Using the Clausius–Clapeyron equation, show why it is possible to remove water and still maintain a low temperature at this pressure.
5. ♦ Many industrial processes for preparing compounds use “continuous-flow reactors,” which are chemical reaction vessels in which the reactants are mixed and allowed to react as they flow along a tube. The products are removed at a certain distance from the starting point, when the reaction is nearly complete. The key operating parameters in a continuous-flow reactor are temperature, reactor volume, and reactant flow rate. As an industrial chemist, you think you have successfully modified a particular process to produce a higher product yield by substituting one reactant for another. The viscosity of the new reactant is, however, greater than that of the initial reactant.
   a. Which of the operating parameters will be most greatly affected by this change?
   b. What other parameter could be changed to compensate for the substitution?
   c. Predict the possible effects on your reactor and your process if you do not compensate for the substitution.

Contributors

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CHAPTER OVERVIEW

Chapter 8: Solids

Chapter 8.1: Crystalline and Amorphous Solids
Chapter 8.2: Arrangement of Atoms in Crystals
Chapter 8.3: Stucture of Simple Binary Compounds
Chapter 8.4: Crystal Defects
Chapter 8.5: Bonding and Properties of Solids
Chapter 8.6: Metals and Semiconductors
Chapter 8.7: Superconductors
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Chapter 8.1: Crystalline and Amorphous Solids

Learning Objective

- To know the characteristic properties of crystalline and amorphous solids.

With few exceptions, the particles that compose a solid material, whether ionic, molecular, covalent, or metallic, are held in place by strong attractive forces between them. When we discuss solids, therefore, we consider the *positions* of the atoms, molecules, or ions, which are essentially fixed in space, rather than their motions (which are more important in liquids and gases). The constituents of a solid can be arranged in two general ways: they can form a regular repeating three-dimensional structure called a crystal latticeA regular repeating three-dimensional structure., thus producing a crystalline solidA solid with a regular repeating three-dimensional structure., or they can aggregate with no particular order, in which case they form an amorphous solidA solid with no particular structural order. (from the Greek *ámorphos*, meaning “shapeless”).

Crystalline solids, or *crystals*, have distinctive internal structures that in turn lead to distinctive flat surfaces, or *faces*. The faces intersect at angles that are characteristic of the substance. When exposed to x-rays, each structure also produces a distinctive pattern that can be used to identify the material (see Section 8.3). The characteristic angles do not depend on the size of the crystal; they reflect the regular repeating arrangement of the component atoms, molecules, or ions in space. When an ionic crystal is cleaved (Figure 8.1.1), for example, repulsive interactions cause it to break along fixed planes to produce new faces that intersect at the same angles as those in the original crystal. In a covalent solid such as a cut diamond, the angles at which the faces meet are also not arbitrary but are determined by the arrangement of the carbon atoms in the crystal.



Crystalline faces. *The faces of crystals can intersect at right angles, as in galena (PbS) and pyrite (FeS_2), or at other angles, as in quartz.*

Cleavage surfaces of an amorphous solid. Obsidian, a volcanic glass with the same chemical composition as granite (typically $KAlSi_3O_8$), tends to have curved, irregular surfaces when cleaved.

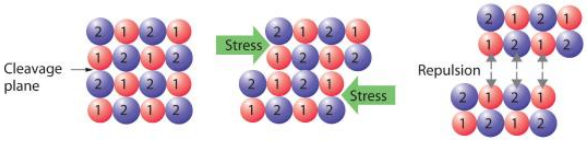
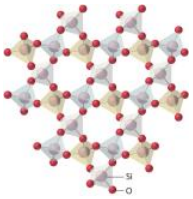




Figure 8.1.1 Cleaving a Crystal of an Ionic Compound along a Plane of Ions *Deformation of the ionic crystal causes one plane of atoms to slide along another. The resulting repulsive interactions between ions with like charges cause the layers to separate.*

Crystals tend to have relatively sharp, well-defined melting points because all the component atoms, molecules, or ions are the same distance from the same number and type of neighbors; that is, the regularity of the crystalline lattice creates local environments that are the same. Thus the intermolecular forces holding the solid together are uniform, and the same amount of thermal energy is needed to break every interaction simultaneously.

Amorphous solids have two characteristic properties. When cleaved or broken, they produce fragments with irregular, often curved surfaces; and they have poorly defined patterns when exposed to x-rays because their components are not arranged in a regular array. An amorphous, translucent solid is called a glassAn amorphous, translucent solid. A glass is a solid that has been cooled too quickly to form ordered crystals.. Almost any substance can solidify in amorphous form if the liquid phase is cooled rapidly enough. Some solids, however, are intrinsically amorphous, because either their components cannot fit together well enough to form a stable crystalline lattice or they contain impurities that disrupt the lattice. For example, although the chemical composition and the basic structural units of a quartz crystal and quartz glass are the same—both are SiO_2 and both consist of linked SiO_4 tetrahedra—the arrangements of the atoms in space are not. Crystalline quartz contains a highly ordered arrangement of silicon and oxygen atoms, but in quartz glass the atoms are arranged almost randomly. When molten SiO_2 is cooled rapidly (4 K/min), it forms quartz glass, whereas the large, perfect quartz crystals sold in mineral shops have had cooling times of thousands of years. In contrast, aluminum crystallizes much more rapidly. Amorphous aluminum forms only when the liquid is cooled at the extraordinary rate of 4×10^{13} K/s, which prevents the atoms from arranging themselves into a regular array.



The lattice of crystalline quartz (SiO_2). *The atoms form a regular arrangement in a structure that consists of linked tetrahedra.*

In an amorphous solid, the local environment, including both the distances to neighboring units and the numbers of neighbors, varies throughout the material. Different amounts of thermal energy are needed to overcome these different interactions. Consequently, amorphous solids tend to soften slowly over a wide temperature range rather than having a well-defined melting point like a crystalline solid. If an amorphous solid is maintained at a temperature just below its melting point for long periods of time, the component molecules, atoms, or ions can gradually rearrange into a more highly ordered crystalline form.

Note the Pattern

Crystals have sharp, well-defined melting points; amorphous solids do not.

Summary

Solids are characterized by an extended three-dimensional arrangement of atoms, ions, or molecules in which the components are generally locked into their positions. The components can be arranged in a regular repeating three-dimensional array (a **crystal lattice**), which results in a **crystalline solid**, or more or less randomly to produce an **amorphous solid**. Crystalline solids have well-defined edges and faces, diffract x-rays, and tend to have sharp melting points. In contrast, amorphous solids have irregular or curved surfaces, do not give well-resolved x-ray diffraction patterns, and melt over a wide range of temperatures.

Key Takeaway

- Crystalline solids have regular ordered arrays of components held together by uniform intermolecular forces, whereas the components of amorphous solids are not arranged in regular arrays.

Conceptual Problems

1. Compare the solid and liquid states in terms of
    1. rigidity of structure.
    2. long-range order.
    3. short-range order.
2. How do amorphous solids differ from crystalline solids in each characteristic? Which of the two types of solid is most similar to a liquid?
    1. rigidity of structure
    2. long-range order

3. short-range order

3. Why is the arrangement of the constituent atoms or molecules more important in determining the properties of a solid than a liquid or a gas?

4. Why are the structures of solids usually described in terms of the positions of the constituent atoms rather than their motion?

5. What physical characteristics distinguish a crystalline solid from an amorphous solid? Describe at least two ways to determine experimentally whether a material is crystalline or amorphous.

6. Explain why each characteristic would or would not favor the formation of an amorphous solid.

   1. slow cooling of pure molten material
   2. impurities in the liquid from which the solid is formed
   3. weak intermolecular attractive forces

7. A student obtained a solid product in a laboratory synthesis. To verify the identity of the solid, she measured its melting point and found that the material melted over a 12°C range. After it had cooled, she measured the melting point of the same sample again and found that this time the solid had a sharp melting point at the temperature that is characteristic of the desired product. Why were the two melting points different? What was responsible for the change in the melting point?

Answers

3. The arrangement of the atoms or molecules is more important in determining the properties of a solid because of the greater
2. persistent long-range order of solids. Gases and liquids cannot readily be described by the spatial arrangement of their
1. components because rapid molecular motion and rearrangement defines many of the properties of liquids and gases.

4.

5.

6.

7. The initial solid contained the desired compound in an amorphous state, as indicated by the wide temperature range over which melting occurred. Slow cooling of the liquid caused it to crystallize, as evidenced by the sharp second melting point observed at the expected temperature.

Contributors

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Chapter 8.2: Arrangement of Atoms in Crystals

Learning Objective

- To recognize the unit cell of a crystalline solid.
- To calculate the density of a solid given its unit cell.

Because a crystalline solid consists of repeating patterns of its components in three dimensions (a **crystal lattice**), we can represent the entire crystal by drawing the structure of the smallest identical units that, when stacked together, form the crystal. This basic repeating unit is called a unit cellThe smallest repeating unit of a crystal lattice.. For example, the unit cell of a sheet of identical postage stamps is a single stamp, and the unit cell of a stack of bricks is a single brick. In this section, we describe the arrangements of atoms in various unit cells.

Unit cells are easiest to visualize in two dimensions. In many cases, more than one unit cell can be used to represent a given structure, as shown for the Escher drawing in the chapter opener and for a two-dimensional crystal lattice in Figure 8.2.1. Usually the smallest unit cell that completely describes the order is chosen. The only requirement for a valid unit cell is that repeating it in space must produce the regular lattice. Thus the unit cell in part (d) in Figure 8.2.1 is not a valid choice because repeating it in space does not produce the desired lattice (there are triangular holes). The concept of unit cells is extended to a three-dimensional lattice in the schematic drawing in Figure 8.2.2 .

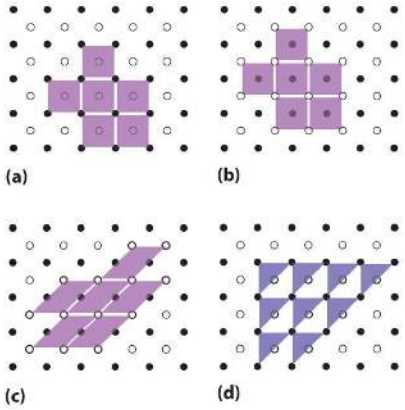


Figure 8.2.1 Unit Cells in Two Dimensions *(a–c) Three two-dimensional lattices illustrate the possible choices of the unit cell. The unit cells differ in their relative locations or orientations within the lattice, but they are all valid choices because repeating them in any direction fills the overall pattern of dots. (d) The triangle is not a valid unit cell because repeating it in space fills only half of the space in the pattern.*

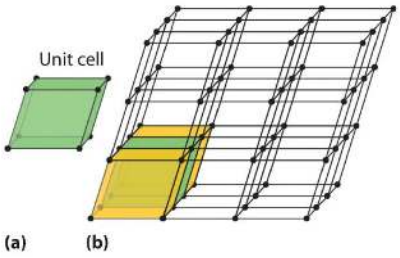


Figure 8.2.2 Unit Cells in Three Dimensions *These images show (a) a three-dimensional unit cell and (b) the resulting regular three-dimensional lattice.*

The Unit Cell

There are seven fundamentally different kinds of unit cells, which differ in the relative lengths of the edges and the angles between them (Figure 8.2.3). Each unit cell has six sides, and each side is a parallelogram. We focus primarily on the cubic unit cells, in

which all sides have the same length and all angles are 90°, but the concepts that we introduce also apply to substances whose unit cells are not cubic.

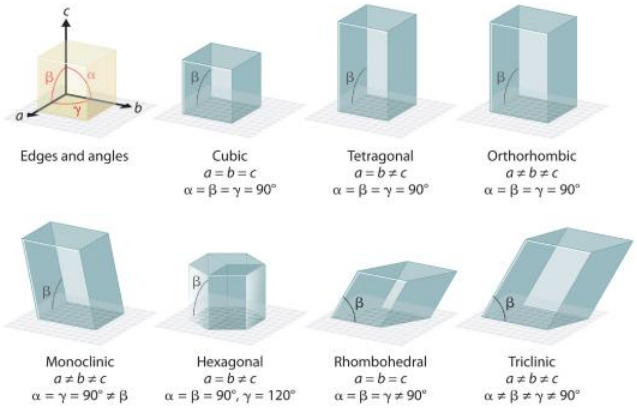


Figure 8.2.3 The General Features of the Seven Basic Unit Cells *The lengths of the edges of the unit cells are indicated by a, b, and c, and the angles are defined as follows: α, the angle between b and c; β, the angle between a and c; and γ, the angle between a and b.*

If the cubic unit cell consists of eight component atoms, molecules, or ions located at the corners of the cube, then it is called simple cubicA cubic unit cell that consists of eight component atoms, molecules, or ions located at the corners of a cube. (part (a) in Figure 8.2.4). If the unit cell also contains an identical component in the center of the cube, then it is body-centered cubic (bcc)A cubic unit cell with eight component atoms, molecules, or ions located at the corners of a cube plus an identical component in the center of the cube. (part (b) in Figure 8.2.4). If there are components in the center of each face in addition to those at the corners of the cube, then the unit cell is face-centered cubic (fcc)A cubic unit cell with eight component atoms, molecules, or ions located at the corners of a cube plus an identical component in the center of each face of the cube. (part (c) in Figure 8.2.4).

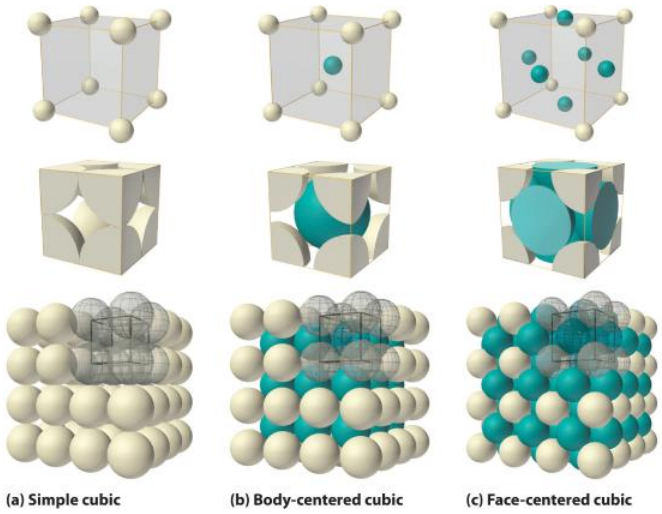


Figure 8.2.4 The Three Kinds of Cubic Unit Cell *For the three kinds of cubic unit cells, simple cubic (a), body-centered cubic (b), and face-centered cubic (c), there are three representations for each: a ball-and-stick model, a space-filling cutaway model that shows the portion of each atom that lies within the unit cell, and an aggregate of several unit cells.*

As indicated in Figure 8.2.4, a solid consists of a large number of unit cells arrayed in three dimensions. Any intensive property of the bulk material, such as its density, must therefore also be related to its unit cell. Because **density** is the mass of substance per unit volume, we can calculate the density of the bulk material from the density of a single unit cell. To do this, we need to know the size of the unit cell (to obtain its volume), the molar mass of its components, and the number of components per unit cell. When we count atoms or ions in a unit cell, however, those lying on a face, an edge, or a corner contribute to more than one unit cell, as shown in Figure 8.2.4. For example, an atom that lies on a face of a unit cell is shared by two adjacent unit cells and is therefore

counted as 1/2 atom per unit cell. Similarly, an atom that lies on the edge of a unit cell is shared by four adjacent unit cells, so it contributes 1/4 atom to each. An atom at a corner of a unit cell is shared by all eight adjacent unit cells and therefore contributes 1/8 atom to each.The statement that atoms lying on an edge or a corner of a unit cell count as 1/4 or 1/8 atom per unit cell, respectively, is true for all unit cells *except* the hexagonal one, in which three unit cells share each vertical edge and six share each corner (Figure 8.2.3), leading to values of 1/3 and 1/6 atom per unit cell, respectively, for atoms in these positions. In contrast, atoms that lie entirely within a unit cell, such as the atom in the center of a body-centered cubic unit cell, belong to only that one unit cell.

Note the Pattern

For all unit cells except hexagonal, atoms on the faces contribute 1/2 atom to each unit cell, atoms on the edges contribute 1/4 atom to each unit cell, and atoms on the corners contribute 1/8 atom to each unit cell.

Example 8.2.1

Metallic gold has a face-centered cubic unit cell (part (c) in Figure 8.2.4). How many Au atoms are in each unit cell?

Given: unit cell

Asked for: number of atoms per unit cell

Strategy:

Using Figure 8.2.4 , identify the positions of the Au atoms in a face-centered cubic unit cell and then determine how much each Au atom contributes to the unit cell. Add the contributions of all the Au atoms to obtain the total number of Au atoms in a unit cell.

Solution:

As shown in Figure 8.2.4, a face-centered cubic unit cell has eight atoms at the corners of the cube and six atoms on the faces. Because atoms on a face are shared by two unit cells, each counts as 1/2 atom per unit cell, giving 6 x 1/2 =3 Au atoms per unit cell. Atoms on a corner are shared by eight unit cells and hence contribute only 1/8 atom per unit cell, giving 8 x 1/8 = 1Au atom per unit cell. The total number of Au atoms in each unit cell is thus 3 + 1 = 4.

Exercise

Metallic iron has a body-centered cubic unit cell (part (b) in Figure 8.2.4). How many Fe atoms are in each unit cell?

Answer: two

Now that we know how to count atoms in unit cells, we can use unit cells to calculate the densities of simple compounds. Note, however, that we are assuming a solid consists of a perfect regular array of unit cells, whereas real substances contain impurities and defects that affect many of their bulk properties, including density. Consequently, the results of our calculations will be close but not necessarily identical to the experimentally obtained values.

Example 8.2.2

Calculate the density of metallic iron, which has a body-centered cubic unit cell (part (b) in Figure 8.2.4) with an edge length of 286.6 pm.

Given: unit cell and edge length

Asked for: density

Strategy:

A. Determine the number of iron atoms per unit cell.
B. Calculate the mass of iron atoms in the unit cell from the molar mass and Avogadro's number. Then divide the mass by the volume of the cell.

Solution:

A We know from Example 1 that each unit cell of metallic iron contains two Fe atoms.

B The molar mass of iron is 55.85 g/mol. Because density is mass per unit volume, we need to calculate the mass of the iron atoms in the unit cell from the molar mass and Avogadro's number and then divide the mass by the volume of the cell (making sure to use

suitable units to get density in g/cm^3):

$$\begin{aligned} mass\ of\ Fe &= \left(2\ \cancel{atoms}\ Fe\right)\left(\frac{1\ \cancel{mol}}{6.022\times10^{23}\ \cancel{atoms}}\right)\left(\frac{55.85\ g}{\cancel{mol}}\right) \\ &= 1.855\times10^{-22}\ g \end{aligned} \qquad \text{(Chapter 8.2.1)}$$

$$\begin{aligned} volume &= \left[(286.6\ pm)\left(\frac{10^{-12}\ \cancel{m}}{\cancel{pm}}\right)\left(\frac{10^{2}\ cm}{\cancel{m}}\right)\right] \\ &= 2.345\times10^{-23}\ cm^3 \end{aligned} \qquad \text{(Chapter 8.2.2)}$$

$$density = \frac{1.855\times10^{-22}\ g}{2.345\times10^{-23}\ cm^3} = 7.880 g/cm^3 \qquad \text{(Chapter 8.2.3)}$$

This result compares well with the tabulated experimental value of 7.874 g/cm^3.

Exercise

Calculate the density of gold, which has a face-centered cubic unit cell (part (c) in Figure 8.2.4) with an edge length of 407.8 pm.

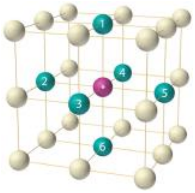
Answer: 19.29 g/cm^3

Packing of Spheres

Our discussion of the three-dimensional structures of solids has considered only substances in which all the components are identical. As we shall see, such substances can be viewed as consisting of identical spheres packed together in space; the way the components are packed together produces the different unit cells. Most of the substances with structures of this type are metals.

Simple Cubic Structure

The arrangement of the atoms in a solid that has a simple cubic unit cell was shown in part (a) in Figure 8.2.4 . Each atom in the lattice has only six nearest neighbors in an octahedral arrangement. Consequently, the simple cubic lattice is an inefficient way to pack atoms together in space: only 52% of the total space is filled by the atoms. The only element that crystallizes in a simple cubic unit cell is polonium. Simple cubic unit cells are, however, common among binary ionic compounds, where each cation is surrounded by six anions and vice versa.



The arrangement of atoms in a simple cubic unit cell. *Each atom in the lattice has six nearest neighbors in an octahedral arrangement.*

Body-Centered Cubic Structure

The body-centered cubic unit cell is a more efficient way to pack spheres together and is much more common among pure elements. Each atom has eight nearest neighbors in the unit cell, and 68% of the volume is occupied by the atoms. As shown in part (b) in Figure 8.2.4, the body-centered cubic structure consists of a single layer of spheres in contact with each other and aligned so that their centers are at the corners of a square; a second layer of spheres occupies the square-shaped “holes” above the spheres in the first layer. The third layer of spheres occupies the square holes formed by the second layer, so that each lies directly above a sphere in the first layer, and so forth. All the alkali metals, barium, radium, and several of the transition metals have body-centered cubic structures.

Hexagonal Close-Packed and Cubic Close-Packed Structures

The most efficient way to pack spheres is the close-packed arrangement, which has two variants. A single layer of close-packed spheres is shown in part (a) in Figure 8.2.5 . Each sphere is surrounded by six others in the same plane to produce a hexagonal

arrangement. Above any set of seven spheres are six depressions arranged in a hexagon. In principle, all six sites are the same, and any one of them could be occupied by an atom in the next layer. Actually, however, these six sites can be divided into two sets, labeled B and C in part (a) in Figure 8.2.5. Sites B and C differ because as soon as we place a sphere at a B position, we can no longer place a sphere in any of the three C positions adjacent to A and vice versa.

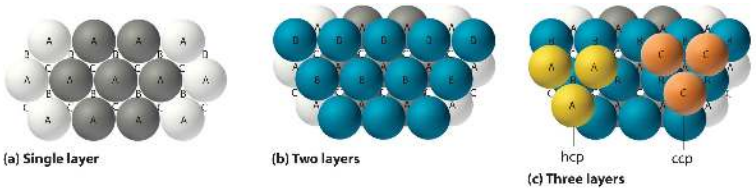


Figure 8.2.5 Close-Packed Layers of Spheres *(a) In this single layer of close-packed spheres, each sphere is surrounded by six others in a hexagonal arrangement. (b) Placing an atom at a B position prohibits placing an atom at any of the adjacent C positions and results in all the atoms in the second layer occupying the B positions. (c) Placing the atoms in the third layer over the atoms at A positions in the first layer gives the hexagonal close-packed structure. Placing the third-layer atoms over the C positions gives the cubic close-packed structure.*

If we place the second layer of spheres at the B positions in part (a) in Figure 8.2.5, we obtain the two-layered structure shown in part (b) in Figure 8.2.5. There are now two alternatives for placing the first atom of the third layer: we can place it directly over one of the atoms in the first layer (an A position) or at one of the C positions, corresponding to the positions that we did *not* use for the atoms in the first or second layers (part (c) in Figure 8.2.5). If we choose the first arrangement and repeat the pattern in succeeding layers, the positions of the atoms alternate from layer to layer in the pattern ABABAB…, resulting in a hexagonal close-packed (hcp) structureOne of two variants of the close-packed arrangement—the most efficient way to pack spheres in a lattice—in which the atomic positions alternate from layer to layer in an ABABAB… pattern. (part (a) in Figure 8.2.6). If we choose the second arrangement and repeat the pattern indefinitely, the positions of the atoms alternate as ABCABC…, giving a cubic close-packed (ccp) structureOne of two variants of the close-packed arrangement—the most efficient way to pack spheres in a lattice—in which the atomic positions alter from layer to layer in an ABCABC… pattern. (part (b) in Figure 8.2.6). Because the ccp structure contains hexagonally packed layers, it does not look particularly cubic. As shown in part (b) in Figure 8.2.6, however, simply rotating the structure reveals its cubic nature, which is identical to a fcc structure. The hcp and ccp structures differ only in the way their layers are stacked. Both structures have an overall packing efficiency of 74%, and in both each atom has 12 nearest neighbors (6 in the same plane plus 3 in each of the planes immediately above and below).

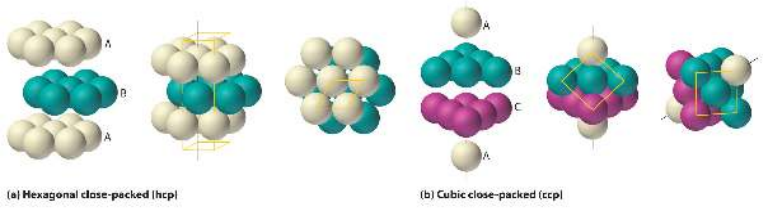


Figure 8.2.6 Close-Packed Structures: hcp and ccp *The illustrations in (a) show an exploded view, a side view, and a top view of the hcp structure. The simple hexagonal unit cell is outlined in the side and top views. Note the similarity to the hexagonal unit cell shown in Figure 8.2.3. The ccp structure in (b) is shown in an exploded view, a side view, and a rotated view. The rotated view emphasizes the fcc nature of the unit cell (outlined). The line that connects the atoms in the first and fourth layers of the ccp structure is the body diagonal of the cube.*

Table 8.2.1 compares the packing efficiency and the number of nearest neighbors for the different cubic and close-packed structures; the number of nearest neighbors is called the coordination numberThe number of nearest neighbors in a solid structure.. Most metals have hcp, ccp, or bcc structures, although several metals exhibit both hcp and ccp structures, depending on temperature and pressure.

Table 8.2.1 Properties of the Common Structures of Metals

Structure	Percentage of Space Occupied by Atoms	Coordination Number
simple cubic	52	6
body-centered cubic	68	8
hexagonal close packed	74	12
cubic close packed (identical to face-centered cubic)	74	12

Summary

The smallest repeating unit of a crystal lattice is the **unit cell**. The **simple cubic** unit cell contains only eight atoms, molecules, or ions at the corners of a cube. A **body-centered cubic (bcc)** unit cell contains one additional component in the center of the cube. A **face-centered cubic (fcc)** unit cell contains a component in the center of each face in addition to those at the corners of the cube. Simple cubic and bcc arrangements fill only 52% and 68% of the available space with atoms, respectively. The **hexagonal close-packed (hcp) structure** has an ABABAB… repeating arrangement, and the **cubic close-packed (ccp) structure** has an ABCABC… repeating pattern; the latter is identical to an fcc lattice. The hcp and ccp arrangements fill 74% of the available space and have a **coordination number** of 12 for each atom in the lattice, the number of nearest neighbors. The simple cubic and bcc lattices have coordination numbers of 6 and 8, respectively.

Key Takeaway

- A crystalline solid can be represented by its unit cell, which is the smallest identical unit that when stacked together produces the characteristic three-dimensional structure.

Conceptual Problems

1. Why is it valid to represent the structure of a crystalline solid by the structure of its unit cell? What are the most important constraints in selecting a unit cell?
2. All unit cell structures have six sides. Can crystals of a solid have more than six sides? Explain your answer.
3. Explain how the intensive properties of a material are reflected in the unit cell. Are all the properties of a bulk material the same as those of its unit cell? Explain your answer.
4. The experimentally measured density of a bulk material is slightly *higher* than expected based on the structure of the pure material. Propose two explanations for this observation.
5. The experimentally determined density of a material is *lower* than expected based on the arrangement of the atoms in the unit cell, the formula mass, and the size of the atoms. What conclusion(s) can you draw about the material?
6. Only one element (polonium) crystallizes with a simple cubic unit cell. Why is polonium the only example of an element with this structure?
7. What is meant by the term *coordination number* in the structure of a solid? How does the coordination number depend on the structure of the metal?
8. Arrange the three types of cubic unit cells in order of increasing packing efficiency. What is the difference in packing efficiency between the hcp structure and the ccp structure?
9. The structures of many metals depend on pressure and temperature. Which structure—bcc or hcp—would be more likely in a given metal at very high pressures? Explain your reasoning.
10. A metal has two crystalline phases. The *transition temperature*, the temperature at which one phase is converted to the other, is 95°C at 1 atm and 135°C at 1000 atm. Sketch a phase diagram for this substance. The metal is known to have either a ccp structure or a simple cubic structure. Label the regions in your diagram appropriately and justify your selection for the structure of each phase.

Numerical Problems

1. Metallic rhodium has an fcc unit cell. How many atoms of rhodium does each unit cell contain?
2. Chromium has a structure with two atoms per unit cell. Is the structure of this metal simple cubic, bcc, fcc, or hcp?
3. The density of nickel is 8.908 g/cm^3. If the metallic radius of nickel is 125 pm, what is the structure of metallic nickel?
4. The density of tungsten is 19.3 g/cm^3. If the metallic radius of tungsten is 139 pm, what is the structure of metallic tungsten?
5. An element has a density of 10.25 g/cm^3 and a metallic radius of 136.3 pm. The metal crystallizes in a bcc lattice. Identify the element.
6. A 21.64 g sample of a nonreactive metal is placed in a flask containing 12.00 mL of water; the final volume is 13.81 mL. If the length of the edge of the unit cell is 387 pm and the metallic radius is 137 pm, determine the packing arrangement and identify the element.
7. A sample of an alkali metal that has a bcc unit cell is found to have a mass of 1.000 g and a volume of 1.0298 cm^3. When the metal reacts with excess water, the reaction produces 539.29 mL of hydrogen gas at 0.980 atm and 23°C. Identify the metal, determine the unit cell dimensions, and give the approximate size of the atom in picometers.
8. A sample of an alkaline earth metal that has a bcc unit cell is found to have a mass 5.000 g and a volume of 1.392 cm^3. Complete reaction with chlorine gas requires 848.3 mL of chlorine gas at 1.050 atm and 25°C. Identify the metal, determine the unit cell dimensions, and give the approximate size of the atom in picometers.
9. Lithium crystallizes in a bcc structure with an edge length of 3.509 Å. Calculate its density. What is the approximate metallic radius of lithium in picometers?
10. Vanadium is used in the manufacture of rust-resistant vanadium steel. It forms bcc crystals with a density of 6.11 g/cm^3 at 18.7°C. What is the length of the edge of the unit cell? What is the approximate metallic radius of the vanadium in picometers?
11. A simple cubic cell contains one metal atom with a metallic radius of 100 pm.
    1. Determine the volume of the atom(s) contained in one unit cell [the volume of a sphere = 4/3 $\pi $ r^3
    2. What is the length of one edge of the unit cell? (Hint: there is no empty space between atoms.)
    3. Calculate the volume of the unit cell.
    4. Determine the packing efficiency for this structure.
    5. Use the steps in Problem 11 to calculate the packing efficiency for a bcc unit cell with a metallic radius of 1.00 Å.

Answers

1. four
2.
3. fcc
4.
5. molybdenum
6.
7. sodium, unit cell edge = 428 pm, r = 185 pm
8.
9. d = 0.5335 g/cm^3, r =151.9 pm
10.
11.

Contributors

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Chapter 8.3: Stucture of Simple Binary Compounds

Learning Objective

- To use the cation:anion radius ratio to predict the structures of simple binary compounds.
- To understand how x-rays are diffracted by crystalline solids.

The structures of most binary compounds can be described using the packing schemes we have just discussed for metals. To do so, we generally focus on the arrangement in space of the largest species present. In ionic solids, this generally means the anions, which are usually arranged in a simple cubic, bcc, fcc, or hcp lattice. Often, however, the anion lattices are not truly “close packed”; because the cations are large enough to prop them apart somewhat, the anions are not actually in contact with one another. In ionic compounds, the cations usually occupy the “holes” between the anions, thus balancing the negative charge. The ratio of cations to anions within a unit cell is required to achieve electrical neutrality and corresponds to the bulk stoichiometry of the compound.

Common Structures of Binary Compounds

As shown in part (a) in Figure 8.3.1, a simple cubic lattice of anions contains only one kind of hole, located in the center of the unit cell. Because this hole is equidistant from all eight atoms at the corners of the unit cell, it is called a cubic holeThe hole located at the center of the simple cubic lattice. The hole is equidistant from all eight atoms or ions at the corners of the unit cell. An atom or ion in a cubic hole has a coordination number of 8.. An atom or ion in a cubic hole therefore has a coordination number of 8. Many ionic compounds with relatively large cations and a 1:1 cation:anion ratio have this structure, which is called the cesium chloride structureThe unit cell for many ionic compounds with relatively large cations and a 1:1 cation:anion ratio. (Figure 8.3.2) because CsCl is a common example.Solid-state chemists tend to describe the structures of new compounds in terms of the structure of a well-known reference compound. Hence you will often read statements such as “Compound X possesses the cesium chloride (or sodium chloride, etc.) structure” to describe the structure of compound X. Notice in Figure 8.3.2 that the $z = 0$ and the $z = 1.0$ planes are always the same. This is because the $z = 1.0$ plane of one unit cell becomes the $z = 0$ plane of the succeeding one. The unit cell in CsCl contains a single Cs^+ ion as well as $8\times1/8$ Cl^-=1 Cl^- ion, for an overall stoichiometry of CsCl. The cesium chloride structure is most common for ionic substances with relatively large cations, in which the ratio of the radius of the cation to the radius of the anion is in the range shown in Table 8.3.1 .

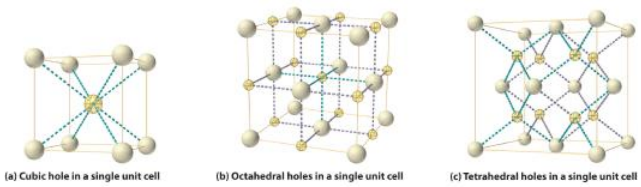


Figure 8.3.1 Holes in Cubic Lattices *The three illustrations show (a) the cubic hole that is in the center of a simple cubic lattice of anions, (b) the locations of the octahedral holes in a face-centered cubic lattice of anions, and (c) the locations of the tetrahedral holes in a face-centered cubic lattice of anions.*

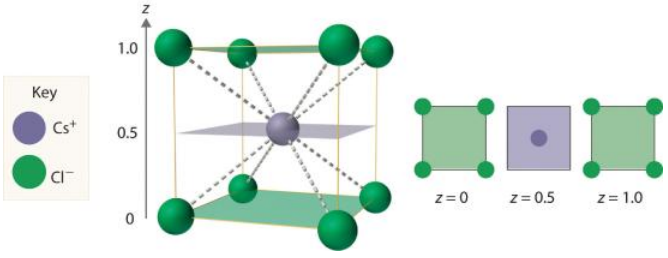


Figure 8.3.2 The Cesium Chloride Structure *The Cs^+ ion occupies the cubic hole in the center of a cube of Cl^- ions. The drawings at the right are horizontal cross-sections through the unit cell at the bottom ($z = 0$) and halfway between the bottom and top ($z = 0.5$). A top cross-section ($z = 1$) is identical to $z = 0$. Such cross-sections often help us visualize the arrangement of atoms or ions in the unit cell more easily.*

Table 8.3.2 Relationship between the Cation:Anion Radius Ratio and the Site Occupied by the Cations

Approximate Range of Cation:Anion Radius Ratio	Hole Occupied by Cation	Cation Coordination Number
0.225–0.414	tetrahedral	4
0.414–0.732	octahedral	6
0.732–1.000	cubic	8

Note the Pattern

Very large cations occupy cubic holes, cations of intermediate size occupy octahedral holes, and small cations occupy tetrahedral holes in the anion lattice.

In contrast, a face-centered cubic (fcc) array of atoms or anions contains two types of holes: octahedral holesOne of two kinds of holes in a face-centered cubic array of atoms or ions (the other is a tetrahedral hole). One octahedral hole is located in the center of the face-centered cubic unit cell, and there is a shared one in the middle of each edge. An atom or ion in an octahedral hole has a coordination number of 6., one in the center of the unit cell plus a shared one in the middle of each edge (part (b) in Figure 8.3.1, and tetrahedral holesOne of two kinds of holes in a face-centered cubic array of atoms or ions (the other is an octahedral hole). Tetrahedral holes are located between an atom at a corner and the three atoms at the centers of the adjacent faces of the face-centered cubic unit cell. An atom or ion in a tetrahedral hole has a coordination number of 4., located between an atom at a corner and the three atoms at the centers of the adjacent faces (part (c) in Figure 8.3.1). As shown in Table 8.3.1, the ratio of the radius of the cation to the radius of the anion is the most important determinant of whether cations occupy the cubic holes in a cubic anion lattice or the octahedral or tetrahedral holes in an fcc lattice of anions. Very large cations occupy cubic holes in a cubic anion lattice, cations of intermediate size tend to occupy the octahedral holes in an fcc anion lattice, and relatively small cations tend to occupy the tetrahedral holes in an fcc anion lattice. In general, larger cations have higher coordination numbers than small cations.

The most common structure based on a fcc lattice is the sodium chloride structureThe solid structure that results when the octahedral holes of an fcc lattice of anions are filled with cations. (Figure 8.3.3), which contains an fcc array of Cl^- ions with Na^+ ions in all the octahedral holes. We can understand the sodium chloride structure by recognizing that filling all the octahedral holes in an fcc lattice of Cl^- ions with Na^+ ions gives a total of 4 Cl^- ions (one on each face gives $6\times1/1=3$ plus one on each corner gives $8\times1/8=1$, for a total of 4) and 4 Na^+ ions (one on each edge gives $11\times1/4=3$ plus one in the middle, for a total of 4). The result is an electrically neutral unit cell and a stoichiometry of NaCl. As shown in Figure 8.3.3, the Na^+ ions in the sodium chloride structure also form an fcc lattice. The sodium chloride structure is favored for substances with two atoms or ions in a 1:1 ratio and in which the ratio of the radius of the cation to the radius of the anion is between 0.414 and 0.732. It is observed in many compounds, including MgO and TiC.

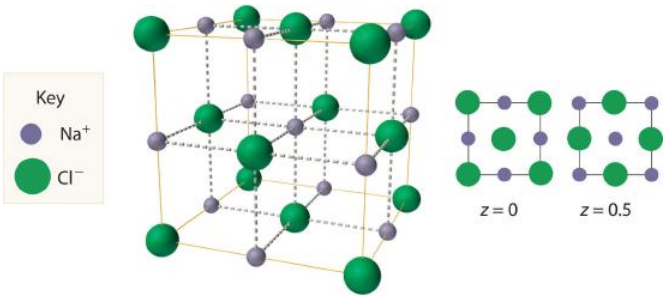


Figure 8.3.3 The Sodium Chloride Structure *In NaCl, the Na^+ ions occupy the octahedral holes in an fcc lattice of Cl^- ions, resulting in an fcc array of Na^+ ions as well.*

The structure shown in Figure 8.3.4 is called the zinc blende structureThe solid structure that results when half of the tetrahedral holes in an fcc lattice of anions are filled with cations with a 1:1 cation:anion ratio and a coordination number of 4., from the common name of the mineral ZnS. It results when the cation in a substance with a 1:1 cation:anion ratio is much smaller than the anion (if the cation:anion radius ratio is less than about 0.414). For example, ZnS contains an fcc lattice of S^{2-} ions, and the cation:anion radius ratio is only about 0.40, so we predict that the cation would occupy either a tetrahedral hole or an octahedral hole. In fact, the relatively small Zn^{2+} cations occupy the tetrahedral holes in the lattice. If all 8 tetrahedral holes in the unit cell

were occupied by Zn^{2+} ions, however, the unit cell would contain 4 S^{2-} and 8 Zn^{2+} ions, giving a formula of Zn_2S and a net charge of +4 per unit cell. Consequently, the Zn^{2+} ions occupy *every other* tetrahedral hole, as shown in Figure 8.3.4, giving a total of 4 Zn^{2+} and 4 S^{2-} ions per unit cell and a formula of ZnS. The zinc blende structure results in a coordination number of 4 for each Zn^{2+} ion and a tetrahedral arrangement of the four S^{2-} ions around each Zn^{2+} ion.

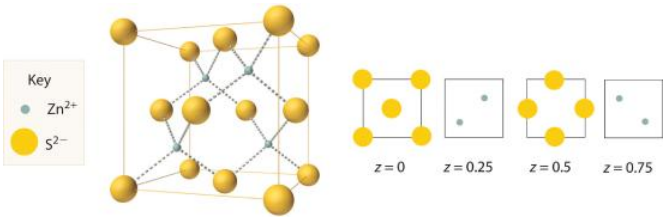


Figure 8.3.4 The Zinc Blende Structure *Zn^{2+} ions occupy every other tetrahedral hole in the fcc array of S^{2-} ions. Each Zn^{2+} ion is surrounded by four S^{2-} ions in a tetrahedral arrangement.*

Example 8.3.1

1. If all the tetrahedral holes in an fcc lattice of anions are occupied by cations, what is the stoichiometry of the resulting compound?
2. Use the ionic radii given in Figure 3.2.7 to identify a plausible oxygen-containing compound with this stoichiometry and structure.

Given: lattice, occupancy of tetrahedral holes, and ionic radii

Asked for: stoichiometry and identity

Strategy:

A Use Figure 8.3.1 to determine the number and location of the tetrahedral holes in an fcc unit cell of anions and place a cation in each.

B Determine the total number of cations and anions in the unit cell; their ratio is the stoichiometry of the compound.

C From the stoichiometry, suggest reasonable charges for the cation and the anion. Use the data in Figure 3.2.7 to identify a cation–anion combination that has a cation:anion radius ratio within a reasonable range.

Solution:

1. **A** Figure 8.3.1 shows that the tetrahedral holes in an fcc unit cell of anions are located entirely within the unit cell, for a total of eight (one near each corner). **B** Because the tetrahedral holes are located entirely within the unit cell, there are eight cations per unit cell. We calculated previously that an fcc unit cell of anions contains a total of four anions per unit cell. The stoichiometry of the compound is therefore M_8Y_4 or, reduced to the smallest whole numbers, M_2Y.
2. **C** The M_2Y stoichiometry is consistent with a lattice composed of M^+ ions and Y^{2-} ions. If the anion is O^{2-} (ionic radius 140 pm), we need a monocation with a radius no larger than about 140 × 0.414 = 58 pm to fit into the tetrahedral holes. According to Figure 3.1.7, none of the monocations has such a small radius; therefore, the most likely possibility is Li^+ at 76 pm. Thus we expect Li_2O to have a structure that is an fcc array of O^{2-} anions with Li^+ cations in all the tetrahedral holes.

Exercise

If only half the octahedral holes in an fcc lattice of anions are filled by cations, what is the stoichiometry of the resulting compound?

Answer: MX_2; an example of such a compound is cadmium chloride ($CdCl_2$), in which the empty cation sites form planes running through the crystal.

We examine only one other structure of the many that are known, the perovskite structureA structure that consists of a bcc array of two metal ions, with one set (M) located at the corners of the cube, and the other set (M′) in the centers of the cube.. *Perovskite* is the generic name for oxides with two different kinds of metal and have the general formula $MM'O_3$, such as $CaTiO_3$. The structure is a body-centered cubic (bcc) array of two metal ions, with one M (Ca in this case) located at the corners of the cube, and the other M′ (in this case Ti) in the centers of the cube. The oxides are in the centers of the square faces (part (a) in Figure 8.3.5). The

stoichiometry predicted from the unit cell shown in part (a) in Figure 8.3.5 agrees with the general formula; each unit cell contains 8×18=1 Ca, 1 Ti, and 6×1/2=3 O atoms. The Ti and Ca atoms have coordination numbers of 6 and 12, respectively. We will return to the perovskite structure when we discuss high-temperature superconductors in Section 8.7.

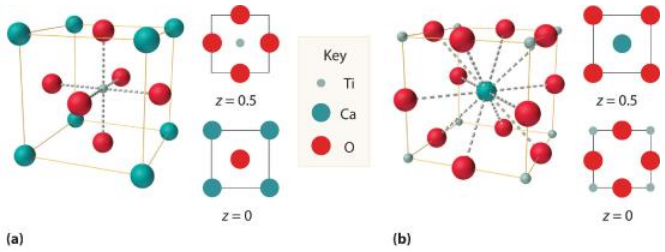


Figure 8.3.5 The Perovskite Structure of $CaTiO_3$ *Two equivalent views are shown: (a) a view with the Ti atom at the center and (b) an alternative view with the Ca atom at the center.*

X-Ray Diffraction

The wavelengths of x-rays are approximately the same magnitude as the distances between atoms in molecules or ions. Consequently, x-rays are a useful tool for obtaining information about the structures of crystalline substances. In a technique called x-ray diffractionAn technique used to obtain information about the structures of crystalline substances by using x-rays., a beam of x-rays is aimed at a sample of a crystalline material, and the x-rays are diffracted by layers of atoms in the crystalline lattice (part (a) in Figure 8.3.6). When the beam strikes photographic film, it produces an x-ray diffraction pattern, which consists of dark spots on a light background (part (b) in Figure 8.3.6). In 1912, the German physicist Max von Laue (1879–1960; Nobel Prize in Physics, 1914) predicted that x-rays should be diffracted by crystals, and his prediction was rapidly confirmed. Within a year, two British physicists, William Henry Bragg (1862–1942) and his son, William Lawrence Bragg (1890–1972), had worked out the mathematics that allows x-ray diffraction to be used to measure interatomic distances in crystals. The Braggs shared the Nobel Prize in Physics in 1915, when the son was only 25 years old. Virtually everything we know today about the detailed structures of solids and molecules in solids is due to the x-ray diffraction technique.

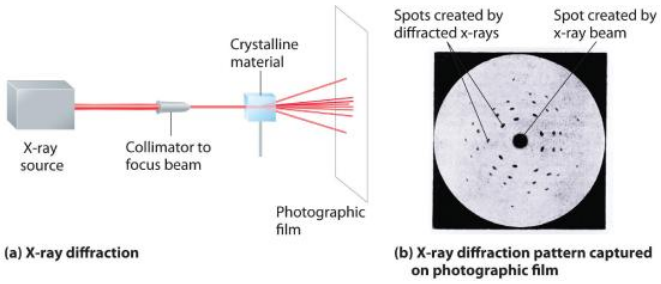


Figure 8.3.6 X-Ray Diffraction *These illustrations show (a) a schematic drawing of x-ray diffraction and (b) the x-ray diffraction pattern of a zinc blende crystalline solid captured on photographic film.*

Recall from Section 2. 2 that two waves that are in phase interfere constructively, thus reinforcing each other and generating a wave with a greater amplitude. In contrast, two waves that are out of phase interfere destructively, effectively canceling each other. When x-rays interact with the components of a crystalline lattice, they are scattered by the electron clouds associated with each atom. As shown in Figure 8.2.4, Figure 8.2.6 , and Figure 8.3.1, the atoms in crystalline solids are typically arranged in planes. Figure 8.3.7 illustrates how two adjacent planes of atoms can scatter x-rays in a way that results in constructive interference. If two x-rays that are initially in phase are diffracted by two planes of atoms separated by a distance d, the lower beam travels the extra distance indicated by the lines BC and CD. The *angle of incidence*, designated as θ, is the angle between the x-ray beam and the planes in the crystal. Because $BC = CD = d \sin\theta$, the extra distance that the lower beam in Figure 8.3.7 must travel compared with the upper beam is $2d \sin\theta$. For these two x-rays to arrive at a detector in phase, the extra distance traveled must be an integral multiple n of the wavelength λ:

$$2d\sin\theta = n\lambda \tag{8.3.1}$$

Equation 8.3.1 is the Bragg equationThe equation that describes the relationship between two x-ray beams diffracted from different planes of atoms: 2d sinθ = nλ. The structures of crystalline substances with both small molecules and ions or very large biological molecules, with molecular masses in excess of 100,000 amu, can now be determined accurately and routinely using x-ray diffraction and the Bragg equation. Example 4 illustrates how to use the Bragg equation to calculate the distance between planes of atoms in crystals.

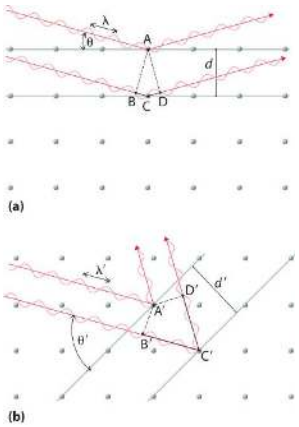


Figure 8.3.7 The Reflection of X-Rays from Two Adjacent Planes of Atoms Can Result in Constructive Interference of the X-Rays *(a) The x-ray diffracted by the lower layer of atoms must travel a distance that is longer by 2d sin θ than the distance traveled by the x-ray diffracted by the upper layer of atoms. Only if this distance (BC plus CD) equals an integral number of wavelengths of the x-rays (i.e., only if λ = 2d sin θ) will the x-rays arrive at the detector in phase. (b) In a solid, many different sets of planes of atoms can diffract x-rays. Each has a different interplanar distance and therefore diffracts the x-rays at a different angle θ, which produces a characteristic pattern of spots.*

Example 8.3.2

X-rays from a copper x-ray tube (λ = 1.54062 Å or 154.062 pm)In x-ray diffraction, the angstrom (Å) is generally used as the unit of wavelength. are diffracted at an angle of 10.89° from a sample of crystalline gold. Assuming that n = 1, what is the distance between the planes that gives rise to this reflection? Give your answer in angstroms and picometers to four significant figures.

Given: wavelength, diffraction angle, and number of wavelengths

Asked for: distance between planes

Strategy:

Substitute the given values into the Bragg equation and solve to obtain the distance between planes.

Solution:

We are given n, θ, and λ and asked to solve for d, so this is a straightforward application of the Bragg equation. For an answer in angstroms, we do not even have to convert units. Solving the Bragg equation for d gives

$$d = \frac{n\lambda}{2\ sin\theta} \qquad \text{(Chapter 8.3.1)}$$

and substituting values gives

$$d = \frac{1 \times 1.54062\ \mathring{A}}{2\ sin\ 10.89^{\circ}} = 4.077\ \mathring{A} = 407.4\ pm \qquad \text{(Chapter 8.3.2)}$$

This value corresponds to the edge length of the fcc unit cell of elemental gold.

Exercise

X-rays from a molybdenum x-ray tube (λ = 0.709300 Å) are diffracted at an angle of 7.11° from a sample of metallic iron. Assuming that n = 1, what is the distance between the planes that gives rise to this reflection? Give your answer in angstroms and picometers to three significant figures.

Answer: 2.87 Å or 287 pm (corresponding to the edge length of the bcc unit cell of elemental iron)

Summary

The structures of most binary compounds are dictated by the packing arrangement of the largest species present (the anions), with the smaller species (the cations) occupying appropriately sized holes in the anion lattice. A simple cubic lattice of anions contains a single **cubic hole** in the center of the unit cell. Placing a cation in the cubic hole results in the **cesium chloride structure**, with a 1:1 cation:anion ratio and a coordination number of 8 for both the cation and the anion. An fcc array of atoms or ions contains both **octahedral holes** and **tetrahedral holes**. If the octahedral holes in an fcc lattice of anions are filled with cations, the result is a **sodium chloride structure**. It also has a 1:1 cation:anion ratio, and each ion has a coordination number of 6. Occupation of half the tetrahedral holes by cations results in the **zinc blende structure**, with a 1:1 cation:anion ratio and a coordination number of 4 for the cations. More complex structures are possible if there are more than two kinds of atoms in a solid. One example is the **perovskite structure**, in which the two metal ions form an alternating bcc array with the anions in the centers of the square faces. Because the wavelength of x-ray radiation is comparable to the interatomic distances in most solids, **x-ray diffraction** can be used to provide information about the structures of crystalline solids. X-rays diffracted from different planes of atoms in a solid reinforce one another if they are in phase, which occurs only if the extra distance they travel corresponds to an integral number of wavelengths. This relationship is described by the **Bragg equation**: $2d \sin \theta = n\lambda$.

Key Takeaway

- The ratio of cations to anions within a unit cell produces electrical neutrality and corresponds to the bulk stoichiometry of a compound, the structure of which can be determined using x-ray diffraction.

Key Equation

Bragg equation

Equation 8.3.1:

$$2dsin\theta = n\lambda \qquad \text{(Chapter 8.3.3)}$$

Conceptual Problems

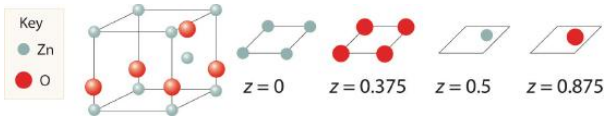
1. Using circles or spheres, sketch a unit cell containing an octahedral hole. Which of the basic structural types possess octahedral holes? If an ion were placed in an octahedral hole, what would its coordination number be?
2. Using circles or spheres, sketch a unit cell containing a tetrahedral hole. Which of the basic structural types possess tetrahedral holes? If an ion were placed in a tetrahedral hole, what would its coordination number be?
3. How many octahedral holes are there in each unit cell of the sodium chloride structure? Potassium fluoride contains an fcc lattice of F^- ions that is identical to the arrangement of Cl^- ions in the sodium chloride structure. Do you expect K^+ ions to occupy the tetrahedral or octahedral holes in the fcc lattice of F^- ions?
4. The unit cell of cesium chloride consists of a cubic array of chloride ions with a cesium ion in the center. Why then is cesium chloride described as having a simple cubic structure rather than a bcc structure? The unit cell of iron also consists of a cubic array of iron atoms with an iron atom in the center of the cube. Is this a bcc or a simple cubic unit cell? Explain your answer.
5. Why are x-rays used to determine the structure of crystalline materials? Could gamma rays also be used to determine crystalline structures? Why or why not?
6. X-rays are higher in energy than most other forms of electromagnetic radiation, including visible light. Why can't you use visible light to determine the structure of a crystalline material?
7. When x-rays interact with the atoms in a crystal lattice, what relationship between the distances between planes of atoms in the crystal structure and the wavelength of the x-rays results in the scattered x-rays being exactly in phase with one another? What difference in structure between amorphous materials and crystalline materials makes it difficult to determine the structures of amorphous materials by x-ray diffraction?
8. It is possible to use different x-ray sources to generate x-rays with different wavelengths. Use the Bragg equation to predict how the diffraction angle would change if a molybdenum x-ray source (x-ray wavelength = 70.93 pm) were used instead of a copper

source (x-ray wavelength = 154.1 pm).

9. Based on the Bragg equation, if crystal A has larger spacing in its diffraction pattern than crystal B, what conclusion can you draw about the spacing between layers of atoms in A compared with B?

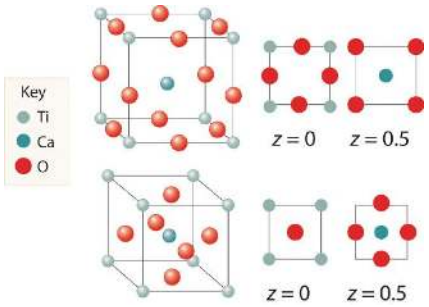
Numerical Problems

1. Thallium bromide crystallizes in the cesium chloride structure. This bcc structure contains a Tl^+ ion in the center of the cube with Br^- ions at the corners. Sketch an alternative unit cell for this compound.
2. Potassium fluoride has a lattice identical to that of sodium chloride. The potassium ions occupy octahedral holes in an fcc lattice of fluoride ions. Propose an alternative unit cell that can also represent the structure of KF.
3. Calcium fluoride is used to fluoridate drinking water to promote dental health. Crystalline CaF_2 (d = 3.1805 g/cm^3) has a structure in which calcium ions are located at each corner and the middle of each edge of the unit cell, which contains eight fluoride ions per unit cell. The length of the edge of this unit cell is 5.463 Å. Use this information to determine Avogadro's number.
4. Zinc and oxygen form a compound that is used as both a semiconductor and a paint pigment. This compound has the following structure:



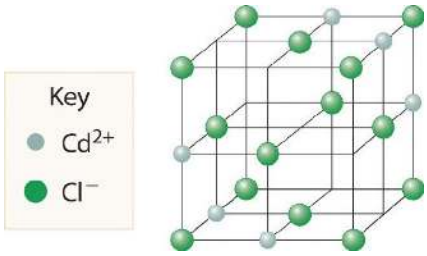
What is the empirical formula of this compound?

5. Here are two representations of the perovskite structure:



Are they identical? What is the empirical formula corresponding to each representation?

6. The salt MX_2 has a cubic close-packed (ccp) structure in which all the tetrahedral holes are filled by anions. What is the coordination number of M? of X?
7. A compound has a structure based on simple cubic packing of the anions, and the cations occupy half of the cubic holes. What is the empirical formula of this compound? What is the coordination number of the cation?
8. Barium and fluoride form a compound that crystallizes in the fluorite structure, in which the fluoride ions occupy all the tetrahedral holes in a ccp array of barium ions. This particular compound is used in embalming fluid. What is its empirical formula?
9. Cadmium chloride is used in paints as a yellow pigment. Is the following structure consistent with an empirical formula of $CdCl_2$? If not, what is the empirical formula of the structure shown?



10. Use the information in the following table to decide whether the cation will occupy a tetrahedral hole, an octahedral hole, or a cubic hole in each case.

Cation Radius (pm)	Anion Radius (pm)
78.0	132
165	133
81	174

11. Calculate the angle of diffraction when x-rays from a copper tube (λ = 154 pm) are diffracted by planes of atoms parallel to the faces of the cubic unit cell for Mg (260 pm), Zn (247 pm), and Ni (216 pm). The length on one edge of the unit cell is given in parentheses; assume first-order diffraction (n = 1).

12. If x-rays from a copper target (λ = 154 pm) are scattered at an angle of 17.23° by a sample of Mg, what is the distance (in picometers) between the planes responsible for this diffraction? How does this distance compare with that in a sample of Ni for which θ = 20.88°?
3. d = 3.1805 g/cm^3; Avogadro's number = 6.023 × 10^{23} mol^{-1}

Answers

2.
4.
1.
5. Both have same stoichiometry, $CaTiO_3$
6.
7. Stoichiometry is MX_2; coordination number of cations is 8
8.
9. No, the structure shown has an empirical formula of Cd_3Cl_8.
10.
11. Mg: 17.2°, Zn: 18.2°, Ni: 20.9°
12.

Contributors

- Anonymous

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Chapter 8.4: Crystal Defects

Learning Objective

- To understand the origin and nature of defects in crystals.

The crystal lattices we have described represent an idealized, simplified system that can be used to understand many of the important principles governing the behavior of solids. In contrast, real crystals contain large numbers of defectsErrors in an idealized crystal lattice. (typically more than 10^4 per milligram), ranging from variable amounts of impurities to missing or misplaced atoms or ions. These defects occur for three main reasons:

1. It is impossible to obtain any substance in 100% pure form. Some impurities are always present.
2. Even if a substance were 100% pure, forming a perfect crystal would require cooling the liquid phase infinitely slowly to allow all atoms, ions, or molecules to find their proper positions. Cooling at more realistic rates usually results in one or more components being trapped in the “wrong” place in a lattice or in areas where two lattices that grew separately intersect.
3. Applying an external stress to a crystal, such as a hammer blow, can cause microscopic regions of the lattice to move with respect to the rest, thus resulting in imperfect alignment.

In this section, we discuss how defects determine some of the properties of solids. We begin with solids that consist of neutral atoms, specifically metals, and then turn to ionic compounds.

Defects in Metals

Metals can have various types of defects. A point defectA defect in a crystal that affects a single point in the lattice. is any defect that involves only a single particle (a lattice point) or sometimes a very small set of points. A line defectA defect in a crystal that affects a row of points in the lattice. is restricted to a row of lattice points, and a plane defectA defect in a crystal that affects a plane of points in the lattice. involves an entire plane of lattice points in a crystal. A vacancyA point defect that consists of a single atom missing from a site in a crystal. occurs where an atom is missing from the normal crystalline array; it constitutes a tiny void in the middle of a solid (Figure 8.4.1). We focus primarily on point and plane defects in our discussion because they are encountered most frequently.

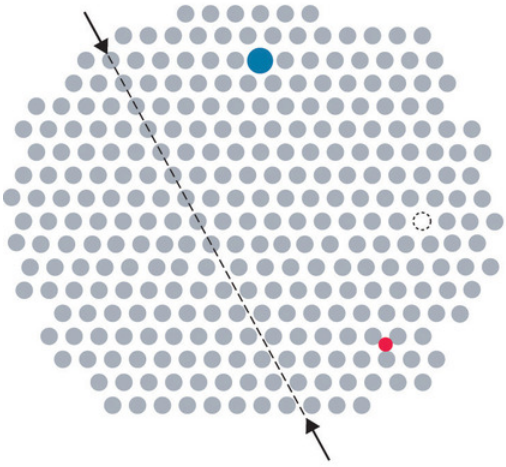


Figure 8.4.1Common Defects in Crystals *In this two-dimensional representation of a crystal lattice containing substitutional and interstitial impurities, vacancies, and line defects, a dashed line and arrows indicate the position of the line defect.*

Impurities

Impurities can be classified as interstitial or substitutional. An interstitial impurityA point defect that results when an impurity atom occupies an octahedral hole or a tetrahedral hole in the lattice between atoms. is usually a smaller atom (typically about 45% smaller than the host) that can fit into the octahedral or tetrahedral holes in the metal lattice (Figure 8.4.1). Steels consist of iron

with carbon atoms added as interstitial impurities (Table 8.4.1). The inclusion of one or more transition metals or semimetals can improve the corrosion resistance of steel.

Table 8.4.1Compositions, Properties, and Uses of Some Types of Steel

Name of Steel	Typical Composition*	Properties	Applications
low-carbon	<0.15% C	soft and ductile	wire
mild carbon	0.15%–0.25% C	malleable and ductile	cables, chains, and nails
high-carbon	0.60%–1.5% C	hard and brittle	knives, cutting tools, drill bits, and springs
stainless	15%–20% Cr, 1%–5% Mn, 5%–10% Ni, 1%–3% Si, 1% C, 0.05% P	corrosion resistant	cutlery, instruments, and marine fittings
invar	36% Ni	low coefficient of thermal expansion	measuring tapes and meter sticks
manganese	10%–20% Mn	hard and wear resistant	armor plate, safes, and rails
high-speed	14%–20% W	retains hardness at high temperatures	high-speed cutting tools
silicon	1%–5% Si	hard, strong, and highly magnetic	magnets in electric motors and transformers

*In addition to enough iron to bring the total percentage up to 100%, most steels contain small amounts of carbon (0.5%–1.5%) and manganese (<2%).

In contrast, a substitutional impurityA point defect that results when an impurity atom occupies a normal lattice site. is a different atom of about the same size that simply replaces one of the atoms that compose the host lattice (Figure 8.4.1 \). Substitutional impurities are usually chemically similar to the substance that constitutes the bulk of the sample, and they generally have atomic radii that are within about 15% of the radius of the host. For example, strontium and calcium are chemically similar and have similar radii, and as a result, strontium is a common impurity in crystalline calcium, with the Sr atoms randomly occupying sites normally occupied by Ca.

Note the Pattern

Interstitial impurities are smaller atoms than the host atom, whereas substitutional impurities are usually chemically similar and are similar in size to the host atom.

Dislocations, Deformations, and Work Hardening

Inserting an extra plane of atoms into a crystal lattice produces an edge dislocationA crystal defect that results from the insertion of an extra plane of atoms into part of the crystal lattice.. A familiar example of an edge dislocation occurs when an ear of corn contains an extra row of kernels between the other rows (Figure 8.4.2). An edge dislocation in a crystal causes the planes of atoms in the lattice to deform where the extra plane of atoms begins (Figure 8.4.2). The edge dislocation frequently determines whether the entire solid will deform and fail under stress.

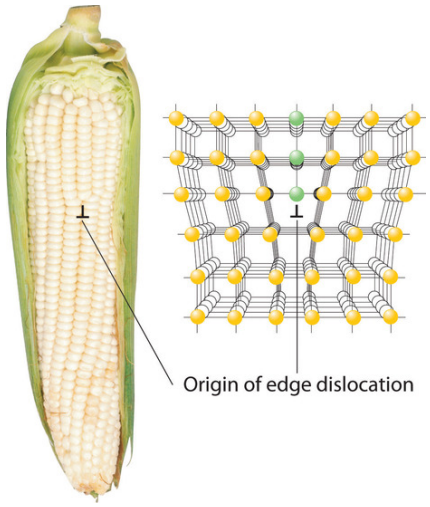


Figure 8.4.2 Edge Dislocations *Shown are two examples of edge dislocations: (a) an edge dislocation in an ear of corn and (b) a three-dimensional representation of an edge dislocation in a solid, illustrating how an edge dislocation can be viewed as a simple line defect arising from the insertion of an extra set of atoms into the lattice. In both cases, the origin of the edge dislocation is indicated by the symbol ⊥*

DeformationA distortion that occurs when a dislocation moves through a crystal. occurs when a dislocation moves through a crystal. To illustrate the process, suppose you have a heavy rug that is lying a few inches off-center on a nonskid pad. To move the rug to its proper place, you could pick up one end and pull it. Because of the large area of contact between the rug and the pad, however, they will probably move as a unit. Alternatively, you could pick up the rug and try to set it back down exactly where you want it, but that requires a great deal of effort (and probably at least one extra person). An easier solution is to create a small wrinkle at one end of the rug (an edge dislocation) and gradually push the wrinkle across, resulting in a net movement of the rug as a whole (part (a) in Figure 8.4.3). Moving the wrinkle requires only a small amount of energy because only a small part of the rug is actually moving at any one time. Similarly, in a solid, the contacts between layers are broken in only one place at a time, which facilitates the deformation process.

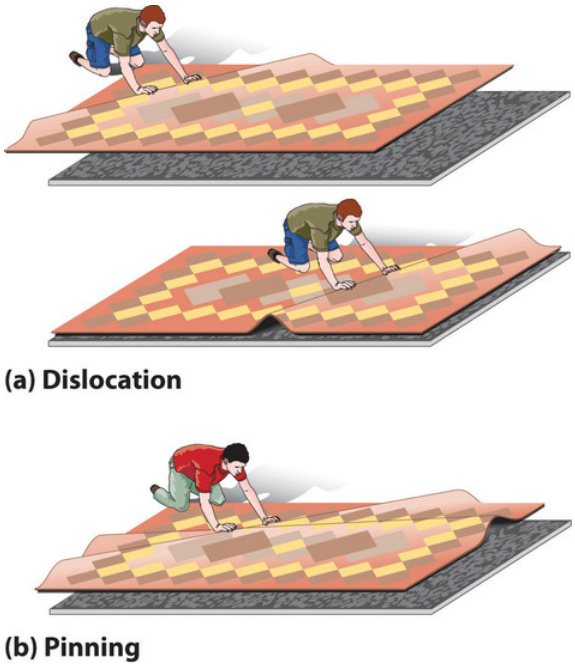


Figure 8.4.3 The Role of Dislocation in the Motion of One Planar Object across Another *(a) Pushing a wrinkle across the rug results in a net movement of the rug with relatively little expenditure of energy because at any given time only a very small amount*

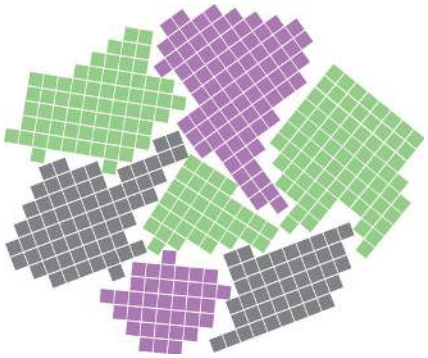
of the rug is not in contact with the floor. (b) A second intersecting wrinkle prevents movement of the first by "pinning" it.

If the rug we have just described has a *second* wrinkle at a different angle, however, it is very difficult to move the first one where the two wrinkles intersect (part (b) in Figure 8.4.3); this process is called pinningA process that increases the mechanical strength of a material by introducing multiple defects into a material so that the presence of one defect prevents the motion of another.. Similarly, intersecting dislocations in a solid prevent them from moving, thereby increasing the mechanical strength of the material. In fact, one of the major goals of materials science is to find ways to pin dislocations to strengthen or harden a material.

Pinning can also be achieved by introducing selected impurities in appropriate amounts. Substitutional impurities that are a mismatch in size to the host prevent dislocations from migrating smoothly along a plane. Generally, the higher the concentration of impurities, the more effectively they block migration, and the stronger the material. For example, bronze, which contains about 20% tin and 80% copper by mass, produces a much harder and sharper weapon than does either pure tin or pure copper. Similarly, pure gold is too soft to make durable jewelry, so most gold jewelry contains 75% (18 carat) or 58% (14 carat) gold by mass, with the remainder consisting of copper, silver, or both.

If an interstitial impurity forms polar covalent bonds to the host atoms, the layers are prevented from sliding past one another, even when only a small amount of the impurity is present. For example, because iron forms polar covalent bonds to carbon, the strongest steels need to contain only about 1% carbon by mass to substantially increase their strength (Table 8.4.1).

Most materials are polycrystalline, which means they consist of many microscopic individual crystals called *grains* that are randomly oriented with respect to one another. The place where two grains intersect is called a grain boundaryThe place where two grains in a solid intersect.. The movement of a deformation through a solid tends to stop at a grain boundary. Consequently, controlling the grain size in solids is critical for obtaining desirable mechanical properties; fine-grained materials are usually much stronger than coarse-grained ones.



Grain boundaries. *As a polycrystalline material solidifies, grains with irregular shapes form. The interfaces between grains constitute grain boundaries. (Squares represent unit cells within grains.)*

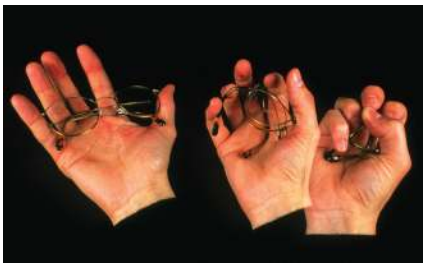
Work hardeningThe practice of introducing a dense network of dislocations throughout a solid, making it very tough and hard. is the introduction of a dense network of dislocations throughout a solid, which makes it very tough and hard. If all the defects in a single 1 cm^3 sample of a work-hardened material were laid end to end, their total length could be 10^6 km! The legendary blades of the Japanese and Moorish swordsmiths owed much of their strength to repeated work hardening of the steel. As the density of defects increases, however, the metal becomes more brittle (less malleable). For example, bending a paper clip back and forth several times increases its brittleness from work hardening and causes the wire to break.

Memory Metal

The compound NiTi, popularly known as "memory metal" or nitinol (*ni*ckel–*ti*tanium *N*aval *O*rdinance *L*aboratory, after the site where it was first prepared), illustrates the importance of deformations. If a straight piece of NiTi wire is wound into a spiral, it will remain in the spiral shape indefinitely, *unless* it is warmed to 50°C–60°C, at which point it will spontaneously straighten out again. The chemistry behind the temperature-induced change in shape is moderately complex, but for our purposes it is sufficient to know that NiTi can exist in two different solid phases.

The high-temperature phase has the cubic cesium chloride structure, in which a Ti atom is embedded in the center of a cube of Ni atoms (or vice versa). The low-temperature phase has a related but kinked structure, in which one of the angles of the unit cell is no

longer 90°. Bending an object made of the low-temperature (kinked) phase creates defects that change the pattern of kinks within the structure. If the object is heated to a temperature greater than about 50°C, the material undergoes a transition to the cubic high-temperature phase, causing the object to return to its original shape. The shape of the object above 50°C is controlled by a complex set of defects and dislocations that can be relaxed or changed only by the thermal motion of the atoms.



Memory metal. *Flexon is a fatigue-resistant alloy of Ti and Ni that is used as a frame for glasses because of its durability and corrosion resistance.*

Memory metal has many other practical applications, such as its use in temperature-sensitive springs that open and close valves in the automatic transmissions of cars. Because NiTi can also undergo pressure- or tension-induced phase transitions, it is used to make wires for straightening teeth in orthodontic braces and in surgical staples that change shape at body temperature to hold broken bones together

Another flexible, fatigue-resistant alloy composed of titanium and nickel is Flexon. Originally discovered by metallurgists who were creating titanium-based alloys for use in missile heat shields, Flexon is now used as a durable, corrosion-resistant frame for glasses, among other uses.

Example 8.4.1

Because steels with at least 4% chromium are much more corrosion resistant than iron, they are collectively sold as “stainless steel.” Referring to the composition of stainless steel in Table 8.4.1 and, if needed, the atomic radii in Figure 3.1.7, predict which type of impurity is represented by each element in stainless steel, excluding iron, that are present in at least 0.05% by mass.

Given: composition of stainless steel and atomic radii

Asked for: type of impurity

Strategy:

Using the data in Table 8.4.1 and the atomic radii in Figure 3.1.7, determine whether the impurities listed are similar in size to an iron atom. Then determine whether each impurity is chemically similar to Fe. If similar in both size and chemistry, the impurity is likely to be a substitutional impurity. If not, it is likely to be an interstitial impurity.

Solution:

According to Table 8.4.1 stainless steel typically contains about 1% carbon, 1%–5% manganese, 0.05% phosphorus, 1%–3% silicon, 5%–10% nickel, and 15%–20% chromium. The three transition elements (Mn, Ni, and Cr) lie near Fe in the periodic table, so they should be similar to Fe in chemical properties and atomic size (atomic radius = 125 pm). Hence they almost certainly will substitute for iron in the Fe lattice. Carbon is a second-period element that is nonmetallic and much smaller (atomic radius = 77 pm) than iron. Carbon will therefore tend to occupy interstitial sites in the iron lattice. Phosphorus and silicon are chemically quite different from iron (phosphorus is a nonmetal, and silicon is a semimetal), even though they are similar in size (atomic radii of 106 and 111 pm, respectively). Thus they are unlikely to be substitutional impurities in the iron lattice or fit into interstitial sites, but they could aggregate into layers that would constitute plane defects.

Exercise

Consider nitrogen, vanadium, zirconium, and uranium impurities in a sample of titanium metal. Which is most likely to form an interstitial impurity? a substitutional impurity?

Answer: nitrogen; vanadium

Defects in Ionic and Molecular Crystals

All the defects and impurities described for metals are seen in ionic and molecular compounds as well. Because ionic compounds contain both cations and anions rather than only neutral atoms, however, they exhibit additional types of defects that are not possible in metals.

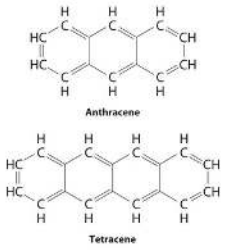
The most straightforward variant is a substitutional impurity in which a cation or an anion is replaced by another of similar charge and size. For example, Br^- can substitute for Cl^-, so tiny amounts of Br^- are usually present in a chloride salt such as $CaCl_2$ or $BaCl_2$. If the substitutional impurity and the host have *different* charges, however, the situation becomes more complicated. Suppose, for example, that Sr^{2+} (ionic radius = 118 pm) substitutes for K^+ (ionic radius = 138 pm) in KCl. Because the ions are approximately the same size, Sr^{2+} should fit nicely into the face-centered cubic (fcc) lattice of KCl. The difference in charge, however, must somehow be compensated for so that electrical neutrality is preserved. The simplest way is for a second K^+ ion to be lost elsewhere in the crystal, producing a vacancy. Thus substitution of K^+ by Sr^{2+} in KCl results in the introduction of *two* defects: a site in which an Sr^{2+} ion occupies a K^+ position and a vacant cation site. Substitutional impurities whose charges do not match the host's are often introduced intentionally to produce compounds with specific properties.

Virtually all the colored gems used in jewelry are due to substitutional impurities in simple oxide structures. For example, α-Al_2O_3, a hard white solid called *corundum* that is used as an abrasive in fine sandpaper, is the primary component, or *matrix*, of a wide variety of gems. Because many trivalent transition metal ions have ionic radii only a little larger than the radius of Al^{3+} (ionic radius = 53.5 pm), they can replace Al^{3+} in the octahedral holes of the oxide lattice. Substituting small amounts of Cr^{3+} ions (ionic radius = 75 pm) for Al^{3+} gives the deep red color of ruby, and a mixture of impurities (Fe^{2+}, Fe^{3+}, and Ti^{4+}) gives the deep blue of sapphire. True amethyst contains small amounts of Fe^{3+} in an SiO_2 (quartz) matrix. The same metal ion substituted into different mineral lattices can produce very different colors. For example, Fe^{3+} ions are responsible for the yellow color of topaz and the violet color of amethyst. The distinct environments cause differences in *d* orbital energies, enabling the Fe^{3+} ions to absorb light of different frequencies.



The same cation in different environments. *An Fe^{3+} substitutional impurity produces substances with strikingly different colors.*

Substitutional impurities are also observed in *molecular* crystals if the structure of the impurity is similar to the host, and they can have major effects on the properties of the crystal. Pure anthracene, for example, is an electrical conductor, but the transfer of electrons through the molecule is much slower if the anthracene crystal contains even very small amounts of tetracene despite their strong structural similarities.



If a cation or an anion is simply missing, leaving a vacant site in an ionic crystal, then for the crystal to be electrically neutral, there must be a corresponding vacancy of the ion with the opposite charge somewhere in the crystal. In compounds such as KCl, the

charges are equal but opposite, so one anion vacancy is sufficient to compensate for each cation vacancy. In compounds such as $CaCl_2$, however, *two* Cl^- anion sites must be vacant to compensate for each missing Ca^{2+} cation. These pairs (or sets) of vacancies are called Schottky defectsA coupled pair of vacancies—one cation and one anion—that maintains the electrical neutrality of an ionic solid. and are particularly common in simple alkali metal halides such as KCl (part (a) in Figure 8.4.4). Many microwave diodes, which are devices that allow a current to flow in a single direction, are composed of materials with Schottky defects.

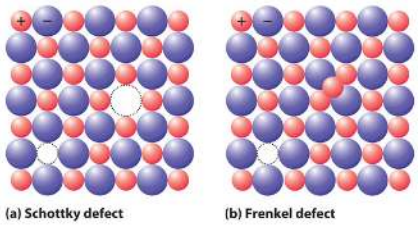


Figure 8.4.4 The Two Most Common Defects in Ionic Solids *(a) A Schottky defect in KCl shows the missing cation/anion pair. (b) A Frenkel defect in AgI shows a misplaced Ag^+ cation.*

Occasionally one of the ions in an ionic lattice is simply in the wrong position. An example of this phenomenon, called a Frenkel defectA defect in an ionic lattice that occurs when one of the ions is in the wrong position., is a cation that occupies a tetrahedral hole rather than an octahedral hole in the anion lattice (part (b) in Figure 8.4.4). Frenkel defects are most common in salts that have a large anion and a relatively small cation. To preserve electrical neutrality, one of the normal cation sites, usually octahedral, must be vacant.

Frenkel defects are particularly common in the silver halides AgCl, AgBr, and AgI, which combine a rather small cation (Ag^+, ionic radius = 115 pm) with large, polarizable anions. Certain more complex salts with a second cation in addition to Ag^+ and Br^- or I^- have so many Ag^+ ions in tetrahedral holes that they are good electrical conductors in the solid state; hence they are called solid electrolytesA solid material with a very high electrical conductivity.. (As you will learn in Chapter 12, most ionic compounds do not conduct electricity in the solid state, although they do conduct electricity when molten or dissolved in a solvent that separates the ions, allowing them to migrate in response to an applied electric field.) In response to an applied voltage, the cations in solid electrolytes can diffuse rapidly through the lattice via octahedral holes, creating Frenkel defects as the cations migrate. Sodium–sulfur batteries use a solid Al_2O_3 electrolyte with small amounts of solid Na_2O. Because the electrolyte cannot leak, it cannot cause corrosion, which gives a battery that uses a solid electrolyte a significant advantage over one with a liquid electrolyte.

Example 8.4.2

In a sample of NaCl, one of every 10,000 sites normally occupied by Na^+ is occupied instead by Ca^{2+}. Assuming that all of the Cl^- sites are fully occupied, what is the stoichiometry of the sample?

Given: ionic solid and number and type of defect

Asked for: stoichiometry

Strategy:

A Identify the unit cell of the host compound. Compute the stoichiometry if 0.01% of the Na^+ sites are occupied by Ca^{2+}. If the overall charge is greater than 0, then the stoichiometry must be incorrect.

B If incorrect, adjust the stoichiometry of the Na^+ ion to compensate for the additional charge.

Solution:

A Pure NaCl has a 1:1 ratio of Na^+ and Cl^- ions arranged in an fcc lattice (the sodium chloride structure). If all the anion sites are occupied by Cl^-, the negative charge is −1.00 per formula unit. If 0.01% of the Na^+ sites are occupied by Ca^{2+} ions, the cation stoichiometry is $Na_{0.99}Ca_{0.01}$. This results in a positive charge of (0.99)(+1) + (0.01)(+2) = +1.01 per formula unit, for a net charge in the crystal of +1.01 + (−1.00) = +0.01 per formula unit. Because the overall charge is greater than 0, this stoichiometry must be incorrect.

B The most plausible way for the solid to adjust its composition to become electrically neutral is for some of the Na^+ sites to be vacant. If one Na^+ site is vacant for each site that has a Ca^{2+} cation, then the cation stoichiometry is $Na_{0.98}Ca_{0.01}$. This results in a

positive charge of (0.98)(+1) + (0.01)(+2) = +1.00 per formula unit, which exactly neutralizes the negative charge. The stoichiometry of the solid is thus $Na_{0.98}Ca_{0.01}Cl_{1.00}$.

Exercise

In a sample of MgO that has the sodium chloride structure, 0.02% of the Mg^{2+} ions are replaced by Na^{+} ions. Assuming that all of the cation sites are fully occupied, what is the stoichiometry of the sample?

Answer: If the formula of the compound is $Mg_{0.98}Na_{0.02}O_{1-x}$, then x must equal 0.01 to preserve electrical neutrality. The formula is thus $Mg_{0.98}Na_{0.02}O_{0.99}$.

Nonstoichiometric Compounds

The law of multiple proportions, states that chemical compounds contain fixed integral ratios of atoms. In fact, nonstoichiometric compoundsA solid that has intrinsically variable stoichiometries without affecting the fundamental structure of the crystal. contain large numbers of defects, usually vacancies, which give rise to stoichiometries that can depart significantly from simple integral ratios *without affecting the fundamental structure of the crystal*. Nonstoichiometric compounds frequently consist of transition metals, lanthanides, and actinides, with polarizable anions such as oxide (O^{2-}) and sulfide (S^{2-}). Some common examples are listed in Table 8.4.1, along with their basic structure type. These compounds are nonstoichiometric because their constituent metals can exist in multiple oxidation states in the solid, which in combination preserve electrical neutrality.

Table 12.4.1 Some Non-stoichiometric Compounds

Compound	Observed Range of x
Oxides*	
Fe_xO	0.85–0.95
Ni_xO	0.97–1.00
TiO_x	0.75–1.45
VO_x	0.9–1.20
NbO_x	0.9–1.04
Sulfides	
Cu_xS	1.77–2.0
Fe_xS	0.80–0.99
ZrS_x	0.9–1.0
*All the oxides listed have the sodium chloride structure.	

One example is iron(II) oxide (ferrous oxide), which produces the black color in clays and is used as an abrasive. Its stoichiometry is *not* FeO because it always contains less than 1.00 Fe per O^{2-} (typically 0.90–0.95). This is possible because Fe can exist in both the +2 and +3 oxidation states. Thus the difference in charge created by a vacant Fe^{2+} site can be balanced by two Fe^{2+} sites that have Fe^{3+} ions instead [+2 vacancy = (3 − 2) + (3 − 2)]. The crystal lattice is able to accommodate this relatively high fraction of substitutions and vacancies with no significant change in structure.

Note the Pattern

Because a crystal must be electrically neutral, any defect that affects the number or charge of the cations *must be compensated* by a corresponding defect in the number or charge of the anions.

Summary

Real crystals contain large numbers of **defects**. Defects may affect only a single point in the lattice (a **point defect**), a row of lattice points (a **line defect**), or a plane of atoms (a **plane defect**). A point defect can be an atom missing from a site in the crystal (a **vacancy**) or an impurity atom that occupies either a normal lattice site (a **substitutional impurity**) or a hole in the lattice between atoms (an **interstitial impurity**). In an **edge dislocation**, an extra plane of atoms is inserted into part of the crystal lattice. Multiple defects can be introduced into materials so that the presence of one defect prevents the motion of another, in a process called **pinning**. Because defect motion tends to stop at **grain boundaries**, controlling the size of the grains in a material controls its mechanical properties. In addition, a process called **work hardening** introduces defects to toughen metals. **Schottky defects** are a coupled pair of vacancies—one cation and one anion—that maintains electrical neutrality. A **Frenkel defect** is an ion that occupies an incorrect site in the lattice. Cations in such compounds are often able to move rapidly from one site in the crystal to another, resulting in high electrical conductivity in the solid material. Such compounds are called **solid electrolytes**. **Nonstoichiometric compounds** have variable stoichiometries over a given range with no dramatic change in crystal structure. This behavior is due to a large number of vacancies or substitutions of one ion by another ion with a different charge.

Key Takeaway

- Defects determine the behavior of solids, but because ionic compounds contain both cations and anions, they exhibit additional types of defects that are not found in metals.

Conceptual Problems

1. How are defects and impurities in a solid related? Can a pure, crystalline compound be free of defects? How can a substitutional impurity produce a vacancy?
2. Why does applying a mechanical stress to a covalent solid cause it to fracture? Use an atomic level description to explain why a metal is ductile under conditions that cause a covalent solid to fracture.
3. How does work hardening increase the strength of a metal? How does work hardening affect the physical properties of a metal?
4. Work-hardened metals and covalent solids such as diamonds are both susceptible to cracking when stressed. Explain how such different materials can both exhibit this property.
5. Suppose you want to produce a ductile material with improved properties. Would impurity atoms of similar or dissimilar atomic size be better at maintaining the ductility of a metal? Why? How would introducing an impurity that forms polar covalent bonds with the metal atoms affect the ductility of the metal? Explain your reasoning.
6. Substitutional impurities are often used to tune the properties of material. Why are substitutional impurities generally more effective at high concentrations, whereas interstitial impurities are usually effective at low concentrations?
7. If an O^{2-} ion (ionic radius = 132 pm) is substituted for an F^{-} ion (ionic radius = 133 pm) in an ionic crystal, what structural changes in the ionic lattice will result?
8. How will the introduction of a metal ion with a different charge as an impurity induce the formation of oxygen vacancies in an ionic metal-oxide crystal?
9. Many nonstoichiometric compounds are transition metal compounds. How can such compounds exist, given that their nonintegral cation:anion ratios apparently contradict one of the basic tenets of Dalton's atomic theory of matter?
10. If you wanted to induce the formation of oxygen vacancies in an ionic crystal, which would you introduce as substitutional impurities—cations with a higher positive charge or a lower positive charge than the cations in the parent structure? Explain your reasoning.

Answers

5. Impurity atoms of similar size and with similar chemical properties would be most likely to maintain the ductility of the metal, because they are unlikely to have a large effect on the ease with which one layer of atoms can move past another under mechanical stress. Larger impurity atoms are likely to form "bumps" or kinks that will make it harder for layers of atoms to move across one another. Interstitial atoms that form polar covalent bonds with the metal atoms tend to occupy spaces between the layers; they act as a "glue" that holds layers of metal atoms together, which greatly decreases the ductility.
6.
7. Since O^{2-} and F^{-} are both very similar in size, substitution is possible without disruption of the ionic packing. The difference in charge, however, requires the formation of a vacancy on another F^{-} site to maintain charge neutrality.

8.
9. Most transition metals form at least two cations that differ by only one electron. Consequently, nonstoichiometric compounds containing transition metals can maintain electrical neutrality by gaining electrons to compensate for the absence of anions or the presence of additional metal ions. Conversely, such compounds can lose electrons to compensate for the presence of additional anions or the absence of metal ions. In both cases, the positive charge on the transition metal is adjusted to maintain electrical neutrality.
10.

Numerical Problems

1. The ionic radius of K^+ is 133 pm, whereas that of Na^+ is 98 pm. Do you expect K^+ to be a common substitutional impurity in compounds containing Na^+? Why or why not?
2. Given Cs (262 pm), Tl (171 pm), and B (88 pm) with their noted atomic radii, which atom is most likely to act as an interstitial impurity in an Sn lattice (Sn atomic radius = 141 pm)? Why?
3. After aluminum, iron is the second most abundant metal in Earth's crust. The silvery-white, ductile metal has a body-centered cubic (bcc) unit cell with an edge length of 286.65 pm.
    1. Use this information to calculate the density of iron.
    2. What would the density of iron be if 0.15% of the iron sites were vacant?
    3. How does the mass of 1.00 cm^3 of iron without defects compare with the mass of 1.00 cm^3 of iron with 0.15% vacancies?
4. Certain ceramic materials are good electrical conductors due to high mobility of oxide ions resulting from the presence of oxygen vacancies. Zirconia (ZrO_2) can be doped with yttrium by adding Y_2O_3. If 0.35 g of Y_2O_3 can be incorporated into 25.0 g of ZrO_2 while maintaining the zirconia structure, what is the percentage of oxygen vacancies in the structure?
5. Which of the following ions is most effective at inducing an O^{2-} vacancy in crystal of CaO? The ionic radii are O^{2-}, 132 pm; Ca^{2+}, 100 pm; Sr^{2+}, 127 pm; F^-, 133 pm; La^{3+}, 104 pm; and K^+, 133 pm. Explain your reasoning.

Answers

1. No. The potassium is much larger than the sodium ion.
2.
3. 1. 7.8744 g/cm^3
    2. 7.86 g/cm^3
    3. Without defects, the mass is 0.15% greater.
4.
5. The lower charge of K^+ makes it the best candidate for inducing an oxide vacancy, even though its ionic radius is substantially larger than that of Ca^{2+}. Substituting two K^+ ions for two Ca^{2+} ions will decrease the total positive charge by two, and an oxide vacancy will maintain electrical neutrality. For example, if 10% of the Ca^{2+} ions are replaced by K^+, we can represent the change as going from $Ca_{20}O_{20}$ to $K_2Ca_{18}O_{20}$, which has a net charge of +2. Loss of one oxide ion would give a composition of $K_2Ca_{18}O_{19}$, which is electrically neutral.

Contributors

- Anonymous

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Chapter 8.5: Bonding and Properties of Solids

Learning Objective

- To understand the correlation between bonding and the properties of solids.

Based on the nature of the forces that hold the component atoms, molecules, or ions together, solids may be formally classified as *ionic*, *molecular*, *covalent* (*network*), or *metallic*. The variation in the relative strengths of these four types of interactions correlates nicely with their wide variation in properties.

Ionic Solids

You learned in Chapter 4 that an ionic solidA solid that consists of positively and negatively charged ions held together by electrostatic forces. consists of positively and negatively charged ions held together by electrostatic forces. (For more information about ionic solids, see Section 4.2) The strength of the attractive forces depends on the charge and size of the ions that compose the lattice and determines many of the physical properties of the crystal.

The **lattice energy**, the energy required to separate 1 mol of a crystalline ionic solid into its component ions in the gas phase, is directly proportional to the product of the ionic charges and inversely proportional to the sum of the radii of the ions. For example, NaF and CaO both crystallize in the face-centered cubic (fcc) sodium chloride structure, and the sizes of their component ions are about the same: Na^+ (102 pm) versus Ca^{2+} (100 pm), and F^- (133 pm) versus O^{2-} (140 pm). Because of the higher charge on the ions in CaO, however, the lattice energy of CaO is almost four times greater than that of NaF (3401 kJ/mol versus 923 kJ/mol). The forces that hold Ca and O together in CaO are much stronger than those that hold Na and F together in NaF, so the heat of fusion of CaO is almost twice that of NaF (59 kJ/mol versus 33.4 kJ/mol), and the melting point of CaO is 2927°C versus 996°C for NaF. In both cases, however, the values are large; that is, simple ionic compounds have high melting points and are relatively hard (and brittle) solids.

Molecular Solids

Molecular solidsA solid that consists of molecules held together by relatively weak forces, such as dipole-dipole interactions, hydrogen bonds, and London dispersion forces. consist of atoms or molecules held to each other by dipole–dipole interactions, London dispersion forces, or hydrogen bonds, or any combination of these, which were discussed in Chapter 7. The arrangement of the molecules in solid benzene is as follows:



The structure of solid benzene. *In solid benzene, the molecules are not arranged with their planes parallel to one another but at 90° angles.*

Because the intermolecular interactions in a molecular solid are relatively weak compared with ionic and covalent bonds, molecular solids tend to be soft, low melting, and easily vaporized (ΔH_{fus} and ΔH_{vap} are low). For similar substances, the strength of the London dispersion forces increases smoothly with increasing molecular mass. For example, the melting points of benzene (C_6H_6), naphthalene ($C_{10}H_8$), and anthracene ($C_{14}H_{10}$), with one, two, and three fused aromatic rings, are 5.5°C, 80.2°C, and 215°C, respectively. The enthalpies of fusion also increase smoothly within the series: benzene (9.95 kJ/mol) < naphthalene (19.1 kJ/mol) < anthracene (28.8 kJ/mol). If the molecules have shapes that cannot pack together efficiently in the crystal, however, then the

melting points and the enthalpies of fusion tend to be unexpectedly low because the molecules are unable to arrange themselves to optimize intermolecular interactions. Thus toluene ($C_6H_5CH_3$) and *m*-xylene [m-$C_6H_4(CH_3)_2$] have melting points of −95°C and −48°C, respectively, which are significantly lower than the melting point of the lighter but more symmetrical analog, benzene.

Self-healing rubber is an example of a molecular solid with the potential for significant commercial applications. The material can stretch, but when snapped into pieces it can bond back together again through reestablishment of its hydrogen-bonding network without showing any sign of weakness. Among other applications, it is being studied for its use in adhesives and bicycle tires that will self-heal.



Toluene and *m*-xylene. *The methyl groups attached to the phenyl ring in toluene and m-xylene prevent the rings from packing together as in solid benzene.*

Covalent Solids

Covalent solidsA solid that consists of two- or three-dimensional networks of atoms held together by covalent bonds. are formed by networks or chains of atoms or molecules held together by covalent bonds. A perfect single crystal of a covalent solid is therefore a single giant molecule. For example, the structure of diamond, shown in part (a) in Figure 8.5.1, consists of sp^3 hybridized carbon atoms, each bonded to four other carbon atoms in a tetrahedral array to create a giant network. The carbon atoms form six-membered rings.



Figure 8.5.1The Structures of Diamond and Graphite *(a) Diamond consists of sp^3 hybridized carbon atoms, each bonded to four other carbon atoms. The tetrahedral array forms a giant network in which carbon atoms form six-membered rings. (b) These side (left) and top (right) views of the graphite structure show the layers of fused six-membered rings and the arrangement of atoms in alternate layers of graphite. The rings in alternate layers are staggered, such that every other carbon atom in one layer lies directly under (and above) the center of a six-membered ring in an adjacent layer.*

The unit cell of diamond can be described as an fcc array of carbon atoms with four additional carbon atoms inserted into four of the tetrahedral holes. It thus has the zinc blende structure described in Section 8.3, except that in zinc blende the atoms that compose the fcc array are sulfur and the atoms in the tetrahedral holes are zinc. Elemental silicon has the same structure, as does silicon carbide (SiC), which has alternating C and Si atoms. The structure of crystalline quartz (SiO_2), shown in Section 8.1, can be viewed as being derived from the structure of silicon by inserting an oxygen atom between each pair of silicon atoms.

All compounds with the diamond and related structures are hard, high-melting-point solids that are not easily deformed. Instead, they tend to shatter when subjected to large stresses, and they usually do not conduct electricity very well. In fact, diamond (melting point = 3500°C at 63.5 atm) is one of the hardest substances known, and silicon carbide (melting point = 2986°C) is used commercially as an abrasive in sandpaper and grinding wheels. It is difficult to deform or melt these and related compounds because strong covalent (C–C or Si–Si) or polar covalent (Si–C or Si–O) bonds must be broken, which requires a large input of energy.

Other covalent solids have very different structures. For example, graphite, the other common allotrope of carbon, has the structure shown in part (b) in Figure 8.5.1. It contains planar networks of six-membered rings of sp^2 hybridized carbon atoms in which each carbon is bonded to three others. This leaves a single electron in an unhybridized $2p_z$ orbital that can be used to form C=C double bonds, resulting in a ring with alternating double and single bonds. Because of its resonance structures, the bonding in graphite is best viewed as consisting of a network of C–C single bonds with one-third of a π bond holding the carbons together, similar to the bonding in benzene.

To completely describe the bonding in graphite, we need a molecular orbital approach similar to the one used for benzene in Chapter 5 . In fact, the C–C distance in graphite (141.5 pm) is slightly longer than the distance in benzene (139.5 pm), consistent with a net carbon–carbon bond order of 1.33. In graphite, the two-dimensional planes of carbon atoms are stacked to form a three-dimensional solid; only London dispersion forces hold the layers together. As a result, graphite exhibits properties typical of both covalent and molecular solids. Due to strong covalent bonding within the layers, graphite has a very high melting point, as expected for a covalent solid (it actually sublimes at about 3915°C). It is also very soft; the layers can easily slide past one another because of the weak interlayer interactions. Consequently, graphite is used as a lubricant and as the “lead” in pencils; the friction between graphite and a piece of paper is sufficient to leave a thin layer of carbon on the paper. Graphite is unusual among covalent solids in that its electrical conductivity is very high parallel to the planes of carbon atoms because of delocalized C–C π bonding. Finally, graphite is black because it contains an immense number of alternating double bonds, which results in a very small energy difference between the individual molecular orbitals. Thus light of virtually all wavelengths is absorbed. Diamond, on the other hand, is colorless when pure because it has no delocalized electrons.

Table 8.5.1 compares the strengths of the intermolecular and intramolecular interactions for three covalent solids, showing the comparative weakness of the interlayer interactions.

Table 8.5.1 A Comparison of Intermolecular (ΔH_{sub}) and Intramolecular Interactions

Substance	ΔH_{sub} (kJ/mol)	Average Bond Energy (kJ/mol)
phosphorus (s)	58.98	201
sulfur (s)	64.22	226
iodine (s)	62.42	149

The Stuctures of Ice

Normal ice has an open hexagonal structure. This explains why the density of liquid water is higher than that of normal ice and why on freezing ice expands. Anyone really interested in the structure of water and ices should reach Martin Chaplin's massive web site at the London South Bank University.

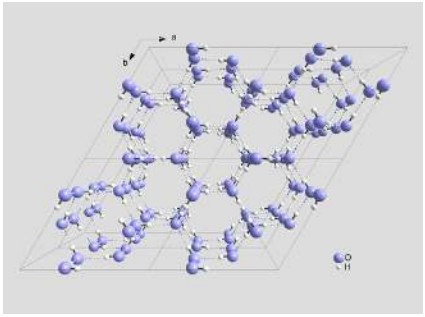


Figure 8.5.2 The Structure of normal ice *Normal ice, called Ice I_h, has an open hexagonal structure held together by hydrogen bonding shown by the dashed lines in this drawing from Wikipedia*

Metallic Solids

Metals are characterized by their ability to reflect light, called lusterThe ability to reflect light. Metals, for instance, have a shiny surface that reflects light (metals are lustrous), whereas nonmetals do not., their high electrical and thermal conductivity, their high

heat capacity, and their malleability and ductility. Every lattice point in a pure metallic element is occupied by an atom of the same metal. The packing efficiency in metallic crystals tends to be high, so the resulting metallic solidsA solid that consists of metal atoms held together by metallic bonds. are dense, with each atom having as many as 12 nearest neighbors.

Bonding in metallic solids is quite different from the bonding in the other kinds of solids we have discussed. Because all the atoms are the same, there can be no ionic bonding, yet metals always contain too few electrons or valence orbitals to form covalent bonds with each of their neighbors. Instead, the valence electrons are delocalized throughout the crystal, providing a strong cohesive force that holds the metal atoms together.

Note the Pattern

Valence electrons in a metallic solid are delocalized, providing a strong cohesive force that holds the atoms together.

The strength of metallic bonds varies dramatically. For example, cesium melts at 28.4°C, and mercury is a liquid at room temperature, whereas tungsten melts at 3680°C. Metallic bonds tend to be weakest for elements that have nearly empty (as in Cs) or nearly full (Hg) valence subshells, and strongest for elements with approximately half-filled valence shells (as in W). As a result, the melting points of the metals increase to a maximum around group 6 and then decrease again from left to right across the *d* block. Other properties related to the strength of metallic bonds, such as enthalpies of fusion, boiling points, and hardness, have similar periodic trends.

A somewhat oversimplified way to describe the bonding in a metallic crystal is to depict the crystal as consisting of positively charged nuclei in an electron seaValence electrons that are delocalized throughout a metallic solid. (Figure 8.5.3). In this model, the valence electrons are not tightly bound to any one atom but are distributed uniformly throughout the structure. Very little energy is needed to remove electrons from a solid metal because they are not bound to a single nucleus. When an electrical potential is applied, the electrons can migrate through the solid toward the positive electrode, thus producing high electrical conductivity. The ease with which metals can be deformed under pressure is attributed to the ability of the metal ions to change positions within the electron sea without breaking any specific bonds. The transfer of energy through the solid by successive collisions between the metal ions also explains the high thermal conductivity of metals. This model does not, however, explain many of the other properties of metals, such as their metallic luster and the observed trends in bond strength as reflected in melting points or enthalpies of fusion. A more complete description of metallic bonding is presented in Section 8.6.



Figure 8.5.3 The Electron-Sea Model of Bonding in Metals *Fixed, positively charged metal nuclei from group 1 (a) or group 2 (b) are surrounded by a "sea" of mobile valence electrons. Because a group 2 metal has twice the number of valence electrons as a group 1 metal, it should have a higher melting point.*

Substitutional Alloys

An alloyA solid solution of two or more metals whose properties differ from those of the constituent elements. is a mixture of metals with metallic properties that differ from those of its constituent elements. Brass (Cu and Zn in a 2:1 ratio) and bronze (Cu and Sn in a 4:1 ratio) are examples of substitutional alloysAn alloy formed by the substitution of one metal atom for another of similar size in the lattice., which are metallic solids with large numbers of substitutional impurities. In contrast, small numbers of interstitial impurities, such as carbon in the iron lattice of steel, give an interstitial alloyAn alloy formed by inserting smaller atoms into holes in the metal lattice.. Because scientists can combine two or more metals in varying proportions to tailor the properties of a material for particular applications, most of the metallic substances we encounter are actually alloys. Examples include the low-melting-point alloys used in solder (Pb and Sn in a 2:1 ratio) and in fuses and fire sprinklers (Bi, Pb, Sn, and Cd in a 4:2:1:1 ratio).

The compositions of most alloys can vary over wide ranges. In contrast, intermetallic compoundsAn alloy that consists of certain metals that combine in only specific proportions and whose properties are frequently quite different from those of their constituent elements. consist of certain metals that combine in only specific proportions. Their compositions are largely determined by the relative sizes of their component atoms and the ratio of the total number of valence electrons to the number of atoms present (the *valence electron density*). The structures and physical properties of intermetallic compounds are frequently quite different from those of their constituent elements, but they may be similar to elements with a similar valence electron density. For example, Cr_3Pt is an intermetallic compound used to coat razor blades advertised as "platinum coated"; it is very hard and dramatically lengthens the useful life of the razor blade. With similar valence electron densities, Cu and PdZn have been found to be virtually identical in their catalytic properties.

Some general properties of the four major classes of solids are summarized in Table 8.5.2.

Table 8.5.2Properties of the Major Classes of Solids

Ionic Solids	Molecular Solids	Covalent Solids	Metallic Solids
poor conductors of heat and electricity	poor conductors of heat and electricity	poor conductors of heat and electricity*	good conductors of heat and electricity
relatively high melting point	low melting point	high melting point	melting points depend strongly on electron configuration
hard but brittle; shatter under stress	soft	very hard and brittle	easily deformed under stress; ductile and malleable
relatively dense	low density	low density	usually high density
dull surface	dull surface	dull surface	lustrous
*Many exceptions exist. For example, graphite has a relatively high electrical conductivity within the carbon planes, and diamond has the highest thermal conductivity of any known substance.			

Note the Pattern

The general order of increasing strength of interactions in a solid is molecular solids < ionic solids ≈ metallic solids < covalent solids.

Example 8.5.1

Classify Ge, RbI, $C_6(CH_3)_6$, and Zn as ionic, molecular, covalent, or metallic solids and arrange them in order of increasing melting points.

Given: compounds

Asked for: classification and order of melting points

Strategy:

A Locate the component element(s) in the periodic table. Based on their positions, predict whether each solid is ionic, molecular, covalent, or metallic.

B Arrange the solids in order of increasing melting points based on your classification, beginning with molecular solids.

Solution:

A Germanium lies in the *p* block just under Si, along the diagonal line of semimetallic elements, which suggests that elemental Ge is likely to have the same structure as Si (the diamond structure). Thus Ge is probably a covalent solid. RbI contains a metal from group 1 and a nonmetal from group 17, so it is an ionic solid containing Rb^+ and I^- ions. The compound $C_6(CH_3)_6$ is a hydrocarbon (hexamethylbenzene), which consists of isolated molecules that stack to form a molecular solid with no covalent bonds between them. Zn is a *d*-block element, so it is a metallic solid.

B Arranging these substances in order of increasing melting points is straightforward, with one exception. We expect $C_6(CH_3)_6$ to have the lowest melting point and Ge to have the highest melting point, with RbI somewhere in between. The melting points of metals, however, are difficult to predict based on the models presented thus far. Because Zn has a filled valence shell, it should not have a particularly high melting point, so a reasonable guess is $C_6(CH_3)_6$ < Zn ~ RbI < Ge. The actual melting points are $C_6(CH_3)_6$, 166°C; Zn, 419°C; RbI, 642°C; and Ge, 938°C. This agrees with our prediction.

Exercise

Classify C_{60}, $BaBr_2$, GaAs, and AgZn as ionic, covalent, molecular, or metallic solids and then arrange them in order of increasing melting points.

Answer: C_{60} (molecular) < AgZn (metallic) ~ $BaBr_2$ (ionic) < GaAs (covalent). The actual melting points are C_{60}, about 300°C; AgZn, about 700°C; $BaBr_2$, 856°C; and GaAs, 1238°C.

Summary

The major types of solids are ionic, molecular, covalent, and metallic. **Ionic solids** consist of positively and negatively charged ions held together by electrostatic forces; the strength of the bonding is reflected in the lattice energy. Ionic solids tend to have high melting points and are rather hard. **Molecular solids** are held together by relatively weak forces, such as dipole–dipole interactions, hydrogen bonds, and London dispersion forces. As a result, they tend to be rather soft and have low melting points, which depend on their molecular structure. **Covalent solids** consist of two- or three-dimensional networks of atoms held together by covalent bonds; they tend to be very hard and have high melting points. **Metallic solids** have unusual properties: in addition to having high thermal and electrical conductivity and being malleable and ductile, they exhibit luster, a shiny surface that reflects light. An **alloy** is a mixture of metals that has bulk metallic properties different from those of its constituent elements. Alloys can be formed by substituting one metal atom for another of similar size in the lattice (**substitutional alloys**), by inserting smaller atoms into holes in the metal lattice (**interstitial alloys**), or by a combination of both. Although the elemental composition of most alloys can vary over wide ranges, certain metals combine in only fixed proportions to form **intermetallic compounds** with unique properties.

Key Takeaway

- Solids can be classified as ionic, molecular, covalent (network), or metallic, where the general order of increasing strength of interactions is molecular < ionic ≈ metallic < covalent.

Conceptual Problems

1. Four vials labeled A–D contain sucrose, zinc, quartz, and sodium chloride, although not necessarily in that order. The following table summarizes the results of the series of analyses you have performed on the contents:

	A	B	C	D
Melting Point	high	high	high	low
Thermal Conductivity	poor	poor	good	poor
Electrical Conductivity in Solid State	moderate	poor	high	poor
Electrical Conductivity in Liquid State	high	poor	high	poor
Hardness	hard	hard	soft	soft
Luster	none	none	high	none

   Match each vial with its contents.

2. Do ionic solids generally have higher or lower melting points than molecular solids? Why? Do ionic solids generally have higher or lower melting points than covalent solids? Explain your reasoning.

3. The strength of London dispersion forces in molecular solids tends to increase with molecular mass, causing a smooth increase in melting points. Some molecular solids, however, have significantly lower melting points than predicted by their molecular

masses. Why?

4. Suppose you want to synthesize a solid that is both heat resistant and a good electrical conductor. What specific types of bonding and molecular interactions would you want in your starting materials?
5. Explain the differences between an interstitial alloy and a substitutional alloy. Given an alloy in which the identity of one metallic element is known, how could you determine whether it is a substitutional alloy or an interstitial alloy?
6. How are intermetallic compounds different from interstitial alloys or substitutional alloys?

Answers

1. 1. NaCl, ionic solid
   2. quartz, covalent solid
   3. zinc, metal
   4. sucrose, molecular solid
2.
3.
4.
5. In a substitutional alloy, the impurity atoms are similar in size and chemical properties to the atoms of the host lattice; consequently, they simply replace some of the metal atoms in the normal lattice and do not greatly perturb the structure and physical properties. In an interstitial alloy, the impurity atoms are generally much smaller, have very different chemical properties, and occupy holes between the larger metal atoms. Because interstitial impurities form covalent bonds to the metal atoms in the host lattice, they tend to have a large effect on the mechanical properties of the metal, making it harder, less ductile, and more brittle. Comparing the mechanical properties of an alloy with those of the parent metal could be used to decide whether the alloy were a substitutional or interstitial alloy.
6.

Numerical Problems

1. Will the melting point of lanthanum(III) oxide be higher or lower than that of ferrous bromide? The relevant ionic radii are as follows: La^{3+}, 104 pm; O^{2-}, 132 pm; Fe^{2+}, 83 pm; and Br^{-}, 196 pm. Explain your reasoning.
2. Draw a graph showing the relationship between the electrical conductivity of metallic silver and temperature.
3. Which has the higher melting point? Explain your reasoning in each case.
   1. Os or Hf
   2. SnO_2 or ZrO_2
   3. Al_2O_3 or SiO_2
4. Draw a graph showing the relationship between the electrical conductivity of a typical semiconductor and temperature.

Answer

3. 1. Osmium has a higher melting point, due to more valence electrons for metallic bonding.
   2. Zirconium oxide has a higher melting point, because it has greater ionic character.
   3. Aluminum oxide has a higher melting point, again because it has greater ionic character.

Contributors

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Chapter 8.6: Metals and Semiconductors

Learning Objective

- To know the relationship between atomic spectra and the electronic structure of atoms.

To explain the observed properties of metals, a more sophisticated approach is needed than the electron-sea model described in Section 8.5 . The molecular orbital theory we used in Chapter 5 to explain the delocalized π bonding in polyatomic ions and molecules such as NO_2^-, ozone, and 1,3-butadiene can be adapted to accommodate the much higher number of atomic orbitals that interact with one another simultaneously in metals.

Band Theory

In a 1 mol sample of a metal, there can be more than 10^{24} orbital interactions to consider. In our molecular orbital description of metals, however, we begin by considering a simple one-dimensional example: a linear arrangement of *n* metal atoms, each containing a single electron in an *s* orbital. We use this example to describe an approach to metallic bonding called band theoryA theory used to describe the bonding in metals and semiconductors., which assumes that the valence orbitals of the atoms in a solid interact, generating a set of molecular orbitals that extend throughout the solid.

One-Dimensional Systems

If the distance between the metal atoms is short enough for the orbitals to interact, they produce bonding, antibonding, and nonbonding molecular orbitals. The left portion of Figure 8.6.1 shows the pattern of molecular orbitals that results from the interaction of *ns* orbitals as *n* increases from 2 to 5.

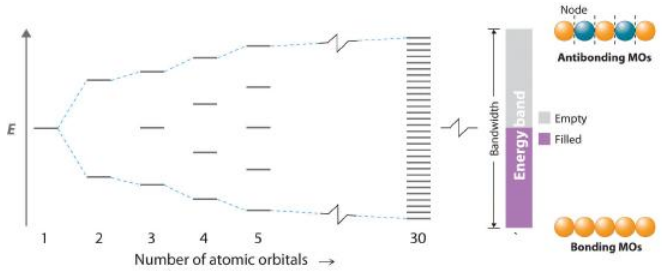


Figure 8.6.1 The Molecular Orbital Energy-Level Diagram for a Linear Arrangement of *n* Atoms, Each of Which Contains a Singly Occupied *s* Orbital. *As n becomes very large, the energy separation between adjacent levels becomes so small that a single continuous band of allowed energy levels results. The lowest-energy molecular orbital corresponds to positive overlap between all the atomic orbitals to give a totally bonding combination, whereas the highest-energy molecular orbital contains a node between each pair of atoms and is thus totally antibonding.*

As we saw in Chapter 5, the lowest-energy orbital is the completely bonding molecular orbital, whereas the highest-energy orbital is the completely antibonding molecular orbital. Molecular orbitals of intermediate energy have fewer nodes than the totally antibonding molecular orbital. The energy separation between adjacent orbitals decreases as the number of interacting orbitals increases. For $n = 30$, there are still discrete, well-resolved energy levels, but as *n* increases from 30 to a number close to Avogadro's number, the spacing between adjacent energy levels becomes almost infinitely small. The result is essentially a continuum of energy levels, as shown on the right in Figure 8.6.1, each of which corresponds to a particular molecular orbital extending throughout the linear array of metal atoms. The levels that are lowest in energy correspond to mostly bonding combinations of atomic orbitals, those highest in energy correspond to mostly antibonding combinations, and those in the middle correspond to essentially nonbonding combinations.

The continuous set of allowed energy levels shown on the right in Figure 8.6.1 is called an energy bandThe continuous set of allowed energy levels generated in band theory when the valence orbitals of the atoms in a solid interact with one another, thus creating a set of molecular orbitals that extend throughout the solid.. The difference in energy between the highest and lowest energy levels is the bandwidthThe difference in energy between the highest and lowest energy levels in an energy band. and is proportional to the strength of the interaction between orbitals on adjacent atoms: the stronger the interaction, the larger the

bandwidth. Because the band contains as many energy levels as molecular orbitals, and the number of molecular orbitals is the same as the number of interacting atomic orbitals, the band in Figure 8.6.1 contains *n* energy levels corresponding to the combining of *s* orbitals from *n* metal atoms. Each of the original *s* orbitals could contain a maximum of two electrons, so the band can accommodate a total of 2*n* electrons. Recall, however, that each of the metal atoms we started with contained only a single electron in each *s* orbital, so there are only *n* electrons to place in the band. Just as with atomic orbitals or molecular orbitals, the electrons occupy the lowest energy levels available. Consequently, only the lower half of the band is filled. This corresponds to filling all of the *bonding* molecular orbitals in the linear array of metal atoms and results in the strongest possible bonding.

Multidimensional Systems

The previous example was a one-dimensional array of atoms that had only *s* orbitals. To extrapolate to two- or three-dimensional systems and atoms with electrons in *p* and *d* orbitals is straightforward in principle, even though in practice the mathematics becomes more complex, and the resulting molecular orbitals are more difficult to visualize. The resulting energy-level diagrams are essentially the same as the diagram of the one-dimensional example in Figure 8.6.1, with the following exception: they contain as many bands as there are different types of interacting orbitals. Because different atomic orbitals interact differently, each band will have a different bandwidth and will be centered at a different energy, corresponding to the energy of the parent atomic orbital of an isolated atom.

Band Gap

Because the 1*s*, 2*s*, and 2*p* orbitals of a period 3 atom are filled core levels, they do not interact strongly with the corresponding orbitals on adjacent atoms. Hence they form rather narrow bands that are well separated in energy (Figure 8.6.2). These bands are completely filled (both the bonding and antibonding levels are completely populated), so they do not make a net contribution to bonding in the solid. The energy difference between the highest level of one band and the lowest level of the next is the band gapThe difference in energy between the highest level of one energy band and the lowest level of the band above it, which represents a set of forbidden energies that do not correspond to any allowed combinations of atomic orbitals.. It represents a set of forbidden energies that do not correspond to any allowed combinations of atomic orbitals.

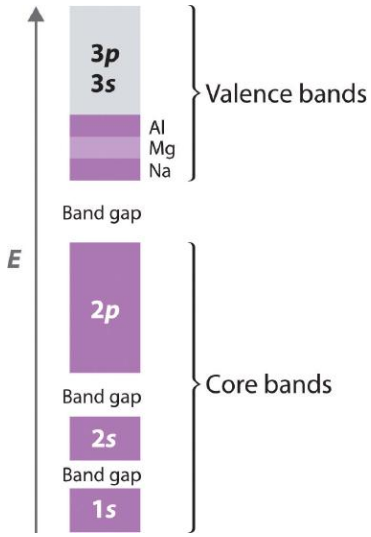


Figure 8.6.2 The Band Structures of the Period 3 Metals Na, Mg, and Al *The 3s and 3p valence bands overlap in energy to form a continuous set of energy levels that can hold a maximum of eight electrons per atom.*

Because they extend farther from the nucleus, the valence orbitals of adjacent atoms (3*s* and 3*p* in Figure 8.6.2) interact much more strongly with one another than do the filled core levels; as a result, the valence bands have a larger bandwidth. In fact, the bands derived from the 3*s* and 3*p* atomic orbitals are wider than the energy gap between them, so the result is overlapping bandsMolecular orbitals derived from two or more different kinds of valence electrons that have similar energies.. These have molecular orbitals derived from two or more valence orbitals with similar energies. As the valence band is filled with one, two, or three electrons per atom for Na, Mg, and Al, respectively, the combined band that arises from the overlap of the 3*s* and 3*p* bands is

also filling up; it has a total capacity of eight electrons per atom (two electrons for each 3*s* orbital and six electrons for each set of 3*p* orbitals). With Na, therefore, which has one valence electron, the combined valence band is one-eighth filled; with Mg (two valence electrons), it is one-fourth filled; and with Al, it is three-eighths filled, as indicated in Figure 8.6.2. The partially filled valence band is absolutely crucial for explaining metallic behavior because it guarantees that there are unoccupied energy levels at an infinitesimally small energy above the highest occupied level.

Band theory can explain virtually all the properties of metals. Metals conduct electricity, for example, because only a very small amount of energy is required to excite an electron from a filled level to an empty one, where it is free to migrate rapidly throughout the crystal in response to an applied electric field. Similarly, metals have high heat capacities (as you no doubt remember from the last time a doctor or a nurse placed a stethoscope on your skin) because the electrons in the valence band can absorb thermal energy by being excited to the low-lying empty energy levels. Finally, metals are lustrous because light of various wavelengths can be absorbed, causing the valence electrons to be excited into any of the empty energy levels above the highest occupied level. When the electrons decay back to low-lying empty levels, they emit light of different wavelengths. Because electrons can be excited from many different filled levels in a metallic solid and can then decay back to any of many empty levels, light of varying wavelengths is absorbed and reemitted, which results in the characteristic shiny appearance that we associate with metals.

Requirements for Metallic Behavior

For a solid to exhibit metallic behavior, it must have a set of delocalized orbitals forming a band of allowed energy levels, and the resulting band must be only partially filled (10%–90%) with electrons. Without a set of delocalized orbitals, there is no pathway by which electrons can move through the solid.

Note the Pattern

Metallic behavior requires a set of delocalized orbitals and a band of allowed energy levels that is partially occupied.

Band theory explains the correlation between the valence electron configuration of a metal and the strength of metallic bonding. The valence electrons of transition metals occupy either their valence *ns*, $(n - 1)d$, and *np* orbitals (with a total capacity of 18 electrons per metal atom) or their *ns* and $(n - 1)d$ orbitals (a total capacity of 12 electrons per metal atom). These atomic orbitals are close enough in energy that the derived bands overlap, so the valence electrons are not confined to a specific orbital. Metals with 6 to 9 valence electrons (which correspond to groups 6–9) are those most likely to fill the valence bands approximately halfway. Those electrons therefore occupy the highest possible number of bonding levels, while the number of antibonding levels occupied is minimal. Not coincidentally, the elements of these groups exhibit physical properties consistent with the presence of the strongest metallic bonding, such as very high melting points.

Insulators

In contrast to metals, electrical insulatorsA material that conducts electricity poorly because its valence bands are full. are materials that conduct electricity poorly because their valence bands are full. The energy gap between the highest filled levels and the lowest empty levels is so large that the empty levels are inaccessible: thermal energy cannot excite an electron from a filled level to an empty one. The valence-band structure of diamond, for example, is shown in part (a) in Figure 8.6.3. Because diamond has only 4 bonded neighbors rather than the 6 to 12 typical of metals, the carbon 2*s* and 2*p* orbitals combine to form two bands in the solid, with the one at lower energy representing bonding molecular orbitals and the one at higher energy representing antibonding molecular orbitals. Each band can accommodate four electrons per atom, so only the lower band is occupied. Because the energy gap between the filled band and the empty band is very large (530 kJ/mol), at normal temperatures thermal energy cannot excite electrons from the filled level into the empty band. Thus there is no pathway by which electrons can move through the solid, so diamond has one of the lowest electrical conductivities known.

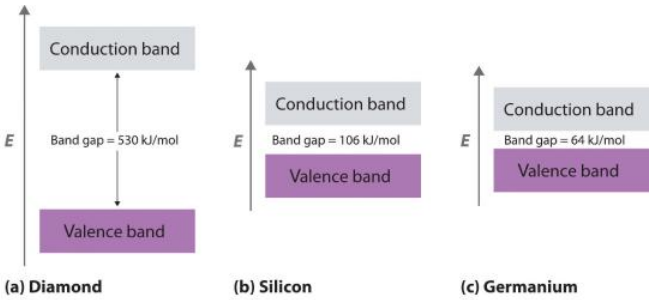


Figure 8.6.3 Energy-Band Diagrams for Diamond, Silicon, and Germanium *The band gap gets smaller from C to Ge.*

Semiconductors

What if the difference in energy between the highest occupied level and the lowest empty level is intermediate between those of electrical conductors and insulators? This is the case for silicon and germanium, which have the same structure as diamond. Because Si–Si and Ge–Ge bonds are substantially weaker than C–C bonds, the energy gap between the filled and empty bands becomes much smaller as we go down group 14 (part (b) and part (c) of Figure 8.6.3). Consequently, thermal energy is able to excite a small number of electrons from the filled valence band of Si and Ge into the empty band above it, which is called the conduction bandThe band of empty molecular orbitals in a semiconductor..

Exciting electrons from the filled valence band to the empty conduction band causes an increase in electrical conductivity for two reasons:

1. The electrons in the previously vacant conduction band are free to migrate through the crystal in response to an applied electric field.
2. Excitation of an electron from the valence band produces a “hole” in the valence band that is equivalent to a *positive* charge. The hole in the valence band can migrate through the crystal in the direction opposite that of the electron in the conduction band by means of a “bucket brigade” mechanism in which an adjacent electron fills the hole, thus generating a hole where the second electron had been, and so forth.

Consequently, Si is a much better electrical conductor than diamond, and Ge is even better, although both are still much poorer conductors than a typical metal (Figure 8.6.4). Substances such as Si and Ge that have conductivities between those of metals and insulators are called semiconductorsA substance such as Si and Ge that has a conductivity between that of metals and insulators.. Many binary compounds of the main group elements exhibit semiconducting behavior similar to that of Si and Ge. For example, gallium arsenide (GaAs) is isoelectronic with Ge and has the same crystalline structure, with alternating Ga and As atoms; not surprisingly, it is also a semiconductor. The electronic structure of semiconductors is compared with the structures of metals and insulators in Figure 8.6.5.

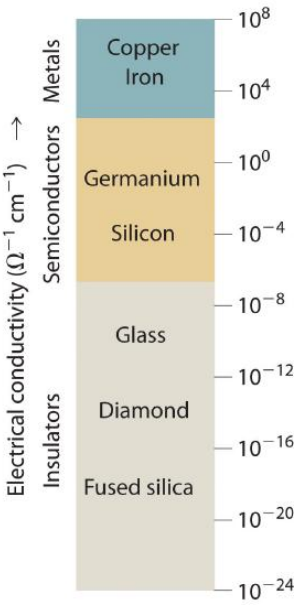


Figure 8.6.4 A Logarithmic Scale Illustrating the Enormous Range of Electrical Conductivities of Solids

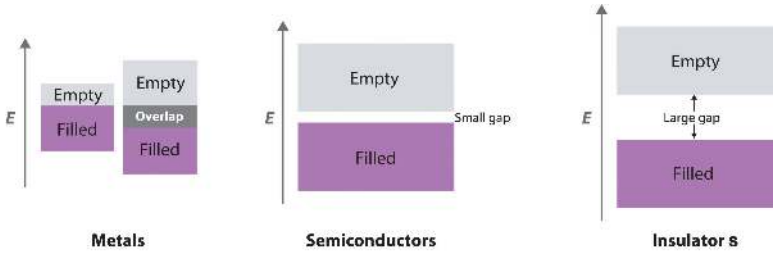


Figure 8.6.5A Comparison of the Key Features of the Band Structures of Metals, Semiconductors, and Insulators *Metallic behavior can arise either from the presence of a single partially filled band or from two overlapping bands (one full and one empty).*

Temperature and Conductivity

Because thermal energy can excite electrons across the band gap in a semiconductor, increasing the temperature increases the number of electrons that have sufficient kinetic energy to be promoted into the conduction band. The electrical conductivity of a semiconductor therefore increases rapidly with increasing temperature, in contrast to the behavior of a purely metallic crystal. In a metal, as an electron travels through the crystal in response to an applied electrical potential, it cannot travel very far before it encounters and collides with a metal nucleus. The more often such encounters occur, the slower the *net* motion of the electron through the crystal, and the *lower* the conductivity. As the temperature of the solid increases, the metal atoms in the lattice acquire more and more kinetic energy. Because their positions are fixed in the lattice, however, the increased kinetic energy increases only the extent to which they vibrate about their fixed positions. At higher temperatures, therefore, the metal nuclei collide with the mobile electrons more frequently and with greater energy, thus *decreasing* the conductivity. This effect is, however, substantially smaller than the increase in conductivity with temperature exhibited by semiconductors. For example, the conductivity of a tungsten wire decreases by a factor of only about two over the temperature range 750–1500 K, whereas the conductivity of silicon increases approximately 100-fold over the same temperature range. These trends are illustrated in Figure 8.6.6.

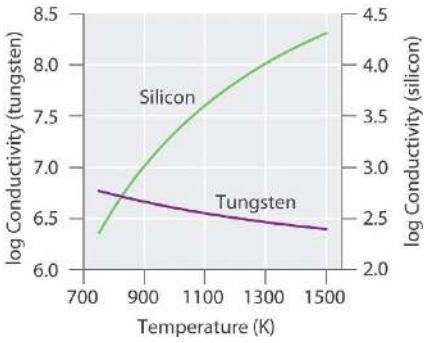


Figure 8.6.6 The Temperature Dependence of the Electrical Conductivity of a Metal versus a Semiconductor *The conductivity of the metal (tungsten) decreases relatively slowly with increasing temperature, whereas the conductivity of the semiconductor (silicon) increases much more rapidly.*

Note the Pattern

The electrical conductivity of a semiconductor *increases* with increasing temperature, whereas the electrical conductivity of a metal *decreases* with increasing temperature.

n- and *p*-Type Semiconductors

DopingThe process of deliberately introducing small amounts of impurities into commercial semiconductors to tune their electrical properties for specific applications. is a process used to tune the electrical properties of commercial semiconductors by deliberately introducing small amounts of impurities. If an impurity contains *more* valence electrons than the atoms of the host lattice (e.g., when small amounts of a group 15 atom are introduced into a crystal of a group 14 element), then the doped solid has more electrons available to conduct current than the pure host has. As shown in part (a) in Figure 8.6.7, adding an impurity such as phosphorus to a silicon crystal creates occasional electron-rich sites in the lattice. The electronic energy of these sites lies between those of the filled valence band and the empty conduction band but closer to the conduction band. Because the atoms that were introduced are surrounded by host atoms, and the electrons associated with the impurity are close in energy to the conduction band, those extra electrons are relatively easily excited into the empty conduction band of the host. Such a substance is called an *n*-type semiconductorA semiconductor that has been doped with an impurity that has more valence electrons than the atoms of the host lattice., with the *n* indicating that the added charge carriers are negative (they are electrons).

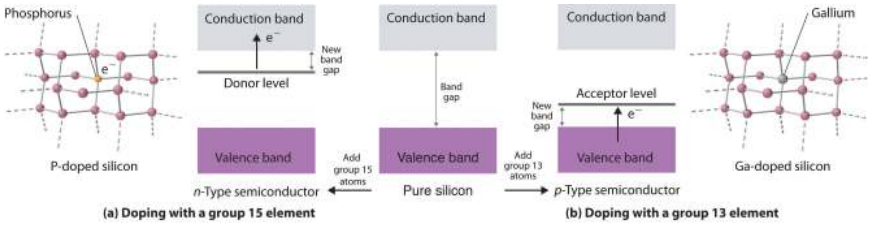


Figure 8.6.7 Structures and Band Diagrams of *n*-Type and *p*-Type Semiconductors *(a) Doping silicon with a group 15 element results in a new filled level between the valence and conduction bands of the host. (b) Doping silicon with a group 13 element results in a new empty level between the valence and conduction bands of the host. In both cases, the effective band gap is substantially decreased, and the electrical conductivity at a given temperature increases dramatically.*

If the impurity atoms contain *fewer* valence electrons than the atoms of the host (e.g., when small amounts of a group 13 atom are introduced into a crystal of a group 14 element), then the doped solid has fewer electrons than the pure host. Perhaps unexpectedly, this also results in *increased* conductivity because the impurity atoms generate holes in the valence band. As shown in part (b) in Figure 8.6.7, adding an impurity such as gallium to a silicon crystal creates isolated electron-deficient sites in the host lattice. The electronic energy of these empty sites also lies between those of the filled valence band and the empty conduction band of the host but much closer to the filled valence band. It is therefore relatively easy to excite electrons from the valence band of the host to the isolated impurity atoms, thus forming holes in the valence band. This kind of substance is called a *p*-type semiconductorA semiconductor that has been doped with an impurity that has fewer valence electrons than the atoms of the host lattice., with the *p*

standing for positive charge carrier (i.e., a hole). Holes in what was a filled band are just as effective as electrons in an empty band at conducting electricity.

Note the Pattern

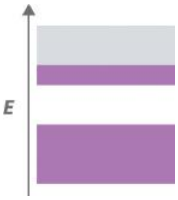
n-Type semiconductors are negative charge carriers; the impurity has *more* valence electrons than the host. *p*-Type semiconductors are positive charge carriers; the impurity has *fewer* valence electrons than the host.

The electrical conductivity of a semiconductor is roughly proportional to the number of charge carriers, so doping is a precise way to adjust the conductivity of a semiconductor over a wide range. The entire semiconductor industry is built on methods for preparing samples of Si, Ge, or GaAs doped with precise amounts of desired impurities and assembling silicon chips and other complex devices with junctions between *n*- and *p*-type semiconductors in varying numbers and arrangements.

Because silicon does not stand up well to temperatures above approximately 100°C, scientists have been interested in developing semiconductors made from diamonds, a more thermally stable material. A new method has been developed based on vapor deposition, in which a gaseous mixture is heated to a high temperature to produce carbon that then condenses on a diamond kernel. This is the same method now used to create cultured diamonds, which are indistinguishable from natural diamonds. The diamonds are heated to more than 2000°C under high pressure to harden them even further. Doping the diamonds with boron has produced *p*-type semiconductors, whereas doping them with boron and deuterium achieves *n*-type behavior. Because of their thermal stability, diamond semiconductors have potential uses as microprocessors in high-voltage applications.

Example 8.6.1

A crystalline solid has the following band structure, with the purple areas representing regions occupied by electrons. The lower band is completely occupied by electrons, and the upper level is about one-third filled with electrons.



1. Predict the electrical properties of this solid.
2. What would happen to the electrical properties if all of the electrons were removed from the upper band? Would you use a chemical oxidant or reductant to effect this change?
3. What would happen to the electrical properties if enough electrons were added to completely fill the upper band? Would you use a chemical oxidant or reductant to effect this change?

Given: band structure

Asked for: variations in electrical properties with conditions

Strategy:

A Based on the occupancy of the lower and upper bands, predict whether the substance will be an electrical conductor. Then predict how its conductivity will change with temperature.

B After all the electrons are removed from the upper band, predict how the band gap would affect the electrical properties of the material. Determine whether you would use a chemical oxidant or reductant to remove electrons from the upper band.

C Predict the effect of a filled upper band on the electrical properties of the solid. Then decide whether you would use an oxidant or a reductant to fill the upper band.

Solution:

1. **A** The material has a partially filled band, which is critical for metallic behavior. The solid will therefore behave like a metal, with high electrical conductivity that decreases slightly with increasing temperature.
2. **B** Removing all of the electrons from the partially filled upper band would create a solid with a filled lower band and an empty upper band, separated by an energy gap. If the band gap is large, the material will be an electrical insulator. If the gap is

relatively small, the substance will be a semiconductor whose electrical conductivity increases rapidly with increasing temperature. Removing the electrons would require an oxidant because oxidants accept electrons.

3. **C** Adding enough electrons to completely fill the upper band would produce an electrical insulator. Without another empty band relatively close in energy above the filled band, semiconductor behavior would be impossible. Adding electrons to the solid would require a reductant because reductants are electron donors.

Exercise

A substance has the following band structure, in which the lower band is half-filled with electrons (purple area) and the upper band is empty.



1. Predict the electrical properties of the solid.
2. What would happen to the electrical properties if all of the electrons were removed from the lower band? Would you use a chemical oxidant or reductant to effect this change?
3. What would happen to the electrical properties if enough electrons were added to completely fill the lower band? Would you use a chemical oxidant or reductant to effect this change?

Answer:

1. The solid has a partially filled band, so it has the electrical properties of a conductor.
2. Removing all of the electrons from the lower band would produce an electrical insulator with two empty bands. An oxidant is required.
3. Adding enough electrons to completely fill the lower level would result in an electrical insulator if the energy gap between the upper and lower bands is relatively large, or a semiconductor if the band gap is relatively small. A reductant is required.

Summary

Band theory assumes that the valence orbitals of the atoms in a solid interact to generate a set of molecular orbitals that extend throughout the solid; the continuous set of allowed energy levels is an **energy band**. The difference in energy between the highest and lowest allowed levels within a given band is the **bandwidth**, and the difference in energy between the highest level of one band and the lowest level of the band above it is the **band gap**. If the width of adjacent bands is larger than the energy gap between them, **overlapping bands** result, in which molecular orbitals derived from two or more kinds of valence orbitals have similar energies. Metallic properties depend on a partially occupied band corresponding to a set of molecular orbitals that extend throughout the solid to form a band of energy levels. If a solid has a filled valence band with a relatively low-lying empty band above it (a **conduction band**), then electrons can be excited by thermal energy from the filled band into the vacant band where they can then migrate through the crystal, resulting in electrical conductivity. **Electrical insulators** are poor conductors because their valence bands are full. **Semiconductors** have electrical conductivities intermediate between those of insulators and metals. The electrical conductivity of semiconductors increases rapidly with increasing temperature, whereas the electrical conductivity of metals decreases slowly with increasing temperature. The properties of semiconductors can be modified by **doping**, or introducing impurities. Adding an element with more valence electrons than the atoms of the host populates the conduction band, resulting in an *n*-**type semiconductor** with increased electrical conductivity. Adding an element with fewer valence electrons than the atoms of the host generates holes in the valence band, resulting in a *p*-**type semiconductor** that also exhibits increased electrical conductivity.

Key Takeaway

- Bonding in metals and semiconductors can be described using band theory, in which a set of molecular orbitals is generated that extends throughout the solid.

Conceptual Problems

1. Can band theory be applied to metals with two electrons in their valence *s* orbitals? with no electrons in their valence *s* orbitals? Why or why not?
2. Given a sample of a metal with 10^{20} atoms, how does the width of the band arising from *p* orbital interactions compare with the width of the band arising from *s* orbital interactions? from *d* orbital interactions?
3. Diamond has one of the lowest electrical conductivities known. Based on this fact, do you expect diamond to be colored? Why? How do you account for the fact that some diamonds are colored (such as “pink” diamond or “green” diamond)?
4. Why do silver halides, used in the photographic industry, have band gaps typical of semiconducting materials, whereas alkali metal halides have very large band gaps?
5. As the ionic character of a compound increases, does its band gap increase or decrease? Why?
6. Why is silicon, rather than carbon or germanium, used in the semiconductor industry?
7. Carbon is an insulator, and silicon and germanium are semiconductors. Explain the relationship between the valence electron configuration of each element and their band structures. Which will have the higher electrical conductivity at room temperature —silicon or germanium?
8. How does doping affect the electrical conductivity of a semiconductor? Draw the effect of doping on the energy levels of the valence band and the conduction band for both an *n*-type and a *p*-type semiconductor.

Answers

1. The low electrical conductivity of diamond implies a very large band gap, corresponding to the energy of a photon of ultraviolet light rather than visible light. Consequently, diamond should be colorless. Pink or green diamonds contain small amounts of highly colored impurities that are responsible for their color.
2.
3.
4. As the ionic character of a compound increases, the band gap will also increase due to a decrease in orbital overlap. Remember that overlap is greatest for orbitals of the same energy, and that the difference in energy between orbitals on adjacent atoms increases as the difference in electronegativity between the atoms increases. Thus, large differences in electronegativity increase the ionic character, decrease the orbital overlap, and increase the band gap.
5.
6.
7.

Numerical Problems

1. Of Ca, N, B, and Ge, which will convert pure silicon into a *p*-type semiconductor when doping? Explain your reasoning.
2. Of Ga, Si, Br, and P, which will convert pure germanium into an *n*-type semiconductor when doping? Explain your reasoning.

Contributors

- Anonymous

Modified by Joshua Halpern, Scott Sinex and Scott Johnson

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Chapter 8.7: Superconductors

Learning Objective

- To become familiar with the properties of superconductors.

The phenomenon of superconductivity was discovered by the Danish physicist H. Kamerlingh Onnes (1853–1926; Nobel Prize in Physics, 1913), who found a way to liquefy helium, which boils at 4.2 K and 1 atm pressure. To exploit the very low temperatures made possible by this new cryogenic fluid, he began a systematic study of the properties of metals, especially their electrical properties. Because the electrical resistance of a sample is technically easier to measure than its conductivity, Onnes measured the *resistivity* of his samples. The resistivity and conductivity of a material are inversely proportional:

$$conductivity = \frac{1}{resistivity} \tag{8.7.1}$$

In 1911, Onnes discovered that at about 4 K, the resistivity of metallic mercury (melting point = 234 K) decreased suddenly to essentially zero, rather than continuing to decrease only slowly with decreasing temperature as expected (Figure 8.7.1). He called this phenomenon superconductivityThe phenomenon in which a solid at low temperatures exhibits zero resistance to the flow of electrical current. because a resistivity of zero means that an electrical current can flow forever. Onnes soon discovered that many other metallic elements exhibit superconductivity at very low temperatures. Each of these superconductorsA solid that at low temperatures exhibits zero resistance to the flow of electrical current. has a characteristic superconducting transition temperature (T_c)The temperature at which the electrical resistance of a material drops to zero. at which its resistivity drops to zero. At temperatures less than their T_c, superconductors also completely expel a magnetic field from their interior (part (a) in Figure 8.7.2). This phenomenon is called the Meissner effectThe phenomenon in which a superconductor completely expels a magnetic field from its interior. after one of its discoverers, the German physicist Walther Meissner, who described the phenomenon in 1933. Due to the Meissner effect, a superconductor will actually “float” over a magnet, as shown in part (b) in Figure 8.7.2.

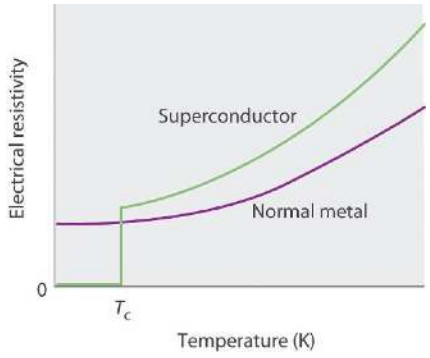
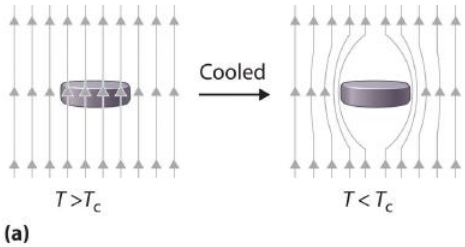


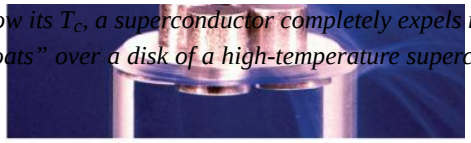
Figure 8.7.1The Temperature Dependence of the Electrical Resistivity of a Normal Metal and a Superconductor *The superconducting transition temperature (T_c) is the temperature at which the resistivity of a superconductor drops to zero.*



(a)



Figure 8.7.2 The Meissner Effect *(a) Below its T_c, a superconductor completely expels magnetic lines of force from its interior. (b) In magnetic levitation, a small magnet "floats" over a disk of a high-temperature superconducting material ($YBa_2Cu_3O_{7-x}$) cooled in liquid nitrogen.*



(b)

BCS Theory

For many years, the phenomenon of superconductivity could not be satisfactorily explained by the laws of conventional physics. In the early 1950s, however, American physicists John Bardeen, Leon Cooper, and John Schrieffer formulated a theory for superconductivity that earned them the Nobel Prize in Physics in 1972. According to the BCS theoryA theory used to explain the phenomenon of superconductivity. (named for the initials of their last names), electrons are able to travel through a solid with zero resistance because of attractive interactions involving two electrons that are at some distance from each other. As one electron moves through the lattice, the surrounding nuclei are attracted to it. The motion of the nuclei can create a transient (short-lived) hole that pulls the second electron in the same direction as the first. The nuclei then return to their original positions to avoid colliding with the second electron as it approaches. The pairs of electrons, called Cooper pairsPairs of electrons that migrate through a superconducting material as a unit., migrate through the crystal as a unit. The electrons in Cooper pairs change partners frequently, like dancers in a ballet.

According to the BCS theory, as the temperature of the solid increases, the vibrations of the atoms in the lattice increase continuously, until eventually the electrons cannot avoid colliding with them. The collisions result in the loss of superconductivity at higher temperatures.

The phenomenon of superconductivity suggested many exciting technological applications. For example, using superconducting wires in power cables would result in zero power losses, even over distances of hundreds of miles. Additionally, because superconductors expel magnetic fields, a combination of magnetic rails and superconducting wheels (or vice versa) could be used to produce *magnetic levitation* of, for example, a train over the track, resulting in friction-free transportation.

Unfortunately, for many years the only superconductors known had serious limitations, especially the need for very low temperatures, which required the use of expensive cryogenic fluids such as liquid He. In addition, the superconducting properties of many substances are destroyed by large electrical currents or even moderately large magnetic fields, making them useless for applications in power cables or high-field magnets. The ability of materials such as NbTi, NbSn, Nb_3Si, and Nb_3Ge to tolerate rather high magnetic fields, however, has led to a number of commercial applications of superconductors, including high-field magnets for nuclear magnetic resonance (NMR) spectrometers and magnetic resonance imaging (MRI) instruments in medicine, which, unlike x-rays, can detect small changes in soft tissues in the body.

High-Temperature Superconductors

Because of these limitations, scientists continued to search for materials that exhibited superconductivity at temperatures greater than 77 K (the temperature of liquid nitrogen, the least expensive cryogenic fluid). In 1986, Johannes G. Bednorz and Karl A. Müller, working for IBM in Zurich, showed that certain mixed-metal oxides containing La, Ba, and Cu exhibited superconductivity above 30 K. These compounds had been prepared by French workers as potential solid catalysts some years earlier, but their electrical properties had never been examined at low temperatures. Although initially the scientific community was extremely skeptical, the compounds were so easy to prepare that the results were confirmed within a few weeks. These high-temperature superconductorsA material that becomes a superconductor at temperatures greater than 30 K. earned Bednorz and Müller the Nobel Prize in Physics in 1987. Subsequent research has produced new compounds with related structures that are superconducting at temperatures as high as 135 K. The best known of these was discovered by Paul Chu and Maw-Kuen Wu Jr. and is called the "Chu–Wu phase" or the 1-2-3 superconductor.

The formula for the 1-2-3 superconductor is $YBa_2Cu_3O_{7-x}$, where x is about 0.1 for samples that superconduct at about 95 K. If $x \approx 1.0$, giving a formula of $YBa_2Cu_3O_6$, the material is an electrical insulator. The superconducting phase is thus a nonstoichiometric compound, with a fixed ratio of metal atoms but a variable oxygen content. The overall equation for the synthesis of this material is as follows:

$$Y_2O_3\,(s) + 4BaCO_3\,(s) + 6CuO\,(s) + \frac{1}{2}O_2\,(g) \xrightarrow{\Delta} 2YBa_2Cu_3O_{7(s)} + 4CO_2\,(g) \tag{8.7.2}$$





If we assume that the superconducting phase is really stoichiometric $YBa_2Cu_3O_7$, then the average oxidation states of O, Y, Ba, and Cu are −2, +3, +2, and +7/3 respectively. The simplest way to view the average oxidation state of Cu is to assume that two Cu atoms per formula unit are present as Cu^{2+} and one is present as the rather unusual Cu^{3+}. In $YBa_2Cu_3O_6$, the insulating form, the oxidation state of Cu is+5/3 so there are two Cu^{2+} and one Cu^{+} per formula unit.

As shown in Figure 8.7.3, the unit cell of the 1-2-3 superconductor is related to the unit cell of the simple perovskite structure (part (b) in Figure 8.7.3). The only difference between the superconducting and insulating forms of the compound is that an O atom has been removed from between the Cu^{3+} ions, which destroys the chains of Cu atoms and leaves the Cu in the center of the unit cell as Cu^{+}. The chains of Cu atoms are crucial to the formation of the superconducting state.

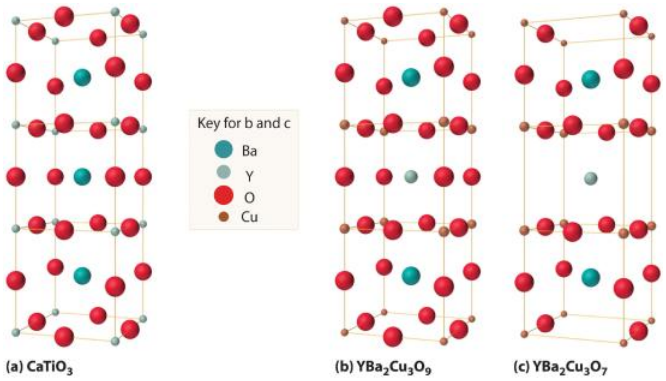


Figure 8.7.3 The Relationship of the Structure of a Superconductor Consisting of Y-Ba-Cu-O to a Simple Perovskite Structure *(a) Stacking three unit cells of the Ca-centered $CaTiO_3$ perovskite structure (part (b) in Figure 8.3.4) together with (b) replacement of all Ti atoms by Cu, replacement of Ca in the top and bottom cubes by Ba, and replacement of Ca in the central cube by Y gives a $YBa_2Cu_3O_9$ stoichiometry. (c) The removal of two oxygen atoms per unit cell gives the nominal $YBa_2Cu_3O_7$ stoichiometry of the superconducting material.*

Table 8.7.1 lists the ideal compositions of some of the known high-temperature superconductors that have been discovered in recent years. Engineers have learned how to process the brittle polycrystalline 1-2-3 and related compounds into wires, tapes, and films that can carry enormous electrical currents. Commercial applications include their use in infrared sensors and in analog signal processing and microwave devices.

Table 8.7.1 The Composition of Various Superconductors

Compound	T_c (K)
$Ba(Pb_{1-x}Bi_x)O_3$	13.5
$(La_{2-x}Sr_x)CuO_4$	35
$YBa_2Cu_3O_{7-x}$	95
$Bi_2(Sr_{2-x}Ca_x)CuO_6$*	80
$Bi_2Ca_2Sr_2Cu_3O_{10}$*	110
$Tl_2Ba_2Ca_2Cu_3O_{10}$*	125
$HgBa_2Ca_2Cu_3O_8$*	133
K_3C_{60}	18
Rb_3C_{60}	30
*Nominal compositions only. Oxygen deficiencies or excesses are common in these compounds.	

Example 8.7.1

Calculate the average oxidation state of Cu in a sample of $YBa_2Cu_3O_{7-x}$ with $x = 0.5$. How do you expect its structure to differ from those shown in Figure 8.7.3 for $YBa_2Cu_3O_9$ and $YBa_2Cu_3O_7$?

Given: stoichiometry

Asked for: average oxidation state and structure

Strategy:

A Based on the oxidation states of the other component atoms, calculate the average oxidation state of Cu that would make an electrically neutral compound.

B Compare the stoichiometry of the structures shown in Figure 8.7.3 with the stoichiometry of the given compound to predict how the structures differ.

Solution:

A The net negative charge from oxygen is (7.0 − 0.5) (−2) = −13, and the sum of the charges on the Y and Ba atoms is [1 × (+3)] + [2 × (+2)] = +7. This leaves a net charge of −6 per unit cell, which must be compensated for by the three Cu atoms, for a net charge of +6/3=+2 per Cu.

B The most likely structure would be one in which every other O atom between the Cu atoms in the Cu chains of $YBa_2Cu_3O_7$ has been removed.

Exercise

Calculate the average oxidation state of Cu in a sample of $HgBa_2Ca_2Cu_3O_8$. Assume that Hg is present as Hg^{2+}.

Answer: +2

Summary

Superconductors are solids that at low temperatures exhibit zero resistance to the flow of electrical current, a phenomenon known as **superconductivity**. The temperature at which the electrical resistance of a substance drops to zero is its **superconducting transition temperature (T_c)**. Superconductors also expel a magnetic field from their interior, a phenomenon known as the **Meissner effect**. Superconductivity can be explained by the **BCS theory**, which says that electrons are able to travel through a solid with no resistance because they couple to form pairs of electrons (Cooper pairs). **High-temperature superconductors** have T_c values greater than 30 K.

Key Takeaway

- Superconductivity can be described using the BCS theory, in which Cooper pairs of electrons migrate through the crystal as a unit.

Conceptual Problems

1. Why does the BCS theory predict that superconductivity is not possible at temperatures above approximately 30 K?
2. How does the formation of Cooper pairs lead to superconductivity?

Answer

1. According to BCS theory, the interactions that lead to formation of Cooper pairs of electrons are so weak that they should be disrupted by thermal vibrations of lattice atoms above about 30 K.
2.

Contributors

- Anonymous

Modified by Joshua Halpern, Scott Sinex and Scott Johnson

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Chapter 8.8: Polymers

Learning Objective

- To understand polymer synthesis.
- To understand the differences between synthetic and biological polymers.

Most of the solids discussed so far have been molecules or ions with low molecular masses, ranging from tens to hundreds of atomic mass units. Many of the molecular materials in consumer goods today, however, have very high molecular masses, ranging from thousands to millions of atomic mass units, and are formed from a carefully controlled series of reactions that produce giant molecules called polymersA giant molecule that consists of many basic structural units (monomers) connected in a chain or network by covalent bonds. (from the Greek *poly* and *meros*, meaning “many parts”). Polymers are used in corrective eye lenses, plastic containers, clothing and textiles, and medical implant devices, among many other uses. They consist of basic structural units called monomersThe basic structural unit of a polymer., which are repeated many times in each molecule. As shown schematically in Figure 8.8.1 , polymerizationA process by which monomers are connected into chains or networks by covalent bonds. is the process by which monomers are connected into chains or networks by covalent bonds. Polymers can form via a *condensation reaction*, in which two monomer molecules are joined by a new covalent bond and a small molecule such as water is eliminated, or by an *addition reaction*, a variant of a condensation reaction in which the components of a species AB are added to adjacent atoms of a multiple bond. Many people confuse the terms *plastics* and *polymers*. PlasticThe property of a material that allows it to be molded into almost any shape. is the property of a material that allows it to be molded into almost any shape. Although many plastics are polymers, many polymers are not plastics. In this section, we introduce the reactions that produce naturally occurring and synthetic polymers.

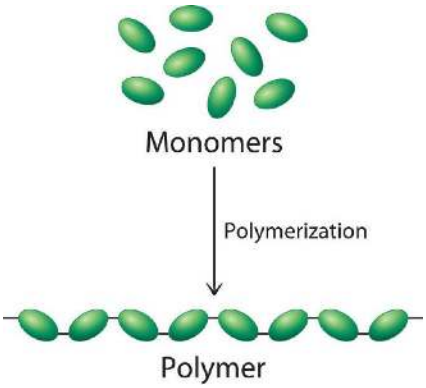


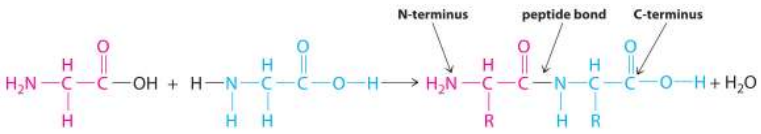
Figure 8.8.1 Polymer formation during a polymerization reaction, *a large number of monomers become connected by covalent bonds to form a single long molecule, a polymer.*

Note the Pattern

Polymers are formed via condensation or addition reactions.

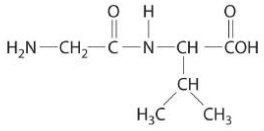
Naturally Occurring Polymers: Peptides and Proteins

Polymers that occur naturally are crucial components of all organisms and form the fabric of our lives. Hair, silk, skin, feathers, muscle, and connective tissue are all primarily composed of proteins, the most familiar kind of naturally occurring, or biological, polymer. The monomers of many biological polymers are the amino acids each called an *amino acid residue*. The residues are linked together by amide bonds, also called peptide bonds, via a condensation reaction where H_2O is eliminated:



In the above equation, R represents an alkyl or aryl group, or hydrogen, depending on the amino acid. We write the structural formula of the product with the free amino group on the left (the *N-terminus*) and the free carboxylate group on the right (the *C-*

terminus). For example, the structural formula for the product formed from the amino acids glycine and valine (glycyl-valine) is as follows:



Glycyl-valine

The most important difference between synthetic and naturally occurring polymers is that the former usually contain very few different monomers, whereas biological polymers can have as many as 20 different kinds of amino acid residues arranged in many different orders. Chains with less than about 50 amino acid residues are called peptidesBiological polymers with less than about 50 amino acid residues., whereas those with more than about 50 amino acid residues are called proteinsBiological polymers with more than 50 amino acid residues linked together by amide bonds.. Many proteins are enzymesCatalysts that occur naturally in living organisms and that catalyze biological reactions., which are catalysts that increase the rate of a biological reaction.

Note the Pattern

Synthetic polymers usually contain only a few different monomers, whereas biological polymers can have many kinds of monomers, such as amino acids arranged in different orders.

Many small peptides have potent physiological activities. The *endorphins*, for example, are powerful, naturally occurring painkillers found in the brain. Other important peptides are the hormones vasopressin and oxytocin. Although their structures and amino acid sequences are similar, vasopressin is a blood pressure regulator, whereas oxytocin induces labor in pregnant women and milk production in nursing mothers. Oxytocin was the first biologically active peptide to be prepared in the laboratory by Vincent du Vigneaud (1901–1978), who was awarded the Nobel Prize in Chemistry in 1955.

Synthetic Polymers

Many of the synthetic polymers we use, such as plastics and rubbers, have commercial advantages over naturally occurring polymers because they can be produced inexpensively. Moreover, many synthetic polymers are actually more desirable than their natural counterparts because scientists can select monomer units to tailor the physical properties of the resulting polymer for particular purposes. For example, in many applications, wood has been replaced by plastics that are more durable, lighter, and easier to shape and maintain. Polymers are also increasingly used in engineering applications where weight reduction and corrosion resistance are required. Steel rods used to support concrete structures, for example, are often coated with a polymeric material when the structures are near ocean environments where steel is vulnerable to corrosion (For more information on corrosion, see Section 17.6.) In fact, the use of polymers in engineering applications is a very active area of research.

Probably the best-known example of a synthetic polymer is *nylon* (Figure 8.8.2). Its monomers are linked by amide bonds (which are called peptide bonds in biological polymers), so its physical properties are similar to those of some proteins because of their common structural unit—the amide group. Nylon is easily drawn into silky fibersA particle of a synthetic polymer that is more than 100 times longer than it is wide. that are more than a hundred times longer than they are wide and can be woven into fabrics. Nylon fibers are so light and strong that during World War II, all available nylon was commandeered for use in parachutes, ropes, and other military items. With polymer chains that are fully extended and run parallel to the fiber axis, nylon fibers resist stretching, just like naturally occurring silk fibers, although the structures of nylon and silk are otherwise different. Replacing the flexible $–CH_2–$ units in nylon by aromatic rings produces a stiffer and stronger polymer, such as the very strong polymer known as Kevlar. Kevlar fibers are so strong and rigid that they are used in lightweight army helmets, bulletproof vests, and even sailboat and canoe hulls, all of which contain multiple layers of Kevlar fabric.

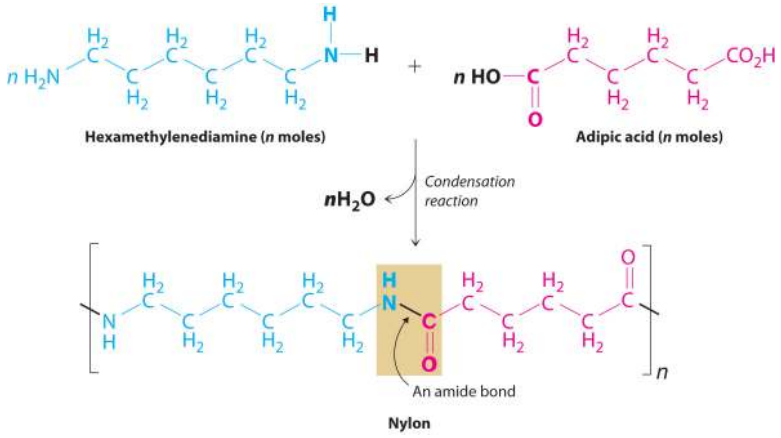


Figure 8.8.2 The Synthesis of Nylon *Nylon is a synthetic condensation polymer created by the reaction of a dicarboxylic acid and a diamine to form amide bonds and water.*

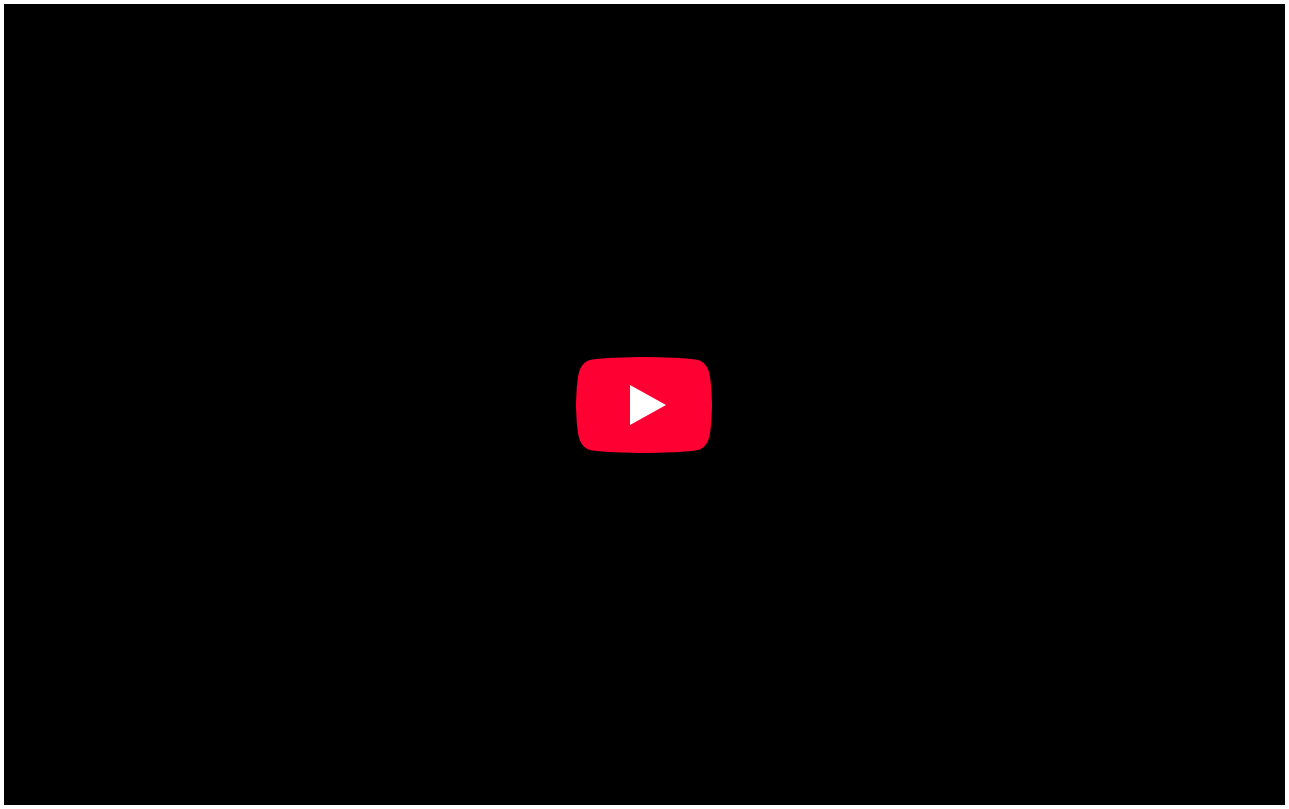




Figure 8.8.3 Synthesis of Nylon: *A video showing the synthesis of nylon 6,10 by Mabakken*

Not all synthetic polymers are linked by amide bonds—for example, *polyesters* contain monomers that are linked by ester bonds. Polyesters are sold under trade names such as Dacron, Kodel, and Fortrel, which are used in clothing, and Mylar, which is used in magnetic tape, helium-filled balloons, and high-tech sails for sailboats. Although the fibers are flexible, properly prepared Mylar films are almost as strong as steel.

Polymers based on skeletons with only carbon are all synthetic. Most of these are formed from ethylene (CH_2=CH_2), a two-carbon building block, and its derivatives. The relative lengths of the chains and any branches control the properties of polyethylene. For

example, higher numbers of branches produce a softer, more flexible, lower-melting-point polymer called low-density polyethylene (LDPE), whereas high-density polyethylene (HDPE) contains few branches. Substances such as glass that melt at relatively low temperatures can also be formed into fibers, producing *fiberglass*.



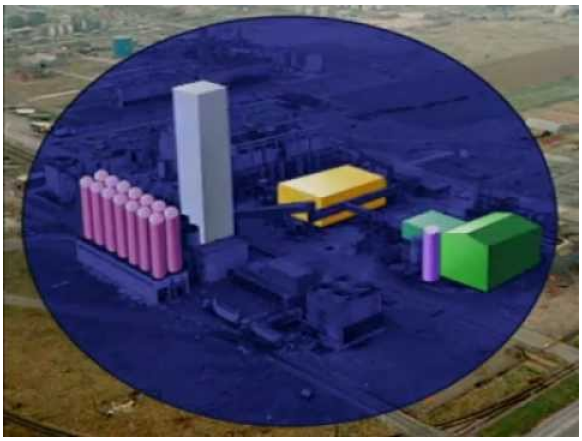


Figure 8.8.4 Commercial Polyethene production: *A video discussing the commercial production of polyethene from the Royal Society of Chemistry*

Because most synthetic fibers are neither soluble nor low melting, multistep processes are required to manufacture them and form them into objects. Graphite fibers are formed by heating a precursor polymer at high temperatures to decompose it, a process called pyrolysisA high-temperature decomposition reaction that can be used to form fibers of synthetic polymers.. The usual precursor for graphite is polyacrylonitrile, better known by its trade name—Orlon. A similar approach is used to prepare fibers of silicon carbide using an organosilicon precursor such as polydimethylsilane $\{[–(CH_3)_2Si–]_n\}$. A new type of fiber consisting of carbon nanotubes, hollow cylinders of carbon just one atom thick, is lightweight, strong, and impact resistant. Its performance has been compared to that of Kevlar, and it is being considered for use in body armor, flexible solar panels, and bombproof trash bins, among other uses.

Because there are no good polymer precursors for elemental boron or boron nitride, these fibers have to be prepared by time-consuming and costly indirect methods. Even though boron fibers are about eight times stronger than metallic aluminum and 10% lighter, they are significantly more expensive. Consequently, unless an application requires boron's greater resistance to oxidation, these fibers cannot compete with less costly graphite fibers.

Example 8.8.1

Polyethylene is used in a wide variety of products, including beach balls and the hard plastic bottles used to store solutions in a chemistry laboratory. Which of these products is formed from the more highly branched polyethylene?

Given: type of polymer

Asked for: application

Strategy:

Determine whether the polymer is LDPE, which is used in applications that require flexibility, or HDPE, which is used for its strength and rigidity.

Solution:

A highly branched polymer is less dense and less rigid than a relatively unbranched polymer. Thus hard, strong polyethylene objects such as bottles are made of HDPE with relatively few branches. In contrast, a beach ball must be flexible so it can be inflated. It is therefore made of highly branched LDPE.

Exercise

Which products are manufactured from LDPE and which from HPDE?

1. lawn chair frames
2. rope
3. disposable syringes
4. automobile protective covers

Answer:

1. HDPE
2. LDPE
3. HDPE
4. LDPE

Summary

Polymers are giant molecules that consist of long chains of units called **monomers** connected by covalent bonds. **Polymerization** is the process of linking monomers together to form a polymer. **Plastic** is the property of a material that allows it to be molded. Biological polymers formed from amino acid residues are called **peptides** or **proteins**, depending on their size. **Enzymes** are proteins that catalyze a biological reaction. A particle that is more than a hundred times longer than it is wide is a **fiber**, which can be formed by a high-temperature decomposition reaction called **pyrolysis**.

Key Takeaway

- Polymers are giant molecules formed from addition or condensation reactions and can be classified as either biological or synthetic polymers.

Conceptual Problems

1. How are amino acids and proteins related to monomers and polymers? Draw the general structure of an amide bond linking two amino acid residues.
2. Although proteins and synthetic polymers (such as nylon) both contain amide bonds, different terms are used to describe the two types of polymer. Compare and contrast the terminology used for the
    1. smallest repeating unit.
    2. covalent bond connecting the units.

Contributors

- Anonymous

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Nylon synthesis from MA Bakken @ YouTube

Polyethylene production from Royal Society of Chemistry @ YouTube

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Chapter 8.9: Modern Materials

Learning Objective

- To become familiar with the properties of some contemporary materials.

In addition to polymers, other materials, such as ceramics, high-strength alloys, and composites, play a major role in almost every aspect of our lives. Until relatively recently, steel was used for any application that required an especially strong and durable material, such as bridges, automobiles, airplanes, golf clubs, and tennis rackets. In the last 15 to 20 years, however, graphite or boron fiber golf clubs and tennis rackets have made wood and steel obsolete for these items. Likewise, a modern jet engine now is largely composed of Ti and Ni by weight rather than steel (Table 8.9.1). The percentage of iron in wings and fuselages is similarly low, which indicates the extent to which other materials have supplanted steel. The Chevrolet Corvette introduced in 1953 was considered unusual because its body was constructed of fiberglass, a composite material, rather than steel; by 1992, Jaguar fabricated an all-aluminum limited-edition vehicle. In fact, the current models of many automobiles have engines that are made mostly of aluminum rather than steel. In this section, we describe some of the chemistry behind three classes of contemporary materials: ceramics, superalloys, and composites.

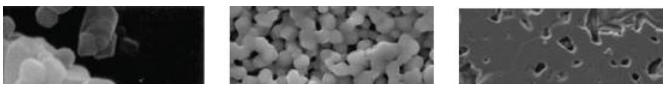
Table 8.9.1 The Approximate Elemental Composition of a Modern Jet Engine

Element	Percentage by Mass
titanium	38
nickel	37
chromium	12
cobalt	6
aluminum	3
niobium	1
tantalum	0.025

Ceramics

A ceramicAny nonmetallic inorganic solid that is strong eneough to be used in structural applications. is any nonmetallic, inorganic solid that is strong enough for use in structural applications. Traditional ceramics, which are based on metal silicates or aluminosilicates, are the materials used to make pottery, china, bricks, and concrete. Modern ceramics contain a much wider range of components and can be classified as either *ceramic oxides*, which are based on metal oxides such as alumina (Al_2O_3), zirconia (ZrO_2), and beryllia (BeO), or *nonoxide ceramics*, which are based on metal carbides such as silicon carbide (carborundum, SiC) and tungsten carbide (WC), or nitrides like silicon nitride (Si_3N_4) and boron nitride (BN).

All modern ceramics are hard, lightweight, and stable at very high temperatures. Unfortunately, however, they are also rather brittle, tending to crack or break under stresses that would cause metals to bend or dent. Thus a major challenge for materials scientists is to take advantage of the desirable properties of ceramics, such as their thermal and oxidative stability, chemical inertness, and toughness, while finding ways to decrease their brittleness to use them in new applications. Few metals can be used in jet engines, for example, because most lose mechanical strength and react with oxygen at the very high operating temperatures inside the engines (approximately 2000°C). In contrast, ceramic oxides such as Al_2O_3 cannot react with oxygen regardless of the temperature because aluminum is already in its highest possible oxidation state (Al^{3+}). Even nonoxide ceramics such as silicon and boron nitrides and silicon carbide are essentially unreactive in air up to about 1500°C. Producing a high-strength ceramic for service use involves a process called sinteringA process that fuses the grains of a ceramic into a dense, strong material. Sintering is used to produce high-strength ceramics., which fuses the grains into a dense and strong material (Figure 8.9.2).



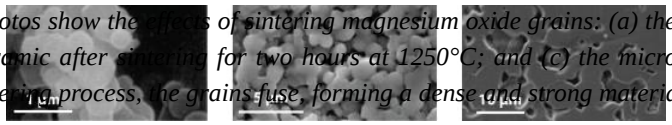


Figure 8.9.2 Sintering *These photos show the effects of sintering magnesium oxide grains: (a) the microstructure before sintering; (b) the microstructure of the ceramic after sintering for two hours at 1250°C; and (c) the microstructure after sintering for two hours at 1450°C. During the sintering process, the grains fuse, forming a dense and strong material.*

Note the Pattern

Ceramics are hard, lightweight, and able to withstand high temperatures, but they are also brittle.

One of the most widely used raw materials for making ceramics is clay. Clay minerals consist of hydrated alumina (Al_2O_3) and silica (SiO_2) that have a broad range of impurities, including barium, calcium, sodium, potassium, and iron. Although the structures of clay minerals are complicated, they all contain layers of metal atoms linked by oxygen atoms. Water molecules fit between the layers to form a thin film of water. When hydrated, clays can be easily molded, but during high-temperature heat treatment, called *firing*, a dense and strong ceramic is produced.

Because ceramics are so hard, they are easily contaminated by the material used to grind them. In fact, the ceramic often grinds the metal surface of the mill almost as fast as the mill grinds the ceramic! The sol-gel processA process used to manufacture ceramics by producing fine powders of ceramic oxides with uniformly sized particles. was developed to address this problem. In this process, a water-soluble precursor species, usually a metal or semimetal alkoxide [$M(OR)_n$] undergoes a hydrolysis reaction to form a cloudy aqueous dispersion called a *sol*. The sol contains particles of the metal or semimetal hydroxide [$M(OH)_n$], which are typically 1–100 nm in diameter. As the reaction proceeds, molecules of water are eliminated from between the $M(OH)_n$ units in a condensation reaction, and the particles fuse together, producing oxide bridges, M–O–M. Eventually, the particles become linked in a three-dimensional network that causes the solution to form a *gel*, similar to a gelatin dessert. Heating the gel to 200°C–500°C causes more water to be eliminated, thus forming small particles of metal oxide that can be amazingly uniform in size. This chemistry starts with highly pure $SiCl_4$ and proceeds via the following reactions starting with the alkoxide formation

$$SiCl_4\,(s) + 4CH_3CH_2OH\,(l) + 4NH_3\,(g) \rightarrow SiO\,(OCH_2CH_3)_4\,(s) + 4NH_4Sl\,(s) \tag{12.8.1}$$

and then the hydrolysis of the alkoxide

$$SiO\,(OCH_2CH_3)_4\,(s) + 4H_2O\,(l) \rightarrow (HO)_3\,Si - OH\,(s) + 4CH_3CH_2OH\,(aq) \tag{12.8.2}$$

ending with the condensation

$$\begin{gathered}(HO_3)\,Si - OH\,(s) + nHO - Si\,(OH)_3\,(s) \\ \rightarrow (HO_3)\,Si\,(-O-Si(OH)_3)_n\,(s) + nH_2O\,(l)\end{gathered} \tag{12.8.3}$$

Nature uses the same process to create opal gemstones.

Superalloys

SuperalloysA high-strength alloy based on cobalt, nickel, and iron, often of complex composition, that is used in applications that require mechanical strength, high surface stability, and resistance to high temperatures. are high-strength alloys, often with a complex composition, that are used in systems requiring mechanical strength, high surface stability (minimal flaking or pitting), and resistance to high temperatures. The aerospace industry, for example, requires materials that have high strength-to-weight ratios to improve the fuel efficiency of advanced propulsion systems, and these systems must operate safely at temperatures greater than 1000°C.

Note the Pattern

Superalloys are used in systems requiring mechanical strength, minimal flaking or pitting, and high-temperature resistance.

Although most superalloys are based on nickel, cobalt, or iron, other metals are used as well. Pure nickel or cobalt is relatively easily oxidized, but adding small amounts of other metals (Al, Co, Cr, Mo, Nb, Ti, and W) results in an alloy that has superior properties. Consequently, most of the internal parts of modern gas turbine jet engines are now made of superalloys based on either nickel (used in blades and disks) or cobalt (used in vanes, combustion chamber liners, and afterburners). The cobalt-based superalloys are not as strong as the nickel-based ones, but they have excellent corrosion resistance at high temperatures.

Other alloys, such as aluminum–lithium and alloys based on titanium, also have applications in the aerospace industry. Because aluminum–lithium alloys are lighter, stiffer, and more resistant to fatigue at high temperatures than aluminum itself, they are used

in engine parts and in the metal “skins” that cover wings and bodies. Titanium’s high strength, corrosion resistance, and lightweight properties are equally desirable for applications where minimizing weight is important (as in airplanes). Unfortunately, however, metallic titanium reacts rapidly with air at high temperatures to form TiN and TiO_2. The welding of titanium or any similar processes must therefore be carried out in an argon or inert gas atmosphere, which adds significantly to the cost. Initially, titanium and its alloys were primarily used in military applications, but more recently, they have been used as components of the airframes of commercial planes, in ship structures, and in biological implants.

Composite Materials

Composite materialsA material that consists of at least two distinct phases: the matrix (which constitutes the bulk of the material) and fibers or granules that are embedded within the matrix. have at least two distinct components: the matrix (which constitutes the bulk of the material) and fibers or granules that are embedded within the matrix and limit the growth of cracks by pinning defects in the bulk material (Figure 8.9.3). The resulting material is stronger, tougher, stiffer, and more resistant to corrosion than either component alone. Composites are thus the nanometer-scale equivalent of reinforced concrete, in which steel rods greatly increase the mechanical strength of the cement matrix, and are extensively used in the aircraft industry, among others. For example, the Boeing 777 is 9% composites by weight, whereas the newly developed Boeing 787 is 50% composites by weight. Not only does the use of composite materials reduce the weight of the aircraft, and therefore its fuel consumption, but it also allows new design concepts because composites can be molded. Moreover, by using composites in the Boeing 787 multiple functions can be integrated into a single system, such as acoustic damping, thermal regulation, and the electrical system.

Three distinct types of composite material are generally recognized, distinguished by the nature of the matrix. These are polymer-matrix composites, metal-matrix composites, and ceramic-matrix composites.

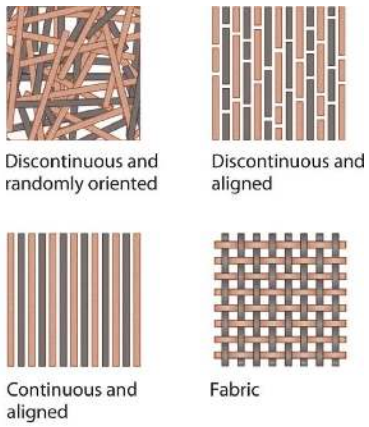


Figure 8.9.3 Some Possible Arrangements of Fibers in Fiber-Reinforced Composite Materials *The arrangements shown range from discontinuous and randomly oriented to continuous and aligned. The fibers limit the growth of cracks by pinning defects within the matrix.*

Note the Pattern

Composites are stronger, tougher, stiffer, and more resistant to corrosion than their components alone.

Fiberglass is a polymer-matrix compositeA compositie that consists of reinforcing fibers embedded in a polymer matrix. that consists of glass fibers embedded in a polymer, forming tapes that are then arranged in layers impregnated with epoxy. The result is a strong, stiff, lightweight material that is resistant to chemical degradation. It is not strong enough, however, to resist cracking or puncturing on impact. Stronger, stiffer polymer-matrix composites contain fibers of carbon (graphite), boron, or polyamides such as Kevlar. High-tech tennis rackets and golf clubs as well as the skins of modern military aircraft such as the “stealth” F-117A fighters and B-2 bombers are made from both carbon fiber–epoxy and boron fiber–epoxy composites. Compared with metals, these materials are 25%–50% lighter and thus reduce operating costs. Similarly, the space shuttle payload bay doors and panels are made of a carbon fiber–epoxy composite. The structure of the Boeing 787 has been described as essentially one giant macromolecule, where everything is fastened through cross-linked chemical bonds reinforced with carbon fiber.

Metal-matrix compositesA composite that consists of reinforcing fibers embedded in a metal or a metal alloy matrix. consist of metals or metal alloys reinforced with fibers. They offer significant advantages for high-temperature applications but pose major manufacturing challenges. For example, obtaining a uniform distribution and alignment of the reinforcing fibers can be difficult, and because organic polymers cannot survive the high temperatures of molten metals, only fibers composed of boron, carbon, or ceramic (such as silicon carbide) can be used. Aluminum alloys reinforced with boron fibers are used in the aerospace industry, where their strength and lightweight properties make up for their relatively high cost. The skins of hypersonic aircraft and structural units in the space shuttle are made of metal-matrix composites.

Ceramic-matrix compositesA composite consisting of reinforcing fibers embedded in a ceramic matrix. contain ceramic fibers in a ceramic matrix material. A typical example is alumina reinforced with silicon carbide fibers. Combining the two very high-melting-point materials results in a composite that has excellent thermal stability, great strength, and corrosion resistance, while the SiC fibers reduce brittleness and cracking. Consequently, these materials are used in very high-temperature applications, such as the leading edge of wings of hypersonic airplanes and jet engine parts. They are also used in the protective ceramic tiles on the space shuttle, which contain short fibers of pure SiO_2 mixed with fibers of an aluminum–boron–silicate ceramic. These tiles are excellent thermal insulators and extremely light (their density is only about 0.2 g/cm^3). Although their surface reaches a temperature of about 1250°C during reentry into Earth's atmosphere, the temperature of the underlying aluminum alloy skin stays below 200°C.

Example 8.9.1

An engineer is tasked with designing a jet ski hull. What material is most suited to this application? Why?

Given: design objective

Asked for: most suitable material

Strategy:

Determine under what conditions the design will be used. Then decide what type of material is most appropriate.

Solution:

A jet ski hull must be lightweight to maximize speed and fuel efficiency. Because of its use in a marine environment, it must also be resistant to impact and corrosion. A ceramic material provides rigidity but is brittle and therefore tends to break or crack under stress, such as when it impacts waves at high speeds. Superalloys provide strength and stability, but a superalloy is probably too heavy for this application. Depending on the selection of metals, it might not be resistant to corrosion in a marine environment either. Composite materials, however, provide strength, stiffness, and corrosion resistance; they are also lightweight materials. This is not a high-temperature application, so we do not need a metal-matrix composite or a ceramic-matrix composite. The best choice of material is a polymer-matrix composite with Kevlar fibers to increase the strength of the composite on impact.

Exercise

In designing a new generation of space shuttle, National Aeronautics and Space Administration (NASA) engineers are considering thermal-protection devices to protect the skin of the craft. Among the materials being considered are titanium- or nickel-based alloys and silicon-carbide ceramic reinforced with carbon fibers. Why are these materials suitable for this application?

Answer: Ti- or Ni-based alloys have a high strength-to-weight ratio, resist corrosion, and are safe at high temperatures. Reinforced ceramic is lightweight; has high thermal and oxidative stability; and is chemically inert, tough, and impact resistant.

Summary

Ceramics are nonmetallic, inorganic solids that are typically strong; they have high melting points but are brittle. The two major classes of modern ceramics are ceramic oxides and nonoxide ceramics, which are composed of nonmetal carbides or nitrides. The production of ceramics generally involves pressing a powder of the material into the desired shape and sintering at a temperature just below its melting point. The necessary fine powders of ceramic oxides with uniformly sized particles can be produced by the **sol-gel process**. **Superalloys** are new metal phases based on cobalt, nickel, or iron that exhibit unusually high temperature stability and resistance to oxidation. **Composite materials** consist of at least two phases: a matrix that constitutes the bulk of the material and fibers or granules that act as a reinforcement. **Polymer-matrix composites** have reinforcing fibers embedded in a polymer

matrix. **Metal-matrix composites** have a metal matrix and fibers of boron, graphite, or ceramic. **Ceramic-matrix composites** use reinforcing fibers, usually also ceramic, to make the matrix phase less brittle.

Key Takeaway

- Materials that have contemporary applications include ceramics, high-strength alloys, and composites, whose properties can be modified as needed.

Conceptual Problems

1. Can a compound based on titanium oxide qualify as a ceramic material? Explain your answer.
2. What features make ceramic materials attractive for use under extreme conditions? What are some potential drawbacks of ceramics?
3. How do composite materials differ from the other classes of materials discussed in this chapter? What advantages do composites have versus other materials?
4. How does the matrix control the properties of a composite material? What is the role of an additive in determining the properties of a composite material?

Contributors

- Anonymous

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Chapter 8. 10: End of Chapter Material

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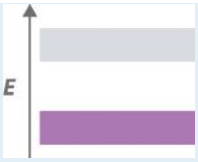
APPLICATION PROBLEMS

Problems marked with a ♦ involve multiple concepts.

1. ♦ Cadmium selenide (CdSe) is a semiconductor used in photoconductors and photoelectric cells that conduct electricity when illuminated. In a related process, a CdSe crystal can absorb enough energy to excite electrons from the valence band to the conduction band, and the excited electrons can return to the valence band by emitting light. The relative intensity and peak wavelength of the emitted light in one experiment are shown in the following table:

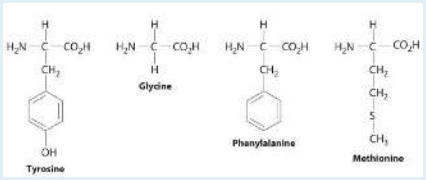
Relative Intensity (%)	Wavelength (nm)	Temperature (°C)
100	720	23
50	725	45
10	730	75

   a. Explain why the emitted light shifts to longer wavelength at higher temperatures. (Hint: consider the expansion of the crystal and the resulting changes in orbital interactions when heated.)
   b. Why does the relative intensity of the emitted light decrease as the temperature increases?
2. A large fraction of electrical energy is currently lost as heat during transmission due to the electrical resistance of transmission wires. How could superconducting technology improve the transmission of electrical power? What are some potential drawbacks of this technology?
3. Light-emitting diodes (LEDs) are semiconductor-based devices that are used in consumer electronics products ranging from digital clocks to fiber-optic telephone transmission lines. The color of the emitted light is determined in part by the band gap of the semiconductor. Electrons can be promoted to the conduction band and return to the valence band by emitting light or by increasing the magnitude of atomic vibrations in the crystal, which increases its temperature. If you wanted to increase the efficiency of an LED display, and thereby the intensity of the emitted light, would you increase or decrease the operating temperature of the LED? Explain your answer.
4. ♦ Strips of pure Au and Al are often used in close proximity to each other on circuit boards. As the boards become warm during use, however, the metals can diffuse, forming a purple alloy known as “the purple plague” between the strips. Because the alloy is electrically conductive, the board short-circuits. A structural analysis of the purple alloy showed that its structure contained a face-centered cubic (fcc) lattice of atoms of one element, with atoms of the other element occupying tetrahedral holes. What type of alloy is this? Which element is most likely to form the fcc lattice? Which element is most likely to occupy the tetrahedral holes? Explain your answers. What is the empirical formula of the “purple plague”?
5. ♦ Glasses are mixtures of oxides, the main component of which is silica (SiO_2). Silica is called the glass *former*, while additives are referred to as glass *modifiers*. The crystalline lattice of the glass former breaks down during heating, producing the random atomic arrangements typical of a liquid. Adding a modifier and cooling the melt rapidly produces a glass. How does the three-dimensional structure of the glass differ from that of the crystalline glass former? Would you expect the melting point of a glass to be higher or lower than that of pure SiO_2? Lead glass, a particular favorite of the Romans, was formed by adding lead oxide as the modifier. Would you expect lead glass to be more or less dense than soda-lime glass formed by adding sodium and potassium salts as modifiers?
6. Many glasses eventually crystallize, rendering them brittle and opaque. Modifying agents such as TiO_2 are frequently added to molten glass to reduce their tendency to crystallize. Why does the addition of small amounts of TiO_2 stabilize the amorphous structure of glass?
7. ♦ The carbon–carbon bond distances in polyacetylene $(–CH=CH–)_n$ alternate between short and long, resulting in the following band structure:



a. Is polyacetylene a metal, a semiconductor, or an insulator?
b. Based on its band structure, how would treating polyacetylene with a potent oxidant affect its electrical conductivity? What would be the effect of treating polyacetylene with small amounts of a powerful reductant? Explain your answers.

8. Enkephalins are pentapeptides, short biopolymers that are synthesized by humans to control pain. Enkephalins bind to certain receptors in brain cells, which are also known to bind morphine and heroin. One enkephalin has the structure tyrosine–glycine–glycine–phenylalanine–methionine. Draw its structure.



9. A polymerization reaction is used to synthesize Saran, a flexible material used in packaging film and seat covers. The monomeric unit for Saran is 1,1-dichloroethylene (CH_2=CCl_2), also known as vinylidene chloride. Draw a reasonable structure for the polymer. Why do pieces of Saran "cling" to one another when they are brought in contact?
10. Polymers are often amorphous solids. Like other materials, polymers can also undergo phase changes. For example, many polymers are flexible above a certain temperature, called the *glass-transition temperature* (T_g). Below the glass transition temperature, the polymer becomes hard and brittle. Biomedical devices that replace or augment parts of the human body often contain a wide variety of materials whose properties must be carefully controlled.
    a. Polydimethylsiloxane has a T_g of −123°C, whereas poly(methylmethacrylate) has a T_g of 105°C. Which of these polymers is likely to be used in dentures, and which is likely to be used for soft-tissue replacement?
    b. If you were designing biomedical devices, which class of biomaterials (alloys, ceramics, or polymers) would you consider for finger joint replacements, eyeball replacements, windpipe replacements, shoulder joint replacements, and bridging bone fractures? Explain your answers.

Contributors

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CHAPTER OVERVIEW

Chapter 9: Solutions

- Chapter 9.1: Forming Soutions
- Chapter 9.2: Solubility and Structure
- Chapter 9.3: Units for Concentration
- Chapter 9.4:Temperature and Pressure Effects
- Chapter 9.5: Colligative Properties
- Chapter 9.6: Aggregate Particles
- Chapter 9.7: End of Chapter Materials

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Chapter 9.1: Forming Soutions

Learning Objective

- To understand the nature of solutions.

In all solutions, whether gaseous, liquid, or solid, the substance present in the greatest amount is the *solvent*, and the substance or substances present in lesser amounts are the *solute(s)*. The solute does not have to be in the same physical state as the solvent, but the physical state of the solvent usually determines the state of the solution. As long as the solute and solvent combine to give a homogeneous solution, the solute is said to be *soluble* in the solvent. Table.9.1.1 lists some common examples of gaseous, liquid, and solid solutions and identifies the physical states of the solute and solvent in each.

Table 9.1.1 Types of Solutions

Solution	Solute	Solvent	Examples
gas	gas	gas	air, natural gas
liquid	gas	liquid	seltzer water (CO_2 gas in water)
liquid	liquid	liquid	alcoholic beverage (ethanol in water), gasoline
liquid	solid	liquid	tea, salt water
solid	gas	solid	H_2 in Pd (used for H_2 storage)
solid	solid	liquid	mercury in silver or gold (amalgam often used in dentistry)

Forming a Solution

The formation of a solution from a solute and a solvent is a physical process, not a chemical one. That is, both solute and solvent can be recovered in chemically unchanged forms using appropriate separation methods. For example, solid zinc nitrate dissolves in water to form an aqueous solution of zinc nitrate:

$$ZnNO_3\,(s) \xrightarrow{H_2O(l)} Zn^{2+}\,(aq) + 2NO_3^-\,(aq)$$

Because $Zn(NO_3)_2$ can be recovered easily by evaporating the water, this is a physical process. In contrast, metallic zinc *appears* to dissolve in aqueous hydrochloric acid. In fact, the two substances undergo a chemical reaction to form an aqueous solution of zinc chloride with evolution of hydrogen gas:

$$Zn\,(s) + 2H^+\,(aq) + 2Cl^-\,(aq) \rightarrow Zn^{2+}\,(aq) + 2Cl^-\,(aq) + H_2\,(g)$$

Solvation is Not Reaction

Dissolution of a solute in a solvent to form a solution does not involve a chemical transformation.

When the solution evaporates, we do not recover metallic zinc, so we cannot say that metallic zinc is *soluble* in aqueous hydrochloric acid because it is chemically transformed when it dissolves. *The dissolution of a solute in a solvent to form a solution does not involve a chemical transformation.*

Substances that form a single homogeneous phase in all proportions are said to be completely miscibleCapable of forming a single homogeneous phase, regardless of the proportions with which the substances are mixed. in one another. Ethanol and water are miscible, just as mixtures of gases are miscible. If two substances are essentially insoluble in each other, such as oil and water, they are *immiscible*. Examples of gaseous solutions include Earth's atmosphere and natural gas.

Aqueous Solutions

The solvent in aqueous solutions is water, which makes up about 70% of the mass of the human body and is essential for life. Many of the chemical reactions that keep us alive depend on the interaction of water molecules with dissolved compounds. Moreover, as we will discuss in Chapter 15.1 the presence of large amounts of water on Earth's surface helps maintain its surface temperature in

a range suitable for life. In this section, we describe some of the interactions of water with various substances and introduce you to the characteristics of aqueous solutions.

Polar Substances

As shown in Figure 9.1.1, the individual water molecule consists of two hydrogen atoms bonded to an oxygen atom in a bent (V-shaped) structure. As is typical of group 16 elements, the oxygen atom in each O–H covalent bond attracts electrons more strongly than the hydrogen atom does. Consequently, the oxygen and hydrogen nuclei do not equally share electrons. Instead, hydrogen atoms are electron poor compared with a neutral hydrogen atom and have a partial positive charge, which is indicated by δ^+. The oxygen atom, in contrast, is more electron rich than a neutral oxygen atom, so it has a partial negative charge. This charge must be twice as large as the partial positive charge on each hydrogen for the molecule to have a net charge of zero. Thus its charge is indicated by $2\delta^-$. This unequal distribution of charge creates a polar bondA chemical bond in which there is an unequal distribution of charge between the bonding atoms., in which one portion of the molecule carries a partial negative charge, while the other portion carries a partial positive charge (Figure 9.1.1). Because of the arrangement of polar bonds in a water molecule, water is described as a polar substance.

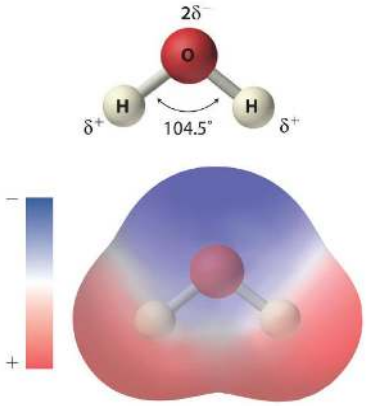


Figure 9.1.1 The Polar Nature of Water *Each water molecule consists of two hydrogen atoms bonded to an oxygen atom in a bent (V-shaped) structure. Because the oxygen atom attracts electrons more strongly than the hydrogen atoms do, the oxygen atom is partially negatively charged ($2\delta^-$; blue) and the hydrogen atoms are partially positively charged (δ^+; red). For the molecule to have a net charge of zero, the partial negative charge on oxygen must be twice as large as the partial positive charge on each hydrogen.*

Because of the asymmetric charge distribution in the water molecule, adjacent water molecules are held together by attractive electrostatic ($\delta^+ \ldots \delta^-$) interactions between the partially negatively charged oxygen atom of one molecule and the partially positively charged hydrogen atoms of adjacent molecules (Figure 9.1.2). Energy is needed to overcome these electrostatic attractions. In fact, without them, water would evaporate at a much lower temperature, and neither Earth's oceans nor we would exist!

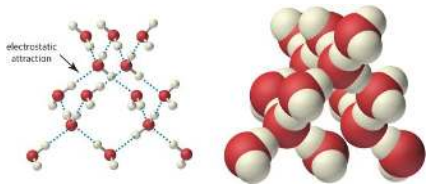


Figure 9.1.2 The Structure of Liquid Water*Two views of a water molecule are shown: (a) a ball-and-stick structure and (b) a space-filling model. Water molecules are held together by electrostatic attractions (dotted lines) between the partially negatively charged oxygen atom of one molecule and the partially positively charged hydrogen atoms on adjacent molecules. As a result, the water molecules in liquid water form transient networks with structures similar to that shown. Because the interactions between water molecules are continually breaking and reforming, liquid water does not have a single fixed structure.*

As you learned in Section 4.1, ionic compounds such as sodium chloride (NaCl) are also held together by electrostatic interactions—in this case, between oppositely charged ions in the highly ordered solid, where each ion is surrounded by ions of the opposite charge in a fixed arrangement. In contrast to an ionic solid, the structure of liquid water is not completely ordered because the interactions between molecules in a liquid are constantly breaking and reforming.

The unequal charge distribution in polar liquids such as water makes them good solvents for ionic compounds. When an ionic solid dissolves in water, the ions *dissociate*. That is, the partially negatively charged oxygen atoms of the H_2O molecules surround the cations (Na^+ in the case of NaCl), and the partially positively charged hydrogen atoms in H_2O surround the anions (Cl^-; Figure 9.1.3). Individual cations and anions that are each surrounded by their own shell of water molecules are called hydrated ionsIndividual cations and anions that are each surrounded by their own shell of water molecules.. We can describe the dissolution of NaCl in water as

$$NaCl(s) \xrightarrow{H_2O(l)} Na^+(aq) + Cl^-(aq)$$

where (aq) indicates that Na^+ and Cl^- are hydrated ions.

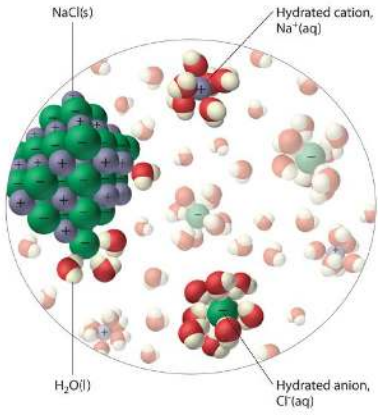


Figure 9.1.3 The Dissolution of Sodium Chloride in Water *An ionic solid such as sodium chloride dissolves in water because of the electrostatic attraction between the cations (Na^+) and the partially negatively charged oxygen atoms of water molecules, and between the anions (Cl^-) and the partially positively charged hydrogen atoms of water.*

Note the Pattern

Polar liquids are good solvents for ionic compounds.

Electrolytes

When electricity, in the form of an *electrical potential*, is applied to a solution, ions in solution migrate toward the oppositely charged rod or plate to complete an electrical circuit, whereas neutral molecules in solution do not (Figure 9.1.4). Thus solutions that contain ions conduct electricity, while solutions that contain only neutral molecules do not. Electrical current will flow through the circuit shown in Figure 9.1.4 and the bulb will glow *only* if ions are present. The lower the concentration of ions in solution, the weaker the current and the dimmer the glow. Pure water, for example, contains only very low concentrations of ions, so it is a poor electrical conductor.

Note the Pattern

Solutions that contain ions conduct electricity.



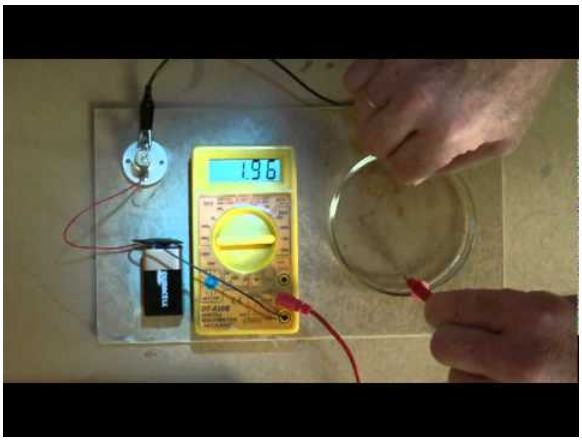


Figure 9.1.4 The Effect of Ions on the Electrical Conductivity of Water *An electrical current will flow and light the bulb only if the solution contains ions. (a) Deionized or distilled water or an aqueous solution of a nonelectrolyte allows almost no current to flow. (b) A weak electrolyte such as tap or river water produces a few ions, allowing some current to flow. (c) A strong electrolyte formed by adding salt produces many ions, allowing more current to flow. Video from MDR Science Academy*

An electrolyteAny compound that can form ions when dissolved in water (c.f. nonelectrolytes). Electrolytes may be strong or weak. is any compound that can form ions when it dissolves in water. When strong electrolytesAn electrolyte that dissociates completely into ions when dissolved in water, thus producing an aqueous solution that conducts electricity very well. dissolve, the constituent ions dissociate completely due to strong electrostatic interactions with the solvent, producing aqueous solutions that conduct electricity very well (Figure 9.1.4). Examples include ionic compounds such as barium chloride ($BaCl_2$) and sodium hydroxide (NaOH), which are both strong electrolytes and dissociate as follows:

$$BaCl_2(s) \xrightarrow{H_2O(l)} Ba^{2+}(aq) + 2Cl^-(aq)$$

$$NaOH(s) \xrightarrow{H_2O(l)} Na^+(aq) + OH^-(aq)$$

The single arrows from reactant to products in Equation 9.1.2 and Equation 9.1.3 indicate that dissociation is complete.

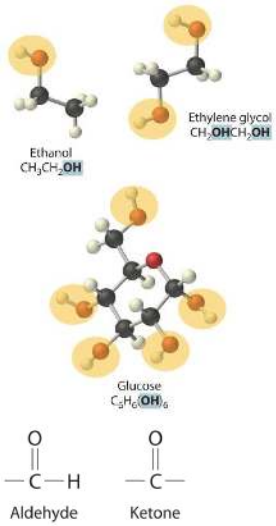
When weak electrolytesA compound that produces relatively few ions when dissolved in water, thus producing an aqueous solution that conducts electricity poorly. dissolve, they produce relatively few ions in solution. This does *not* mean that the compounds do not dissolve readily in water; many weak electrolytes contain polar bonds and are therefore very soluble in a polar solvent such as water. They do not completely dissociate to form ions, however, because of their weaker electrostatic interactions with the solvent.

Because very few of the dissolved particles are ions, aqueous solutions of weak electrolytes do not conduct electricity as well as solutions of strong electrolytes. One such compound is acetic acid (CH_3CO_2H), which contains the $–CO_2H$ unit. Although it is soluble in water, it is a weak acid and therefore also a weak electrolyte. Similarly, ammonia (NH_3) is a weak base and therefore a weak electrolyte. The behavior of weak acids and weak bases will be described in more detail when we discuss acid–base reactions in Section 12.5.

NonelectrolytesA substance that dissolves in water to form neutral molecules and has essentially no effect on electrical conductivity. that dissolve in water do so as neutral molecules and thus have essentially no effect on conductivity. Examples of nonelectrolytes that are very soluble in water but that are essentially nonconductive are ethanol, ethylene glycol, glucose, and sucrose, all of which contain the –OH group that is characteristic of alcohols. In Chapter 4, we discussed why alcohols and carboxylic acids behave differently in aqueous solution due to the nature of their electrostatic interactions with the water molecules but we can simply look for the –OH and $–CO_2H$ functional groups when trying to predict whether a substance is a strong electrolyte, a weak electrolyte, or a nonelectrolyte. In addition to alcohols, two other classes of organic compounds that are nonelectrolytes are aldehydesA class of organic compounds that has the general form RCHO, in which the carbon atom of the carbonyl group is bonded to a hydrogen atom and an R group. The R group may be either another hydrogen atom or an alkyl group (c.f. ketone). and ketonesA class of organic compounds with the general form RC(O)R', in which the carbon atom of the carbonyl group is bonded to two alkyl groups (c.f. aldehyde). The alkyl groups may be the same or different., whose general structures are shown here. The distinctions between soluble and insoluble substances and between strong, weak, and nonelectrolytes are illustrated in Figure 9.1.5.

Note the Pattern

Ionic substances and carboxylic acids are electrolytes; alcohols, aldehydes, and ketones are nonelectrolytes.



General structure of an aldehyde and a ketone. Notice that both contain the C=O group.

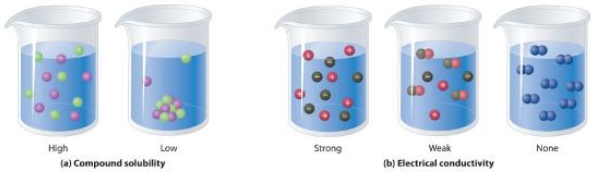
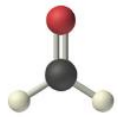


Figure 9.1.5 The Difference between Soluble and Insoluble Compounds (a) and Strong, Weak, and Nonelectrolytes (b)*When a soluble compound dissolves, its constituent atoms, molecules, or ions disperse throughout the solvent. In contrast, the constituents of an insoluble compound remain associated with one another in the solid. A soluble compound is a strong electrolyte if it dissociates completely into ions, a weak electrolyte if it dissociates only slightly into ions, and a nonelectrolyte if it dissolves to produce only neutral molecules.*

Example 9.1.1

Predict whether each compound is a strong electrolyte, a weak electrolyte, or a nonelectrolyte in water.

1. formaldehyde


Formaldehyde, CH_2O

2. cesium chloride

Given: compound

Asked for: relative ability to form ions in water

Strategy:

A Classify the compound as ionic or covalent.

B If the compound is ionic and dissolves, it is a strong electrolyte that will dissociate in water completely to produce a solution that conducts electricity well. If the compound is covalent and organic, determine whether it contains the carboxylic acid group. If the compound contains this group, it is a weak electrolyte. If not, it is a nonelectrolyte.

Solution:

1. **A** Formaldehyde is an organic compound, so it is covalent. **B** It contains an aldehyde group, not a carboxylic acid group, so it should be a nonelectrolyte.
2. **A** Cesium chloride (CsCl) is an ionic compound that consists of Cs^+ and Cl^- ions. **B** Like virtually all other ionic compounds that are soluble in water, cesium chloride will dissociate completely into $Cs^+(aq)$ and $Cl^-(aq)$ ions. Hence it should be a strong electrolyte.

Exercise

Predict whether each compound is a strong electrolyte, a weak electrolyte, or a nonelectrolyte in water.

1. $(CH_3)_2CHOH$ (2-propanol)


2-Propanol (isopropyl alcohol), $(CH_3)_2CHOH$

2. ammonium sulfate

Answer:

1. nonelectrolyte
2. strong electrolyte

Summary

Solutions are homogeneous mixtures of two or more substances whose components are uniformly distributed on a microscopic scale. The component present in the greatest amount is the *solvent*, and the components present in lesser amounts are the *solute(s)*. The formation of a solution from a solute and a solvent is a physical process, not a chemical one. Substances that are **miscible**, such as gases, form a single phase in all proportions when mixed. Substances that form separate phases are *immiscible*. **Solvation** is the process in which solute particles are surrounded by solvent molecules. When the solvent is water, the process is called **hydration**.

Most chemical reactions are carried out in *solutions*, which are homogeneous mixtures of two or more substances. In a solution, a *solute* (the substance present in the lesser amount) is dispersed in a *solvent* (the substance present in the greater amount). *Aqueous*

solutions contain water as the solvent, whereas *nonaqueous solutions* have solvents other than water.

Polar substances, such as water, contain asymmetric arrangements of **polar bonds**, in which electrons are shared unequally between bonded atoms. Polar substances and ionic compounds tend to be most soluble in water because they interact favorably with its structure. In aqueous solution, dissolved ions become **hydrated**; that is, a shell of water molecules surrounds them.

Substances that dissolve in water can be categorized according to whether the resulting aqueous solutions conduct electricity. **Strong electrolytes** dissociate completely into ions to produce solutions that conduct electricity well. **Weak electrolytes** produce a relatively small number of ions, resulting in solutions that conduct electricity poorly. **Nonelectrolytes** dissolve as uncharged molecules and have no effect on the electrical conductivity of water.

Key Takeaway

- Aqueous solutions can be classified as polar or nonpolar depending on how well they conduct electricity.

Conceptual Problems

Answers

1. Homogeneous mixtures: aqueous ammonia, liquid decongestant, vinegar, and gasoline. Heterogeneous mixtures: seawater and fog.
2.
3.
4.
5. Ionic compounds such as NaCl are held together by electrostatic interactions between oppositely charged ions in the highly ordered solid. When an ionic compound dissolves in water, the partially negatively charged oxygen atoms of the H_2O molecules surround the cations, and the partially positively charged hydrogen atoms in H_2O surround the anions. The favorable electrostatic interactions between water and the ions compensate for the loss of the electrostatic interactions between ions in the solid.
6.
7.
8.
9.
10.
11. Acetic acid contains a carboxylic acid group attached to a small alkyl group (a methyl group). Consequently, the polar characteristics of the carboxylic acid group will be dominant, and acetic acid will form a homogenous solution with water.
12. Because most sodium salts are soluble, sodium acetate should form a homogenous solution with water.
13.
14.
15.
16. Because toluene is an aromatic hydrocarbon that lacks polar groups, it is unlikely to form a homogenous solution in water.
17.
18. An *electrolyte* is any compound that can form ions when it dissolves in water. When a strong electrolyte dissolves in water, it dissociates completely to give the constituent ions. In contrast, when a weak electrolyte dissolves in water, it produces relatively few ions in solution.
19.
20.
21.
22.
23.
24.
25.

1. Classify each of the following as a heterogeneous mixture or homogeneous mixture. Explain your rationale in each case.
    1. aqueous ammonia
    2. liquid decongestant
    3. vinegar
    4. seawater
    5. gasoline
    6. fog
2. Solutions and heterogeneous mixtures are at the extreme ends of the solubility scale. Name one type of mixture that is intermediate on this scale. How are the properties of the mixture you have chosen different from those of a solution or a heterogeneous mixture?
3. Classify each process as simple dissolution or a chemical reaction.
    1. a naphthalene mothball dissolving in benzene
    2. a sample of a common drain cleaner that has a mixture of NaOH crystals and Al chunks dissolving in water to give H_2 gas and an aqueous solution of Na^+, OH^-, and Al^{3+} ions
    3. an iron ship anchor slowly dissolving in seawater
    4. sodium metal dissolving in liquid ammonia
4. Classify each process as simple dissolution or a chemical reaction.
    1. a sugar cube dissolving in a cup of hot tea
    2. SO_3 gas dissolving in water to produce sulfuric acid
    3. calcium oxide dissolving in water to produce a basic solution
    4. metallic gold dissolving in a small quantity of liquid mercury
5. You notice that a gas is evolved as you are dissolving a solid in a liquid. Will you be able to recover your original solid by evaporation? Why or why not?

    What are the advantages to carrying out a reaction in solution rather than simply mixing the pure reactants?

    What types of compounds dissolve in polar solvents?
6. Describe the charge distribution in liquid water. How does this distribution affect its physical properties?
7. Must a molecule have an asymmetric charge distribution to be polar? Explain your answer.
8. Why are many ionic substances soluble in water?
9. Explain the phrase *like dissolves like*.
10. What kinds of covalent compounds are soluble in water?
11. Why do most aromatic hydrocarbons have only limited solubility in water? Would you expect their solubility to be higher, lower, or the same in ethanol compared with water? Why?
12. Predict whether each compound will dissolve in water and explain why.
    1. toluene
    2. acetic acid
    3. sodium acetate
    4. butanol
    5. pentanoic acid
13. Predict whether each compound will dissolve in water and explain why.
    1. ammonium chloride
    2. 2-propanol
    3. heptane
    4. potassium dichromate

5. 2-octanol

14. Given water and toluene, predict which is the better solvent for each compound and explain your reasoning.
    1. sodium cyanide
    2. benzene
    3. acetic acid
    4. sodium ethoxide (CH_3CH_2ONa)
15. Of water and toluene, predict which is the better solvent for each compound and explain your reasoning.
    1. *t*-butanol
    2. calcium chloride
    3. sucrose
    4. cyclohexene
16. Compound *A* is divided into three equal samples. The first sample does not dissolve in water, the second sample dissolves only slightly in ethanol, and the third sample dissolves completely in toluene. What does this suggest about the polarity of *A*?
17. You are given a mixture of three solid compounds—*A*, *B*, and *C*—and are told that *A* is a polar compound, *B* is slightly polar, and *C* is nonpolar. Suggest a method for separating these three compounds.
18. A laboratory technician is given a sample that contains only sodium chloride, sucrose, and cyclodecanone (a ketone). You must tell the technician how to separate these three compounds from the mixture. What would you suggest?
19. Many over-the-counter drugs are sold as ethanol/water solutions rather than as purely aqueous solutions. Give a plausible reason for this practice.
20. What distinguishes a weak electrolyte from a strong electrolyte?
21. Which organic groups result in aqueous solutions that conduct electricity?
22. It is considered highly dangerous to splash barefoot in puddles during a lightning storm. Why?
23. Which solution(s) would you expect to conduct electricity well? Explain your reasoning.
    1. an aqueous solution of sodium chloride
    2. a solution of ethanol in water
    3. a solution of calcium chloride in water
    4. a solution of sucrose in water
24. Which solution(s) would you expect to conduct electricity well? Explain your reasoning.
    1. an aqueous solution of acetic acid
    2. an aqueous solution of potassium hydroxide
    3. a solution of ethylene glycol in water
    4. a solution of ammonium chloride in water
25. Which of the following is a strong electrolyte, a weak electrolyte, or a nonelectrolyte in an aqueous solution? Explain your reasoning.
    1. potassium hydroxide
    2. ammonia
    3. calcium chloride
    4. butanoic acid
26. Which of the following is a strong electrolyte, a weak electrolyte, or a nonelectrolyte in an aqueous solution? Explain your reasoning.
    1. magnesium hydroxide
    2. butanol
    3. ammonium bromide

4. pentanoic acid

27. Which of the following is a strong electrolyte, a weak electrolyte, or a nonelectrolyte in aqueous solution? Explain your reasoning.

    1. H_2SO_4
    2. diethylamine
    3. 2-propanol
    4. ammonium chloride
    5. propanoic acid

Answers

1. Homogeneous mixtures: aqueous ammonia, liquid decongestant, vinegar, and gasoline. Heterogeneous mixtures: seawater and fog.
2.
3.
4.
5.

Contributors

- Anonymous

Modified by Joshua Halpern, Scott Sinex and Scott Johnson

Conductivity video from science videos @ YouTube

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Chapter 9.2: Solubility and Structure

Learning Objective

- To understand the relationship between solubility and molecular structure.

When a solute dissolves, its individual atoms, molecules, or ions interact with the solvent, become solvated, and are able to diffuse independently throughout the solution (part (a) in Figure 9.2.1). This is not, however, a unidirectional process. If the molecule or ion happens to collide with the surface of a particle of the undissolved solute, it may adhere to the particle in a process called *crystallization*. Dissolution and crystallization continue as long as excess solid is present, resulting in a *dynamic equilibrium* analogous to the equilibrium that maintains the vapor pressure of a liquid. (For more information about vapor pressure, see Section 7.4) We can represent these opposing processes as follows:

$$\textit{solute} + \textit{solvent} \rightleftharpoons \textit{crystallization dissolution solution}$$

Although the terms *precipitation* and *crystallization* are both used to describe the separation of solid solute from a solution, *crystallization* refers to the formation of a solid with a well-defined crystalline structure, whereas *precipitation* refers to the formation of any solid phase, often one with very small particles.

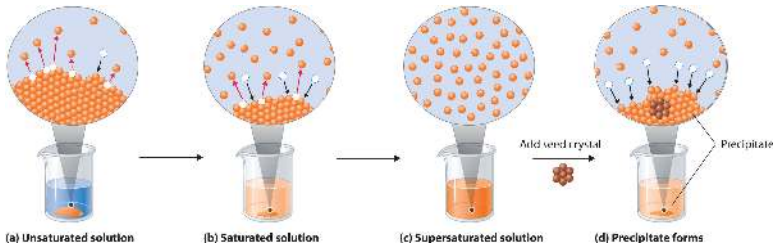


Figure 9.2.1 Dissolution and Precipitation *(a) When a solid is added to a solvent in which it is soluble, solute particles leave the surface of the solid and become solvated by the solvent, initially forming an unsaturated solution. (b) When the maximum possible amount of solute has dissolved, the solution becomes saturated. If excess solute is present, the rate at which solute particles leave the surface of the solid equals the rate at which they return to the surface of the solid. (c) A supersaturated solution can usually be formed from a saturated solution by filtering off the excess solute and lowering the temperature. (d) When a seed crystal of the solute is added to a supersaturated solution, solute particles leave the solution and form a crystalline precipitate.*

Factors Affecting Solubility

The maximum amount of a solute that can dissolve in a solvent at a specified temperature and pressure is its solubilityA measure of the how much of a solid substance remains dissolved in a given amount of a specified liquid at a specified temperature and pressure.. Solubility is often expressed as the mass of solute per volume (g/L) or mass of solute per mass of solvent (g/g), or as the moles of solute per volume (mol/L). Even for very soluble substances, however, there is usually a limit to how much solute can dissolve in a given quantity of solvent. In general, the solubility of a substance depends on not only the energetic factors we have discussed but also the temperature and, for gases, the pressure. At 20°C, for example, 177 g of NaI, 91.2 g of NaBr, 35.9 g of NaCl, and only 4.1 g of NaF dissolve in 100 g of water. At 70°C, however, the solubilities increase to 295 g of NaI, 119 g of NaBr, 37.5 g of NaCl, and 4.8 g of NaF. As you learned in Chapter 4, the lattice energies of the sodium halides increase from NaI to NaF..

A solution with the maximum possible amount of solute is saturatedA solution with the maximum possible amount of a solute under a given set of conditions.. If a solution contains less than the maximum amount of solute, it is *unsaturated*. When a solution is saturated and excess solute is present, the rate of dissolution is exactly equal to the rate of crystallization (part (b) in Figure 9.1.1). Using the value just stated, a saturated aqueous solution of NaCl, for example, contains 35.9 g of NaCl per 100 mL of water at 20°C. We can prepare a homogeneous saturated solution by adding excess solute (in this case, greater than 35.9 g of NaCl) to the solvent (water), stirring until the maximum possible amount of solute has dissolved, and then removing undissolved solute by filtration.

Note the Pattern

The solubility of most solids increases with increasing temperature.

Because the solubility of most solids increases with increasing temperature, a saturated solution that was prepared at a higher temperature usually contains more dissolved solute than it would contain at a lower temperature. When the solution is cooled, it can therefore become supersaturatedAn unstable solution with more dissolved solute than it would normally contain under the given set of conditions. (part (c) in Figure 9.1.1). Like a supercooled or superheated liquid, a supersaturated solution is unstable. Consequently, adding a small particle of the solute, a seed crystalA solid sample of a substance that can be added to a supercooled liquid or a supersaturated solution to help induce crystallization., will usually cause the excess solute to rapidly precipitate or crystallize, sometimes with spectacular results.





Figure 9.2.2 Crystallization of Sodium Acetate out of a Supersaturated Solution: *The crystallization of sodium acetate out of a supersaturated solution can be spectacular. In this video from Mike Shin a small seed crystal is introduced into the middle of the solution*

If the rate of crystallization in Equation 9.2.1 is greater than the rate of dissolution, crystals or a precipitate will form (part (d) in Figure 9.2.1). In contrast, adding a seed crystal to a saturated solution reestablishes the dynamic equilibrium, and the *net* quantity of dissolved solute no longer changes.

Interactions in Liquid Solutions

The interactions that determine the solubility of a substance in a liquid depend largely on the chemical nature of the solute (such as whether it is ionic or molecular) rather than on its physical state (solid, liquid, or gas). We will first describe the general case of forming a solution of a molecular species in a liquid solvent and then describe the formation of a solution of an ionic compound. We postpone until Chapters 16 and 17 deeper analysis of the equilibria between phases based on thermodynamics.

Solutions of Molecular Substances in Liquids

The London dispersion forces, dipole–dipole interactions, and hydrogen bonds that hold molecules to other molecules are generally weak. Even so, energy is required to disrupt these interactions.

For solutions of gases in liquids, we can safely ignore the energy required to separate the solute molecules because the molecules in the gas phase are already separated. Thus we need to consider only the energy required to separate the solvent molecules and the energy released by new solute–solvent interactions.

Nonpolar gases such as N_2, O_2, and Ar have no dipole moment and cannot engage in dipole–dipole interactions or hydrogen bonding. Consequently, the only way they can interact with a solvent is by means of London dispersion forces, which may be weaker than the solvent–solvent interactions in a polar solvent. It is not surprising, then, that nonpolar gases are most soluble in nonpolar solvents. The interactions between the solvent molecules and the solvent-solute interactions are both London dispersion forces and of roughly equal size.

When solvent-solvent and solvent-solute interactions are the same one calls the solution ideal. In an ideal gas, the molecules do not interact at all. In an ideal liquid the molecules must interact to hold the fluid together, but the interaction between the solvent molecules and those between the solvent and solute molecules are the same.

In contrast, for a solution of a nonpolar gas in a polar solvent, the interaction of the polar solvent molecules is far greater than the interaction of the polar solvent molecules with the non-polar solute molecules. As a result, nonpolar gases are less soluble in polar solvents than in nonpolar solvents. For example, the concentration of N_2 in a saturated solution of N_2 in water, a polar solvent, is only 7.07×10^{-4} M compared with 4.5×10^{-3} M for a saturated solution of N_2 in benzene, a nonpolar solvent.

The solubilities of nonpolar gases in water generally increase as the molecular mass of the gas increases, as shown in Table 9.2.1 This is precisely the trend expected: as the gas molecules become larger, the strength of the solvent–solute interactions due to London dispersion forces increases, approaching the strength of the solvent–solvent interactions.

Table 9.2.1 Solubilities of Selected Gases in Water at 20°C and 1 atm Pressure

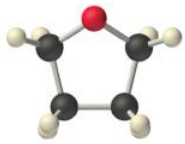
Gas	Solubility (M) $\times 10^{-4}$
He	3.90
Ne	4.65
Ar	15.2
Kr	27.9
Xe	50.2
H_2	8.06
N_2	7.07
CO	10.6
O_2	13.9
N_2O	281
CH_4	15.5

Virtually all common organic liquids, whether polar or not, are miscible. The strengths of the intermolecular attractions are comparable; and the solutions are close to ideal. Another factor, which we will discuss in Chapter 17, the increase in disorder (entropy), drives the formation of a solution. If the predominant intermolecular interactions in two liquids are very different from one another, however, they may be immiscible. For example, organic liquids such as benzene, hexane, CCl_4, and CS_2 (S=C=S) are nonpolar and have no ability to act as hydrogen bond donors or acceptors with hydrogen-bonding solvents such as H_2O, HF, and NH_3; hence they are immiscible in these solvents. When shaken with water, they form separate phases or layers separated by an *interface* (Figure 9.2.3), the region between the two layers. Just because two liquids are immiscible, however, does *not* mean that they are completely insoluble in each other. For example, 188 mg of benzene dissolves in 100 mL of water at 23.5°C. Adding more benzene results in the separation of an upper layer consisting of benzene with a small amount of dissolved water (the solubility of water in benzene is only 178 mg/100 mL of benzene).



Figure 9.2.3 Water is immiscible with with perfluoroheptane (and most halogenated compounds). *Because water is less dense than the perfluoroheptane, the water layer floats on top. The goldfish is swimming in the water layer. Figure from the Wikipedia.*.

The solubilities of simple alcohols in water are given in Table 9.2.2. Only the three lightest alcohols (methanol, ethanol, and *n*-propanol) are completely miscible with water. As the molecular mass of the alcohol increases, so does the proportion of hydrocarbon in the molecule. Correspondingly, the importance of hydrogen bonding and dipole–dipole interactions in the pure alcohol decreases, while the importance of London dispersion forces increases, which leads to progressively fewer favorable electrostatic interactions with water. Organic liquids such as acetone, ethanol, and tetrahydrofuran are sufficiently polar to be completely miscible with water yet sufficiently nonpolar to be completely miscible with all organic solvents.

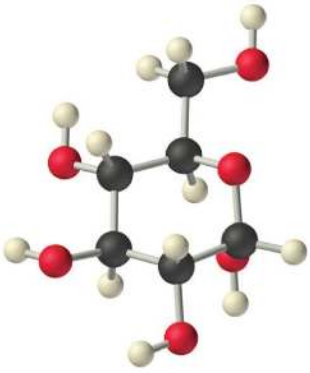


Tetrahydrofuran (THF)

Table 9.2.2 Solubilities of Straight-Chain Organic Alcohols in Water at 20°C

Alcohol	Solubility (mol/100 g of H_2O)
methanol	completely miscible
ethanol	completely miscible
n-propanol	completely miscible
n-butanol	0.11
n-pentanol	0.030
n-hexanol	0.0058
n-heptanol	0.0008

The same principles govern the solubilities of molecular solids in liquids. For example, elemental sulfur is a solid consisting of cyclic S_8 molecules that have no dipole moment. Because the S_8 rings in solid sulfur are held to other rings by London dispersion forces, elemental sulfur is insoluble in water. It is, however, soluble in nonpolar solvents that have comparable London dispersion forces, such as CS_2 (23 g/100 mL). In contrast, glucose contains five –OH groups that can form hydrogen bonds. Consequently, glucose is very soluble in water (91 g/120 mL of water) but essentially insoluble in nonpolar solvents such as benzene. The structure of one isomer of glucose is shown here.



D-Glucose

Low-molecular-mass hydrocarbons with highly electronegative and polarizable halogen atoms, such as chloroform ($CHCl_3$) and methylene chloride (CH_2Cl_2), have both significant dipole moments and relatively strong London dispersion forces. These hydrocarbons are therefore powerful solvents for a wide range of polar and nonpolar compounds. Naphthalene, which is nonpolar, and phenol (C_6H_5OH), which is polar, are very soluble in chloroform. In contrast, the solubility of ionic compounds is largely determined not by the polarity of the solvent but rather by its *dielectric constant*, a measure of its ability to separate ions in solution, as you will soon see.

Example 9.2.1

Identify the most important solute–solvent interactions in each solution.

1. iodine in benzene
2. aniline ($C_6H_5NH_2$) in dichloromethane (CH_2Cl_2)



Aniline

3. iodine in water

Given: components of solutions

Asked for: predominant solute–solvent interactions

Strategy:

Identify all possible intermolecular interactions for both the solute and the solvent: London dispersion forces, dipole–dipole interactions, or hydrogen bonding. Determine which is likely to be the most important factor in solution formation.

Solution:

1. Benzene and I_2 are both nonpolar molecules. The only possible attractive forces are London dispersion forces.
2. Aniline is a polar molecule with an $–NH_2$ group, which can act as a hydrogen bond donor. Dichloromethane is also polar, but it has no obvious hydrogen bond acceptor. Therefore, the most important interactions between aniline and CH_2Cl_2 are likely to be London interactions.

3. Water is a highly polar molecule that engages in extensive hydrogen bonding, whereas I_2 is a nonpolar molecule that cannot act as a hydrogen bond donor or acceptor. The slight solubility of I_2 in water (1.3×10^{-3} mol/L at 25°C) is due to London dispersion forces.

Exercise

Identify the most important interactions in each solution:

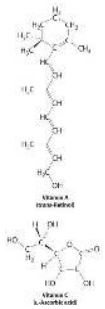
1. ethylene glycol ($HOCH_2CH_2OH$) in acetone
2. acetonitrile ($CH_3C{\equiv}N$) in acetone
3. *n*-hexane in benzene

Answer:

1. hydrogen bonding
2. London interactions
3. London dispersion forces

Hydrophilic and Hydrophobic Solutes

A solute can be classified as hydrophilicA substance attracted to water. Hydrophilic substances are polar and can form hydrogen bonds to water. (literally, “water loving”), meaning that it has an electrostatic attraction to water, or hydrophobicA substance that repels water. Hydrophobic substances do not interact favorably with water. (“water fearing”), meaning that it repels water. A hydrophilic substance is polar and often contains O–H or N–H groups that can form hydrogen bonds to water. For example, glucose with its five O–H groups is hydrophilic. In contrast, a hydrophobic substance may be polar but usually contains C–H bonds that do not interact favorably with water, as is the case with naphthalene and *n*-octane. Hydrophilic substances tend to be very soluble in water and other strongly polar solvents, whereas hydrophobic substances are essentially insoluble in water and soluble in nonpolar solvents such as benzene and cyclohexane.

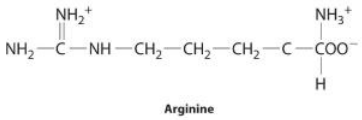


The difference between hydrophilic and hydrophobic substances has substantial consequences in biological systems. For example, vitamins can be classified as either *fat soluble* or *water soluble*. Fat-soluble vitamins, such as vitamin A, are mostly nonpolar, hydrophobic molecules. As a result, they tend to be absorbed into fatty tissues and stored there. In contrast, water-soluble vitamins, such as vitamin C, are polar, hydrophilic molecules that circulate in the blood and intracellular fluids, which are primarily aqueous. Water-soluble vitamins are therefore excreted much more rapidly from the body and must be replenished in our daily diet. A comparison of the chemical structures of vitamin A and vitamin C quickly reveals why one is hydrophobic and the other hydrophilic.

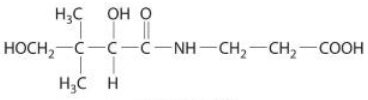
Because water-soluble vitamins are rapidly excreted, the risk of consuming them in excess is relatively small. Eating a dozen oranges a day is likely to make you tired of oranges long before you suffer any ill effects due to their high vitamin C content. In contrast, fat-soluble vitamins constitute a significant health hazard when consumed in large amounts. For example, the livers of polar bears and other large animals that live in cold climates contain large amounts of vitamin A, which have occasionally proven fatal to humans who have eaten them.

Example 9.2.2

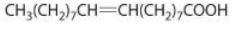
The following substances are essential components of the human diet:



Arginine



Pantothenic acid



Oleic acid

Using what you know of hydrophilic and hydrophobic solutes, classify each as water soluble or fat soluble and predict which are likely to be required in the diet on a daily basis.

1. arginine
2. pantothenic acid
3. oleic acid

Given: chemical structures

Asked for: classification as water soluble or fat soluble; dietary requirement

Strategy:

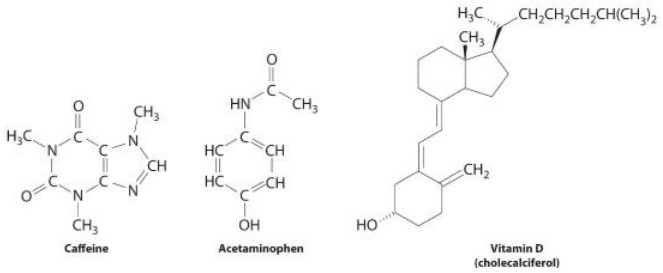
Based on the structure of each compound, decide whether it is hydrophilic or hydrophobic. If it is hydrophilic, it is likely to be required on a daily basis.

Solution:

1. Arginine is a highly polar molecule with two positively charged groups and one negatively charged group, all of which can form hydrogen bonds with water. As a result, it is hydrophilic and required in our daily diet.
2. Although pantothenic acid contains a hydrophobic hydrocarbon portion, it also contains several polar functional groups (–OH and $–CO_2H$) that should interact strongly with water. It is therefore likely to be water soluble and required in the diet. (In fact, pantothenic acid is almost always a component of multiple-vitamin tablets.)
3. Oleic acid is a hydrophobic molecule with a single polar group at one end. It should be fat soluble and not required daily.

Exercise

These compounds are consumed by humans: caffeine, acetaminophen, and vitamin D. Identify each as primarily hydrophilic (water soluble) or hydrophobic (fat soluble), and predict whether each is likely to be excreted from the body rapidly or slowly.



Answer: Caffeine and acetaminophen are water soluble and rapidly excreted, whereas vitamin D is fat soluble and slowly excreted.

Solid Solutions

Solutions are not limited to gases and liquids; solid solutions also exist. For example, amalgams are solutions of metals in liquid mercury. Because most metals are soluble in mercury, amalgams are used in gold mining, dentistry, and many other applications. A major difficulty when mining gold is separating very small particles of pure gold from tons of crushed rock. One way to accomplish this is to agitate a suspension of the crushed rock with liquid mercury, which dissolves the gold (as well as any metallic silver that might be present). The very dense liquid gold–mercury amalgam is then isolated and the mercury distilled away.

An alloy is a solid or liquid solution that consists of one or more elements in a metallic matrix. A solid alloy has a single homogeneous phase in which the crystal structure of the solvent remains unchanged by the presence of the solute. Thus the microstructure of the alloy is uniform throughout the sample. Examples are substitutional and interstitial alloys such as brass or solder. (For more information about alloys, see Section 8.5) Liquid alloys include sodium/potassium and gold/mercury. In contrast, a *partial* alloy solution has two or more phases that can be homogeneous in the distribution of the components, but the microstructures of the two phases are *not* the same. As a liquid solution of lead and tin is cooled, for example, different crystalline phases form at different cooling temperatures. As you learned in Section 8.5, alloys usually have properties that differ from those of the component elements.

Network solids such as diamond, graphite, and SiO_2 are insoluble in all solvents with which they do not react chemically. The covalent bonds that hold the network or lattice together are simply too strong to be broken under normal conditions. They are certainly much stronger than any conceivable combination of intermolecular interactions that might occur in solution. Most metals are insoluble in virtually all solvents for the same reason: the delocalized metallic bonding is much stronger than any favorable metal atom–solvent interactions. Many metals react with solutions such as aqueous acids or bases to produce a solution. However, as we saw in these instances the metal undergoes a chemical transformation that cannot be reversed by simply removing the solvent.

Note the Pattern

Solids with very strong intermolecular bonding tend to be insoluble.

Solubilities of Ionic Substances in Liquids

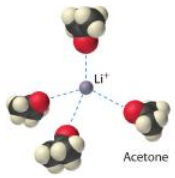
Ionic substances are generally most soluble in polar solvents; the higher the lattice energy, the more polar the solvent must be to overcome the lattice energy and dissolve the substance. Because of its high polarity, water is the most common solvent for ionic compounds. Many ionic compounds are soluble in other polar solvents, however, such as liquid ammonia, liquid hydrogen fluoride, and methanol. Because all these solvents consist of molecules that have relatively large dipole moments, they can interact favorably with the dissolved ions.

The interaction of water with Na^+ and Cl^- ions in an aqueous solution of NaCl is shown whenever you sprinkle salt into water, for example when you are cooking. The ion–dipole interactions between Li^+ ions and acetone molecules in a solution of LiCl in acetone are shown in Figure 9.2.4 The energetically favorable Li^+–acetone interactions make the solvent solute interaction sufficiently negative to overcome the positive lattice energy of the LiCl and the acetone-acetone interactions. Because the dipole moment of acetone (2.88 D), and thus its polarity, is actually larger than that of water (1.85 D), one might even expect that LiCl would be more soluble in acetone than in water. In fact, the opposite is true: 83 g of LiCl dissolve in 100 mL of water at 20°C, but only about 4.1 g of LiCl dissolve in 100 mL of acetone. This apparent contradiction arises from the fact that the dipole moment is a property of a single molecule in the gas phase. A more useful measure of the ability of a solvent to dissolve ionic compounds is its dielectric constant (ε) which is the ability of a bulk substance to decrease the electrostatic forces between two charged particles. By definition, the dielectric constant of a vacuum is 1. In essence, a solvent with a high dielectric constant causes the charged particles to behave as if they have been moved farther apart. At 25°C, the dielectric constant of water is 80.1, one of the highest known, and that of acetone is only 21.0. Hence water is better able to decrease the electrostatic attraction between Li^+ and Cl^- ions, so LiCl is more soluble in water than in acetone. This behavior is in contrast to that of molecular substances, for which polarity is the dominant factor governing solubility.

Note the Pattern

A solvent's dielectric constant is the most useful measure of its ability to dissolve ionic compounds. A solvent's polarity is the dominant factor in dissolving molecular substances.

Figure 9.2.4 Ion–Dipole Interactions in the Solvation of Li^+ Ions by Acetone, a Polar Solvent



It is also possible to dissolve ionic compounds in organic solvents using crown ethersCyclic polyether with four or more oxygen atoms separated by two or three carbon atoms. All crown ethers have a central cavity that can accommodate a metal ion coordinated to the ring of oxygen atoms., cyclic compounds with the general formula $(OCH_2CH_2)_n$. Crown ethers are named using both the total number of atoms in the ring and the number of oxygen atoms. Thus 18-crown-6 is an 18-membered ring with six oxygen atoms (part (a) in Figure 9.2.5). The cavity in the center of the crown ether molecule is lined with oxygen atoms and is large enough to be occupied by a cation, such as K^+. The cation is stabilized by interacting with lone pairs of electrons on the surrounding oxygen atoms. Thus crown ethers solvate cations inside a hydrophilic cavity, whereas the outer shell, consisting of C–H bonds, is hydrophobic. Crown ethers are useful for dissolving ionic substances such as $KMnO_4$ in organic solvents such as

isopropanol [$(CH_3)_2CHOH$] (Figure 9.2.5). The availability of crown ethers with cavities of different sizes allows specific cations to be solvated with a high degree of selectivity.

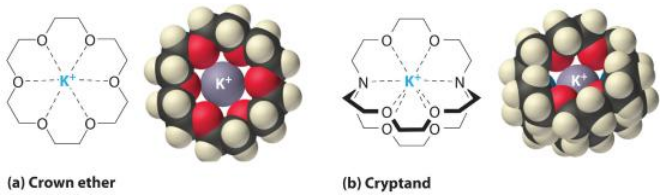


Figure 9.2.5 Crown Ethers and Cryptands (a) The potassium complex of the crown ether 18-crown-6. Note how the cation is nestled within the central cavity of the molecule and interacts with lone pairs of electrons on the oxygen atoms. (b) The potassium complex of 2,2,2-cryptand, showing how the cation is almost hidden by the cryptand. Cryptands solvate cations via lone pairs of electrons on both oxygen and nitrogen atoms.



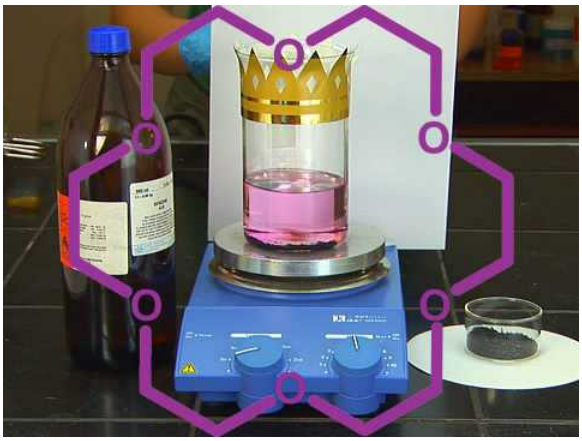


Figure 9.2.6. Effect of a Crown Ether on the Solubility of $KMnO_4$ in Benzene. *Normally which is intensely purple, is completely insoluble in benzene which has a relatively low dielectric constant. In the presence of a small amount of crown ether, $KMnO_4$ dissolves in benzene as shown by the reddish purple color caused by the permanganate ions in solution. Video from Chem Toddler*

Cryptands Consisting of three $(OCH)_2CH_2O–)_n$ chains connected by two nitrogen atoms, cryptands have a central cavity that can encapsulate a metal ion coordinated to the oxygen and nitrogen atoms. (from the Greek *kryptós*, meaning “hidden”) are compounds

that can completely surround a cation with lone pairs of electrons on oxygen and nitrogen atoms (part (b) in Figure 9.2.5). The number in the name of the cryptand is the number of oxygen atoms in each strand of the molecule. Like crown ethers, cryptands can be used to prepare solutions of ionic compounds in solvents that are otherwise too nonpolar to dissolve them.

Summary

The **solubility** of a substance is the maximum amount of a solute that can dissolve in a given quantity of solvent; it depends on the chemical nature of both the solute and the solvent and on the temperature and pressure. When a solution contains the maximum amount of solute that can dissolve under a given set of conditions, it is a **saturated solution**. Otherwise, it is *unsaturated*. **Supersaturated solutions**, which contain more dissolved solute than allowed under particular conditions, are not stable; the addition of a **seed crystal**, a small particle of solute, will usually cause the excess solute to crystallize. A system in which crystallization and dissolution occur at the same rate is in *dynamic equilibrium*. The solubility of a substance in a liquid is determined by intermolecular interactions, which also determine whether two liquids are miscible. Solutes can be classified as **hydrophilic** (water loving) or **hydrophobic** (water fearing). Vitamins with hydrophilic structures are water soluble, whereas those with hydrophobic structures are fat soluble. Many metals dissolve in liquid mercury to form **amalgams**. Covalent network solids and most metals are insoluble in nearly all solvents. The solubility of ionic compounds is largely determined by the **dielectric constant (ε)** of the solvent, a measure of its ability to decrease the electrostatic forces between charged particles. Solutions of many ionic compounds in organic solvents can be dissolved using **crown ethers**, cyclic polyethers large enough to accommodate a metal ion in the center, or **cryptands**, compounds that completely surround a cation.

Key Takeaway

- The strength of intramolecular bonding determines the solubility of a solute in a given solvent.

Conceptual Problems

1. If a compound is only slightly soluble in a particular solvent, what are the relative strengths of the solvent–solvent and solute–solute interactions versus the solute–solvent interactions?
2. Predict whether each of the following sets of conditions favors formation of a solution:

Intermolecular Attractive Forces (Solute)	Intermolecular Attractive Forces (Solvent)	ΔH_{soln}
London dispersion	hydrogen bonding	slightly positive
dipole–dipole	hydrogen bonding	very negative
ionic	dipole–dipole	slightly positive
ionic	London dispersion	positive

3. Arrange the following liquids in order of increasing solubility in water: *t*-butanol [$(CH_3)_3COH$], benzene, ammonia, and heptane. Justify your answer.
4. Which compound in each pair will be more soluble in water? Explain your reasoning in each case.
    1. toluene (C_7H_8) or ethyl ether ($C_2H_5OC_2H_5$)
    2. chloroform ($CHCl_3$) or acetone (CH_3COCH_3)
    3. carbon tetrachloride (CCl_4) or tetrahydrofuran (C_4H_8O)
    4. $CaCl_2$ or CH_2Cl_2
5. Which compound in each pair will be more soluble in benzene? Explain your reasoning in each case.
    1. cyclohexane or methanol
    2. I_2 or $MgCl_2$
    3. methylene chloride (CH_2Cl_2) or acetic acid
6. Two water-insoluble compounds—*n*-decylamine [$CH_3(CH_2)_9NH_2$] and *n*-decane—can be separated by the following procedure: The compounds are dissolved in a solvent such as toluene that is immiscible with water. When adding an aqueous

HCl solution to the mixture and stirring vigorously, the HCl reacts with one of the compounds to produce a salt. When the stirring is stopped and the mixture is allowed to stand, two layers are formed. At this point, each layer contains only one of the two original compounds. After the layers are separated, adding aqueous NaOH to the aqueous layer liberates one of the original compounds, which can then be removed by stirring with a second portion of toluene to extract it from the water.

   1. Identify the compound that is present in each layer following the addition of HCl. Explain your reasoning.
   2. How can the original compounds be recovered from the toluene solution?

7. Bromine and iodine are both soluble in CCl_4, but bromine is much more soluble. Why?
8. A solution is made by mixing 50.0 mL of liquid A with 75.0 mL of liquid B. Which is the solute, and which is the solvent? Is it valid to assume that the volume of the resulting solution will be 125 mL? Explain your answer.
9. The compounds NaI, NaBr, and NaCl are far more soluble in water than NaF, a substance that is used to fluoridate drinking water. In fact, at 25°C the solubility of NaI is 184 g/100 mL of water, versus only 4.2 g/100 mL of water for NaF. Why is sodium iodide so much more soluble in water? Do you expect KCl to be more soluble or less soluble in water than NaCl?
10. When water is mixed with a solvent with which it is immiscible, the two liquids usually form two separate layers. If the density of the nonaqueous solvent is 1.75 g/mL at room temperature, sketch the appearance of the heterogeneous mixture in a beaker and label which layer is which. If you were not sure of the density and the identity of the other liquid, how might you be able to identify which is the aqueous layer?
11. When two liquids are immiscible, the addition of a third liquid can occasionally be used to induce the formation of a homogeneous solution containing all three.

    1. Ethylene glycol ($HOCH_2CH_2OH$) and hexane are immiscible, but adding acetone [$(CH_3)_2CO$] produces a homogeneous solution. Why does adding a third solvent produce a homogeneous solution?
    2. Methanol and *n*-hexane are immiscible. Which of the following solvents would you add to create a homogeneous solution—water, *n*-butanol, or cyclohexane? Justify your choice.

12. Some proponents of vitamin therapy for combating illness encourage the consumption of large amounts of fat-soluble vitamins. Why can this be dangerous? Would it be as dangerous to consume large amounts of water-soluble vitamins? Why or why not?
13. Why are most metals insoluble in virtually all solvents?
14. Because sodium reacts violently with water, it is difficult to weigh out small quantities of sodium metal for a reaction due to its rapid reaction with small amounts of moisture in the air. Would a Na/Hg amalgam be as sensitive to moisture as metallic sodium? Why or why not? A Na/K alloy is a liquid at room temperature. Will it be more or less sensitive to moisture than solid Na or K?
15. Dental amalgams often contain high concentrations of Hg, which is highly toxic. Why isn't dental amalgam toxic?
16. Arrange 2,2,3-trimethylpentane, 1-propanol, toluene (C_7H_8), and dimethyl sulfoxide [$(CH_3)_2S{=}O$] in order of increasing dipole moment. Explain your reasoning.
17. Arrange acetone, chloroform, cyclohexane, and 2-butanol in order of increasing dielectric constant. Explain your reasoning.
18. Dissolving a white crystalline compound in ethanol gave a blue solution. Evaporating the ethanol from the solution gave a bluish-crystalline product, which slowly transformed into the original white solid on standing in the air for several days. Explain what happened. How does the mass of the initial bluish solid compare with the mass of the white solid finally recovered?
19. You have been asked to develop a new drug that could be used to bind Fe^{3+} ions in patients who suffer from iron toxicity, allowing the bound iron to be excreted in the urine. Would you consider a crown ether or a cryptand to be a reasonable candidate for such a drug? Explain your answer.
20. Describe two different situations in which fractional crystallization will not work as a separation technique when attempting to isolate a single compound from a mixture.
21. You have been given a mixture of two compounds—A and B—and have been told to isolate pure A. You know that pure A has a lower solubility than pure B and that the solubilities of both A and B increase with temperature. Outline a procedure to isolate

7. London dispersion forces increase with increasing atomic mass. Iodine is a solid while bromine is a liquid due to the greater
6. intermolecular interactions between the heavier iodine atoms. Iodine is less soluble than bromine in virtually all solvents
5. because it requires more energy to separate I_2 molecules than Br_2 molecules.

8. pure A. If B had the lower solubility, could you use the same procedure to isolate pure A? Why or why not?

Answers

1. A third solvent with intermediate polarity and/or dielectric constant can effectively dissolve both of the immiscible solvents, creating a single liquid phase.
2. *n*-butanol—it is intermediate in polarity between methanol and *n*-hexane, while water is more polar than either and cyclohexane is comparable to *n*-hexane.

15. In dental amalgam, the mercury atoms are locked in a solid phase that does not undergo corrosion under physiological conditions; hence, the mercury atoms cannot readily diffuse to the surface where they could vaporize or undergo chemical reaction.

21. Dissolve the mixture of A and B in a solvent in which they are both soluble when hot and relatively insoluble when cold, filter off any undissolved B, and cool slowly. Pure A should crystallize, while B stays in solution. If B were less soluble, it would be impossible to obtain pure A by this method in a single step, because some of the less soluble compound (B) will always be present in the solid that crystallizes from solution.

Contributors

- Anonymous

Modified by Joshua Halpern, Scott Sinex and Scott Johnson

Sodium acetate precipitation from Mike Shin @Youtube

Crown ether video from ChemToddler @ YouTube

Thumbnail from Wikimedia

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Chapter 9.3: Units for Concentration

Learning Objective

- To describe the concentration of a solution in the way that is most appropriate for a particular problem or application.

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

Molarity

The most common unit of concentration is *molarity*, which is also the most useful for calculations involving the stoichiometry of reactions in solution. The molarity (M) is a common unit of concentration and is the number of moles of solute present in exactly $1L$ of solution (mol/L) of a solution is the number of moles of solute present in exactly $1L$ of solution. Molarity is also the number of millimoles of solute present in exactly 1 mL of solution:

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

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

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

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

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

or

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

Mole Fraction

We can also describe the concentration of a molecule as the mole fraction, We had previously defined mole fraction in describing mixtures of gases in Section 6.5.

The mole fraction (X) of any component of a mixture is the ratio of the number of moles of that component to the total number of moles of all the species present in the mixture (n_t):

$$x_A = \frac{\text{moles of A}}{\text{total moles}} = \frac{n_A}{n_{tot}} = \frac{n_A}{n_A + n_B + \cdots} \tag{9.3.4}$$

The mole fraction is a dimensionless quantity between 0 and 1. If $X_A = 1.0$, then the sample is pure A, not a mixture. If $X_A = 0$, then no A is present in the mixture. The sum of the mole fractions of all the components present must equal 1.

Example 9.3.1

Commercial vinegar is essentially a solution of acetic acid in water. A bottle of vinegar has 3.78 g of acetic acid per 100.0 g of solution. Assume that the density of the solution is 1.00 g/mL.

1. What is its molarity?
2. What is its mole fraction?

Given: mass of substance and mass and density of solution

Asked for: molarity and mole fraction

Strategy:

A Calculate the number of moles of acetic acid in the sample. Then calculate the number of liters of solution from its mass and density. Use these results to determine the molarity of the solution.

B Determine the mass of the water in the sample and calculate the number of moles of water. Then determine the mole fraction of acetic acid by dividing the number of moles of acetic acid by the total number of moles of substances in the sample.

Solution:

1. **A** The molarity is the number of moles of acetic acid per liter of solution. We can calculate the number of moles of acetic acid as its mass divided by its molar mass. The volume of the solution equals its mass divided by its density. The calculations follow:

$$moles\ CH_3CO_2H = \frac{3.78\ \cancel{g}\ CH_3CO_2H}{60.05\ \cancel{g}/mol} = 0.0629\ mol$$

$$volume = \frac{mass}{density} = \frac{100.0\ \cancel{g}\ solution}{1.00\ \cancel{g}/\cancel{mL}} = 100.00\ mL$$

$$molarity\ of\ CH_3CO_2H = \frac{moles\ CH_3CO_2H}{liter\ solution} = \frac{0.0629\ mol\ CH_3CO_2H}{\left(100\ \cancel{mL}\right)\left(1L/\cancel{mL}\right)} = 0.629\ M\ CH_3CO_2H$$

2. This result makes intuitive sense. If 100.0 g of aqueous solution (equal to 100 mL) contains 3.78 g of acetic acid, then 1 L of solution will contain 37.8 g of acetic acid, which is a little more than 1/2 mole. Keep in mind, though, that the mass and volume of a solution are related by its density; concentrated aqueous solutions often have densities greater than 1.00 g/mL.

3. **B** To calculate the mole fraction of acetic acid in the solution, we need to know the number of moles of both acetic acid and water. The number of moles of acetic acid is 0.0629 mol, as calculated in part (a). We know that 100.0 g of vinegar contains 3.78 g of acetic acid; hence the solution also contains (100.0 g − 3.78 g) = 96.2 g of water. We have

$$moles\ H_2O = \frac{96.2\ \cancel{g}\ H_2O}{18.02\ \cancel{g}/mol} = 5.34\ mol\ H_2O$$

The mole fraction *X* of acetic acid is the ratio of the number of moles of acetic acid to the total number of moles of substances present:

$$X_{CH_3CO_2H} = \frac{moles\ \ CH_3CO_2H}{moles\ \ CH_3CO_2H + moles\ H_2O} = \frac{0.0629\ mol}{0.0629\ mol + 5.34\ mol} = 0.0116$$

This answer makes sense, too. There are approximately 100 times as many moles of water as moles of acetic acid, so the ratio should be approximately 0.01.

Exercise

A solution of HCl gas dissolved in water (sold commercially as “muriatic acid,” a solution used to clean masonry surfaces) has 20.22 g of HCl per 100.0 g of solution, and its density is 1.10 g/mL.

1. What is its molarity?
2. What is its mole fraction?

Answer:

1. 6.10 M HCl
2. X_{HCl} = 0.111

Molality

While molarity is ideal for preparing solutions using volumetric flasks it has the disadvantage that volume varies with temperature and also can be affected by composition and pressure. The concentration of a solution can also be described by its molality (*m*)The number of moles of solute present in exactly 1 kg of solvent., the number of moles of solute per *kilogram* of solvent:

$$molality\,(m) = \frac{(moles\ solute)}{(kilograms\ solvent)}$$

Molality, therefore, has the same numerator as molarity (the number of moles of solute) but a different denominator (kilogram of solvent rather than liter of solution). Molality is independent of temperature, pressure and composition.

For dilute aqueous solutions, the molality and molarity are nearly the same because dilute solutions are mostly solvent. Thus because the density of water under standard conditions is very close to 1.0 g/mL, the volume of 1.0 kg of H_2O under these conditions is very close to 1.0 L, and a 0.50 M solution of KBr in water, for example, has approximately the same concentration as a 0.50 *m* solution.

Mass Percent

Another common way of describing concentration is as the ratio of the mass of the solute to the total mass of the solution. The result can be expressed as mass percentageThe ratio of the total mass of the solute to the total mass of the solution., parts per million (ppm)Milligrams of solute per kilogram of solvent., or parts per billion (ppb)Micrograms of solute per kilogram of solvent.:

$$mass\ percentage = \frac{(mass\ of\ solute)}{(mass\ of\ solution)} \times 100$$

$$parts\ per\ million\,(ppm) = \frac{(mass\ of\ solute)}{(mass\ of\ solution)} \times 10^6$$

$$parts\ per\ billion\,(ppb) = \frac{(mass\ of\ solute)}{(mass\ of\ solution)} \times 10^9$$

In the health sciences, the concentration of a solution is typically expressed as parts per thousand (ppt)Grams of solute per kilogram of solvent, primarily used in the health sciences., indicated as a proportion. For example, adrenalin, the hormone produced in high-stress situations, is available in a 1:1000 solution, or one gram of adrenalin per 1000 g of solution.

The labels on bottles of commercial reagents often describe the contents in terms of mass percentage. Sulfuric acid, for example, is sold as a 95% aqueous solution, or 95 g of H_2SO_4 per 100 g of solution. Parts per million and parts per billion are used to describe concentrations of highly dilute solutions. These measurements correspond to milligrams and micrograms of solute per kilogram of solution, respectively. For dilute aqueous solutions, this is equal to milligrams and micrograms of solute per liter of solution (assuming a density of 1.0 g/mL).

Mixing Ratio

To confuse things, many fields use mixing ratios, the ratio of the number of molecules or moles of one species to the total number in a fixed volume. For example, the concentration of CO_2 in the atmosphere today is 400 ppm, or there are 400 CO_2 molecules in every million molecules in the air. More properly this should be written as 400 ppmV, that is 400 parts per million by volume, because Avogadro's principle tells us that equal volumes of gas contain equal numbers of molecules.

Example 9.3.2

Several years ago, millions of bottles of mineral water were contaminated with benzene at ppm levels. This incident received a great deal of attention because the lethal concentration of benzene in rats is 3.8 ppm. A 250 mL sample of mineral water has 13.7 ppm of benzene. Because the contaminated mineral water is a very dilute aqueous solution, we can assume that its density is approximately 1.00 g/mL.

1. What is the molarity of the solution?
2. What is the mass of benzene in the sample?

Given: volume of sample, solute concentration, and density of solution

Asked for: molarity of solute and mass of solute in 250 mL

Strategy:

A Use the concentration of the solute in parts per million to calculate the molarity.

B Use the concentration of the solute in parts per million to calculate the mass of the solute in the specified volume of solution.

Solution:

1. **A** To calculate the molarity of benzene, we need to determine the number of moles of benzene in 1 L of solution. We know that the solution contains 13.7 ppm of benzene. Because 13.7 ppm is equivalent to 13.7 mg/1000 g of solution and the density of the solution is 1.00 g/mL, the solution contains 13.7 mg of benzene per liter (1000 mL). The molarity is therefore

$$molarity = \frac{moles}{liter} = \frac{\left(12.7\ \cancel{mg}\right)\left(1\ \cancel{g}/1000\ \cancel{mg}\right)\left(1\ mol/78.114\ \cancel{g}\right)}{1000\ mL} = 1.63\times 10^{-4}\ M$$

2. **B** We are given that there are 13.7 mg of benzene per 1000 g of solution, which is equal to 13.7 mg/L of solution. Hence the mass of benzene in 250 mL (250 g) of solution is

$$mass\ of\ benzene = \frac{(12.7\ mg\ benzene)\left(250\ \cancel{mL}\right)}{1000\ \cancel{mL}} = 3.18\ mg\ benzene$$

Exercise

The maximum allowable concentration of lead in drinking water is 9.0 ppb. What is the molarity of Pb^{2+} in a 9.0 ppb aqueous solution? Use your calculated concentration to determine how many grams of Pb^{2+} are in an 8 oz glass of water.

Answer: 4.3×10^{-8} M; 2×10^{-6} g

Choosing Units to Use

How do chemists decide which units of concentration to use for a particular application? Although molarity is commonly used to express concentrations for reactions in solution or for titrations, it does have one drawback—molarity is the number of moles of solute divided by the volume of the solution, and the volume of a solution depends on its density, which is a function of temperature. Because volumetric glassware is calibrated at a particular temperature, typically 20°C, the molarity may differ from the original value by several percent if a solution is prepared or used at a significantly different temperature, such as 40°C or 0°C. For many applications this may not be a problem, but for precise work these errors can become important. In contrast, mole fraction, molality, and mass percentage depend on only the masses of the solute and solvent, which are independent of temperature.

Mole fraction is not very useful for experiments that involve quantitative reactions, but it is convenient for calculating the partial pressure of gases in mixtures, as we saw in Section 6.5. Molality is particularly useful for determining how properties such as the freezing or boiling point of a solution vary with solute concentration. Because mass percentage and parts per million or billion are simply different ways of expressing the ratio of the mass of a solute to the mass of the solution, they enable us to express the concentration of a substance even when the molecular mass of the substance is unknown. Units of ppb or ppm are also used to express very low concentrations, such as those of residual impurities in foods or of pollutants in environmental studies.

Table 9.3.1 summarizes the different units of concentration and typical applications for each. When the molar mass of the solute and the density of the solution are known, it becomes relatively easy with practice to convert among the units of concentration we have discussed, as illustrated in Example 6.

Table 9.3.1 Different Units for Expressing the Concentrations of Solutions*

Unit	Definition	Application
molarity (M)	moles of solute/liter of solution (mol/L)	Used for quantitative reactions in solution and titrations; mass and molecular mass of solute and volume of solution are known.
mole fraction (X)	moles of solute/total moles present (mol/mol)	Used for partial pressures of gases and vapor pressures of some solutions; mass and molecular mass of each component are known.
molality (m)	moles of solute/kg of solvent (mol/kg)	Used in determining how colligative properties vary with solute concentration; masses and molecular mass of solute are known.
mass percentage (%)	[mass of solute (g)/mass of solution (g)] × 100	Useful when masses are known but molecular masses are unknown.
parts per thousand (ppt)	[mass of solute/mass of solution] × 10^3 (g solute/kg solution)	Used in the health sciences, ratio solutions are typically expressed as a proportion, such as 1:1000.
parts per million (ppm)	[mass of solute/mass of solution] × 10^6 (mg solute/kg solution)	Used for trace quantities; masses are known but molecular masses may be unknown.
parts per billion (ppb)	[mass of solute/mass of solution] × 10^9 (µg solute/kg solution)	Used for trace quantities; masses are known but molecular masses may be unknown.

*The molarity of a solution is temperature dependent, but the other units shown in this table are independent of temperature.

Example 9.3.3

Vodka is essentially a solution of pure ethanol in water. Typical vodka is sold as “80 proof,” which means that it contains 40.0% ethanol by volume. The density of pure ethanol is 0.789 g/mL at 20°C. If we assume that the volume of the solution is the sum of the volumes of the components (which is not strictly correct), calculate the following for the ethanol in 80-proof vodka.

1. the mass percentage
2. the mole fraction
3. the molarity
4. the molality

Given: volume percent and density

Asked for: mass percentage, mole fraction, molarity, and molality

Strategy:

A Use the density of the solute to calculate the mass of the solute in 100.0 mL of solution. Calculate the mass of water in 100.0 mL of solution.

B Determine the mass percentage of solute by dividing the mass of ethanol by the mass of the solution and multiplying by 100.

C Convert grams of solute and solvent to moles of solute and solvent. Calculate the mole fraction of solute by dividing the moles of solute by the total number of moles of substances present in solution.

D Calculate the molarity of the solution: moles of solute per liter of solution. Determine the molality of the solution by dividing the number of moles of solute by the kilograms of solvent.

Solution:

The key to this problem is to use the density of pure ethanol to determine the mass of ethanol (CH_3CH_2OH), abbreviated as EtOH, in a given volume of solution. We can then calculate the number of moles of ethanol and the concentration of ethanol in any of the required units.

A Because we are given a percentage by volume, we assume that we have 100.0 mL of solution. The volume of ethanol will thus be 40.0% of 100.0 mL, or 40.0 mL of ethanol, and the volume of water will be 60.0% of 100.0 mL, or 60.0 mL of water. The mass of ethanol is obtained from its density:

$$mass\ of\ EtOH = \left(40.0\ \cancel{mL}\right)\left(\frac{0.789\ g}{\cancel{mL}}\right) = 31.6\ g\ EtOH$$

If we assume the density of water is 1.00 g/mL, the mass of water is 60.0 g. We now have all the information we need to calculate the concentration of ethanol in the solution.

B The mass percentage of ethanol is the ratio of the mass of ethanol to the total mass of the solution, expressed as a percentage:

$$\%\ EtOH = \left(\frac{mass\ EtOH}{mass\ of\ solution}\right)(100) = \left(\frac{31.6\ \cancel{g}\ EtOH}{31.6\ \cancel{g}\ EtOH + 60.0\ \cancel{g}\ H_2O}\right)(100) = 34.5\ \%$$

C The mole fraction of ethanol is the ratio of the number of moles of ethanol to the total number of moles of substances in the solution. Because 40.0 mL of ethanol has a mass of 31.6 g, we can use the molar mass of ethanol (46.07 g/mol) to determine the number of moles of ethanol in 40.0 mL:

$$moles\ EtOH = \left(31.6\ \cancel{g\ EtOH}\right)\left(\frac{1\ mol}{46.07\ \cancel{g\ EtOH}}\right) = 0.686\ mol\ EtOH$$

Similarly, the number of moles of water is

$$moles\ H_2O = \left(60.0\ \cancel{g\ H_2O}\right)\left(\frac{1\ mol}{18.02\ \cancel{g\ H_2O}}\right) = 3.33\ mol\ H_2O$$

The mole fraction of ethanol is thus

$$X_{EtOH} = \left(\frac{0.686\ \cancel{mol}}{0.686\ \cancel{mol} + 3.33\ \cancel{mol}}\right) = 0.171$$

D The molarity of the solution is the number of moles of ethanol per liter of solution. We already know the number of moles of ethanol per 100.0 mL of solution, so the molarity is

$$M_{EtOH} = \left(\frac{0.686\ mol}{100\ \cancel{mL}}\right)\left(\frac{1000\ \cancel{mL}}{L}\right) = 6.86\ M$$

The molality of the solution is the number of moles of ethanol per kilogram of solvent. Because we know the number of moles of ethanol in 60.0 g of water, the calculation is again straightforward:

$$m_{EtOH} = \left(\frac{0.686\ mol\ EtOH}{60.0\ \cancel{g}\ H_2O}\right)\left(\frac{1000\ \cancel{g}}{kg}\right) = \frac{11.4\ mol\ EtOH}{kg\ H_2O} = 11.46.86\ m$$

Exercise

A solution is prepared by mixing 100.0 mL of toluene with 300.0 mL of benzene. The densities of toluene and benzene are 0.867 g/mL and 0.874 g/mL, respectively. Assume that the volume of the solution is the sum of the volumes of the components. Calculate the following for toluene.

1. mass percentage
2. mole fraction
3. molarity
4. molality

Answer:

1. mass percentage toluene = 24.8%
2. X_{toluene} = 0.219
3. 2.35 M toluene
4. 3.59 *m* toluene

Summary

The **concentration** of a solution is the quantity of solute in a given quantity of solution. It can be expressed in several ways: molarity (moles of solute per liter of solution); *mole fraction*, the ratio of the number of moles of solute to the total number of

moles of substances present; **mass percentage**, the ratio of the mass of the solute to the mass of the solution times 100; **parts per thousand (ppt)**, grams of solute per kilogram of solution; **parts per million (ppm)**, milligrams of solute per kilogram of solution; **parts per billion (ppb)**, micrograms of solute per kilogram of solution; and **molality (*m*)**, the number of moles of solute per kilogram of solvent.

Key Takeaway

- Different units are used to express the concentrations of a solution depending on the application.

Key Equations

molarity

Equation 9.3.1:

$$molarity = \frac{moles\ of\ solute}{liters\ of\ solution} = \frac{mmoles\ of\ solute}{milliliters\ of\ solution} \tag{Chapter 9.3.1}$$

molality

Equation 9.3.5:

$$molality\,(m) = \frac{(moles\ solute)}{(kilograms\ solvent)} \tag{Chapter 9.3.2}$$

mass percentage

Equation 9.3.6:

$$mass\ percentage = \frac{(mass\ of\ solute)}{(mass\ of\ solution)} \times 100 \tag{Chapter 9.3.3}$$

parts per million by mass

Equation 9.3.7:

$$parts\ per\ million\ (ppm) = \frac{(mass\ of\ solute)}{(mass\ of\ solution)} \times 10^6 \tag{Chapter 9.3.4}$$

relationship among volume, molarity, and moles

Equation 9.3.2:

$$V_L M_{mol/L} = \cancel{L}\left(\frac{mol}{\cancel{L}}\right) = moles \tag{Chapter 9.3.5}$$

Conceptual Problems

1. Does the molality have the same numerical value as the molarity for a highly concentrated aqueous solution of fructose ($C_6H_{12}O_6$) (approximately 3.2 M)? Why or why not?
2. Explain why the molality and molarity of an aqueous solution are not always numerically identical. Will the difference between the two be greater for a dilute or a concentrated solution? Explain your answer.
3. Under what conditions are molality and molarity likely to be equal? Is the difference between the two greater when water is the solvent or when the solvent is not water? Why?
4. What is the key difference between using mole fraction or molality versus molarity to describe the concentration of a solution? Which unit(s) of concentration is most appropriate for experiments that must be carried out at several different temperatures?
5. An experiment that relies on very strict control of the reaction stoichiometry calls for adding 50.0 mL of a 0.95 M solution of A to 225 mL of a 1.01 M solution of B, followed by heating for 1 h at 60°C. To save time, a student decided to heat solution B to 60°C *before* measuring out 225 mL of solution B, transferring it to the flask containing solution A, and proceeding normally. This change in procedure caused the yield of product to be less than usual. How could such an apparently minor change in procedure have resulted in a decrease in the yield?

Numerical Problems

1. Complete the following table for aqueous solutions of the compounds given.

Compound	Molarity (M)	Solution Density (g/mL)	Mole Fraction (X)
H_2SO_4	18.0	1.84	
CH_3COOH		1.00	7.21×10^{-3}
KOH	3.60	1.16	

2. Complete the following table for each compound given.

Compound	Mass (g)	Volume of Solution (mL)	Molarity (M)
Na_2SO_4	7.80	225	
KNO_3		125	1.27
NaO_2CCH_3	18.64		0.95

3. How would you prepare 100.0 mL of an aqueous solution with 0.40 M KI? a solution with 0.65 M NaCN?
4. Calculate the molality of a solution with 775 mg of NaCl in 500.0 g of water. Do you expect the molarity to be the same as the molality? Why or why not?
5. What is the molarity of each solution?
    1. 12.8 g of glucose ($C_6H_{12}O_6$) in water, total volume 150.0 mL
    2. 9.2 g of Na_3PO_4 in water, total volume 200.0 mL
    3. 843 mg of I_2 in EtOH, total volume 150.0 mL
6. A medication used to treat abnormal heart rhythms is labeled “Procainamide 0.5 g/250 cc.” Express this concentration in parts per thousand.
7. Meperidine is a medication used for pain relief. A bottle of meperidine is labeled as 50 mg/mL. Express this concentration in parts per thousand.
8. An aqueous solution that is 4.61% NaOH by mass has a density of 1.06 g/mL. Calculate the molarity of the solution, the mole fraction of NaOH, and the molality of the solution.
9. A solution of concentrated phosphoric acid contains 85.0% H_3PO_4 by mass and has a density of 1.684 g/mL. Calculate the following.
    1. the molarity of the solution
    2. the mole fraction of H_3PO_4
    3. the molality of the solution
10. A solution of commercial concentrated nitric acid is 16 M HNO_3 and has a density of 1.42 g/mL. What is the percentage of HNO_3 in the solution by mass? What is the molality?
11. A commercial aqueous ammonia solution contains 28.0% NH_3 by massand has a density of 0.899 g/mL. Calculate the following.
    1. the molarity
    2. the mole fraction
12. Concentrated, or glacial, acetic acid is pure acetic acid and has a density of 1.053 g/mL. It is widely used in organic syntheses, in the manufacture of rayon and plastics, as a preservative in foods, and occasionally to treat warts. What volume of glacial

acetic acid is required to prepare 5.00 L of a 1.75 M solution of acetic acid in ethanol?

13. Solutions of sodium carbonate decahydrate, also known as washing soda, are used as skin cleansers. The solubility of this compound in cold water is 21.52 g/100 mL. If a saturated solution has a density of 1.20 g/mL, what is its molarity? What is the mole fraction of sodium carbonate decahydrate in this solution?
14. Hydrogen peroxide (H_2O_2) is usually sold over the counter as an aqueous solution that is 3% by mass. Assuming a solution density of 1.01 g/mL, what is the molarity of hydrogen peroxide? What is the molar concentration of a solution that is 30% hydrogen peroxide by mass (density = 1.112 g/mL)? How would you prepare 100.0 mL of a 3% solution from the 30% solution?
15. Determine the concentration of a solution with 825 mg of Na_2HPO_4 dissolved in 450.0 mL of H_2O at 20°C in molarity, molality, mole fraction, and parts per million. Assume that the density of the solution is the same as that of water. Which unit of concentration is most convenient for calculating vapor pressure changes? Why?
16. How many moles of Cl^- are there in 25.0 mL of a 0.15 M $CaCl_2$ solution?
17. How many moles of Na^+ are there in 25.0 g of a 1.33×10^{-3} *m* Na_2HPO_4 solution? What is the sodium concentration of this solution in ppb?
18. How many grams of copper are there in 30.0 mL of a 0.100 M $CuSO_4$ solution?
19. How many grams of nitrate ion are there in 75.0 g of a 1.75×10^{-4} *m* $Pb(NO_3)_2$ solution? What is the nitrate concentration of the solution in ppb?
20. How many milliliters of a 0.750 M solution of K_2CrO_4 are required to deliver 250 mg of chromate ion?
21. How many milliliters of a 1.95×10^{-6} M solution of Ag_3PO_4 are required to deliver 14.0 mg of Ag^+?
22. Iron reacts with bromine according to the following equation:

    $2Fe(s) + 3Br_2(aq) \rightarrow 2FeBr_3(aq)$

    How many milliliters of a 5.0×10^{-2} M solution of bromine in water are required to react completely with 750.0 mg of iron metal?
23. Aluminum reacts with HCl according to the following equation:

    $2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$

    If 25.0 mL of a solution of HCl in water is required to react completely with 1.05 g of aluminum metal, what is the molarity of the HCl solution?
24. The precipitation of silver chloride is a diagnostic test for the presence of chloride ion. If 25.0 mL of 0.175 M $AgNO_3$ are required to completely precipitate the chloride ions from 10.0 mL of an NaCl solution, what was the original concentration of NaCl?
25. Barium sulfate is virtually insoluble. If a 10.0 mL solution of 0.333 M $Ba(NO_3)_2$ is stirred with 40.0 mL of a 0.100 M Na_2SO_4, how many grams of barium sulfate will precipitate? Which reactant is present in excess? What is its final concentration?

Answers

1.

Compound	Molarity (M)	Solution Density (g/mL)	Mole Fraction (*X*)
H_2SO_4	18.0	1.84	**0.82**
CH_3COOH	**0.393**	1.00	7.21×10^{-3}
KOH	3.60	1.16	$\mathbf{6.33 \times 10^{-2}}$

2.

3. 100.0 ml of 0.40 M KI: dissolve 6.64 g of KI in enough water to make 100.0 mL of solution; 100.0 ml of 0.65 M NaCN: dissolve 3.18 g of NaCN in enough water to make 100.0 mL of solution.
4.
5. 1. 0.474 M glucose
   2. 0.28 M Na_3PO_4
   3. 0.0221 M I_2
6.
7.
8.
9. 1. 14.6 M
   2. $X = 0.510$
   3. 57.7 *m*
10.
11. 1. 14.8 M
    2. $X = 0.292$
12.
13. The molarity is 0.745 M, and the mole fraction is 0.0134.
14.
15. The molarity is 0.0129 M, the molality is 0.0129 *m*, the mole fraction is 2.33×10^{-4}, and the solution contains 1830 ppm Na_2HPO_4. Mole fraction is most useful for calculating vapor pressure, because Raoult's law states that the vapor pressure of a solution containing a non-volatile solute is equal to the mole fraction of solvent times the vapor pressure of the pure solvent. The mole fraction of the solvent is just one minus the mole fraction of solute.
16.
17. 6.65×10^{-5} mol sodium; 6.14×10^{4} ppb
18.
19. 1.63×10^{-3} g; 2.17×10^{4} ppb
20.
21. 2.22×10^{4} mL or 22.2 L
22.
23. 4.68 M HCl
24.
25. 0.777 g $BaSO_4$; Na_2SO_4; 0.0134 M Na_2SO_4

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Chapter 9.4:Temperature and Pressure Effects

Learning Objective

- To understand the relationship among temperature, pressure, and solubility.

Experimentally it is found that the solubility of most compounds depends strongly on temperature and, if a gas, on pressure as well. As we shall see, the ability to manipulate the solubility by changing the temperature and pressure has several important consequences.

Effect of Temperature on the Solubility of Solids

Figure 9.4.1 shows plots of the solubilities of several organic and inorganic compounds in water as a function of temperature. Although the solubility of a solid generally increases with increasing temperature, there is no simple relationship between the structure of a substance and the temperature dependence of its solubility. Many compounds (such as glucose and CH_3CO_2Na) exhibit a dramatic increase in solubility with increasing temperature. Others (such as NaCl and K_2SO_4) exhibit little variation, and still others (such as Li_2SO_4) become less soluble with increasing temperature.

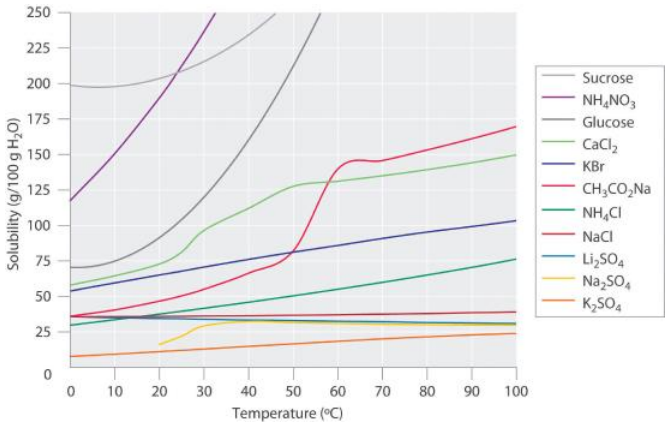


Figure 9.4.1 Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature *Solubility may increase or decrease with temperature; the magnitude of this temperature dependence varies widely among compounds.*

Notice in particular the curves for NH_4NO_3 and $CaCl_2$. The dissolution of ammonium nitrate in water is endothermic, that is the solution cools on mixing (ΔH_{soln} = +25.7 kJ/mol), whereas the dissolution of calcium chloride is exothermic, the solution warms while mixing (ΔH_{soln} = −68.2 kJ/mol), yet Figure 9.4.1 shows that the solubility of both compounds increases sharply with increasing temperature. The reasons for this are complex and will be discussed when we meet thermodynamics in Chapter 16. Because the solubility of a compound is ultimately determined by relatively small differences between large numbers, there is generally no good way to predict how the solubility will vary with temperature.

The variation of solubility with temperature has been measured for a wide range of compounds, and the results are published in many standard reference books. Chemists are often able to use this information to separate the components of a mixture by fractional crystallizationThe separation of compounds based on their relative solubilities in a given solvent., the separation of compounds on the basis of their solubilities in a given solvent. For example, if we have a mixture of 150 g of sodium acetate (CH_3CO_2Na) and 50 g of KBr, we can separate the two compounds by dissolving the mixture in 100 g of water at 80°C and then cooling the solution slowly to 0°C. According to the temperature curves in Figure 9.4.1, both compounds dissolve in water at 80°C, and all 50 g of KBr remains in solution at 0°C. Only about 36 g of CH_3CO_2Na are soluble in 100 g of water at 0°C, however, so approximately 114 g (150 g − 36 g) of CH_3CO_2Na crystallizes out on cooling. The crystals can then be separated by filtration. Thus fractional crystallization allows us to recover about 75% of the original CH_3CO_2Na in essentially pure form in only one step.

Fractional crystallization is a common technique for purifying compounds as diverse as those shown in Figure 9.4.1 and from antibiotics to enzymes. For the technique to work properly, the compound of interest must be more soluble at high temperature than at low temperature, so that lowering the temperature causes it to crystallize out of solution. In addition, the impurities must be *more* soluble than the compound of interest (as was KBr in this example) and preferably present in relatively small amounts.

Effect of Temperature on the Solubility of Gases

The solubility of gases in liquids decreases with increasing temperature, as shown in Figure 9.4.2. Attractive intermolecular interactions in the gas phase are essentially zero for most substances. When a gas dissolves, it does so because its molecules interact with solvent molecules. Because heat is released when these new attractive interactions form, dissolving most gases in liquids is an exothermic process ($\Delta H_{soln} < 0$). Conversely, adding heat to the solution provides thermal energy that overcomes the attractive forces between the gas and the solvent molecules, thereby decreasing the solubility of the gas.The phenomenon is similar to that involved in the increase in vapor pressure of a pure liquid with increasing temperature, as discussed in Chapter 8. In the case of vapor pressure, however, it is attractive forces between *solvent* molecules that are being overcome by the added thermal energy when the temperature is increased.

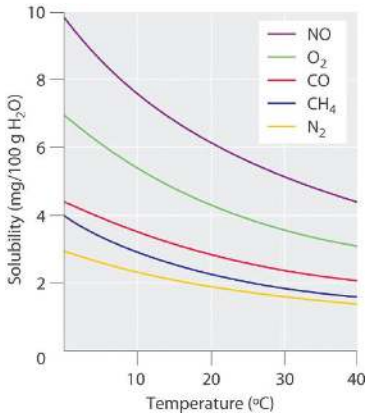


Figure 9.4.2 Solubilities of Several Common Gases in Water as a Function of Temperature at Partial Pressure of 1 atm *The solubilities of all gases decrease with increasing temperature.*

The decrease in the solubilities of gases at higher temperatures has both practical and environmental implications. Anyone who routinely boils water in a teapot or electric kettle knows that a white or gray deposit builds up on the inside and must eventually be removed. The same phenomenon occurs on a much larger scale in the giant boilers used to supply hot water or steam for industrial applications, where it is called "boiler scale," a deposit that can seriously decrease the capacity of hot water pipes (Figure 9.4.3). The problem is not a uniquely modern one: aqueducts that were built by the Romans 2000 years ago to carry cold water from alpine regions to warmer, drier regions in southern France were clogged by similar deposits. The chemistry behind the formation of these deposits is moderately complex, but the driving force is the loss of dissolved CO_2 from solution. Hard water contains dissolved Ca^{2+} and HCO_3^- (bicarbonate) ions. Calcium bicarbonate [$Ca(HCO_3)_2$] is rather soluble in water, but calcium carbonate ($CaCO_3$) is quite insoluble. A solution of bicarbonate ions can react to form carbon dioxide, carbonate ion, and water:

$$2HCO_3^-(aq) \rightarrow CO_2^{2-}(aq) + H_2O(l) + CO_2(aq)$$

Heating the solution decreases the solubility of CO_2, which escapes into the gas phase above the solution. In the presence of calcium ions, the carbonate ions precipitate as insoluble calcium carbonate, the major component of boiler scale.



Figure 9.4.3 Boiler Scale in a Water Pipe *Calcium carbonate ($CaCO_3$) deposits in hot water pipes can significantly reduce pipe capacity. These deposits, called boiler scale, form when dissolved CO_2 is driven into the gas phase at high temperatures.*

In *thermal pollution*, lake or river water that is used to cool an industrial reactor or a power plant is returned to the environment at a higher temperature than normal. Because of the reduced solubility of O_2 at higher temperatures (Figure 9.4.2), the warmer water contains less dissolved oxygen than the water did when it entered the plant. Fish and other aquatic organisms that need dissolved oxygen to live can literally suffocate if the oxygen concentration of their habitat is too low. Because the warm, oxygen-depleted

water is less dense, it tends to float on top of the cooler, denser, more oxygen-rich water in the lake or river, forming a barrier that prevents atmospheric oxygen from dissolving. Eventually even deep lakes can be suffocated if the problem is not corrected. Additionally, most fish and other nonmammalian aquatic organisms are cold-blooded, which means that their body temperature is the same as the temperature of their environment. Temperatures substantially greater than the normal range can lead to severe stress or even death. Cooling systems for power plants and other facilities must be designed to minimize any adverse effects on the temperatures of surrounding bodies of water.

A similar effect is seen in the rising temperatures of bodies of water such as the Chesapeake Bay, the largest estuary in North America, where global warming has been implicated as the cause. For each 1.5°C that the bay's water warms, the capacity of water to dissolve oxygen decreases by about 1.1%. Many marine species that are at the southern limit of their distributions have shifted their populations farther north. In 2005, the eelgrass, which forms an important nursery habitat for fish and shellfish, disappeared from much of the bay following record high water temperatures. Presumably, decreased oxygen levels decreased populations of clams and other filter feeders, which then decreased light transmission to allow the eel grass to grow. The complex relationships in ecosystems such as the Chesapeake Bay are especially sensitive to temperature fluctuations that cause a deterioration of habitat quality.

Effect of Pressure on the Solubility of Gases: Henry's Law

External pressure has very little effect on the solubility of liquids and solids. In contrast, the solubility of gases increases as the partial pressure of the gas above a solution increases. This point is illustrated in Figure 9.4.4 which shows the effect of increased pressure on the dynamic equilibrium that is established between the dissolved gas molecules in solution and the molecules in the gas phase above the solution. Because the concentration of molecules in the gas phase increases with increasing pressure, the concentration of dissolved gas molecules in the solution at equilibrium is also higher at higher pressures.

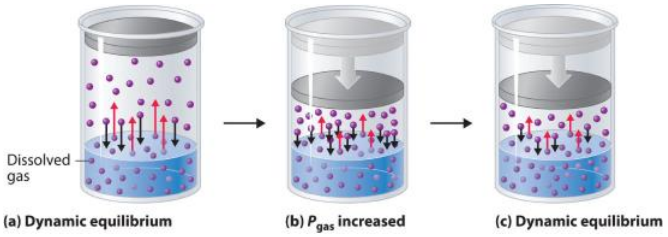


Figure 9.4.4 A Model Depicting Why the Solubility of a Gas Increases as the Partial Pressure Increases at Constant Temperature*(a) When a gas comes in contact with a pure liquid, some of the gas molecules (purple spheres) collide with the surface of the liquid and dissolve. When the concentration of dissolved gas molecules has increased so that the rate at which gas molecules escape into the gas phase is the same as the rate at which they dissolve, a dynamic equilibrium has been established, as depicted here. This equilibrium is entirely analogous to the one that maintains the vapor pressure of a liquid. (For more information on vapor pressure, see Section 7.4) (b) Increasing the pressure of the gas increases the number of molecules of gas per unit volume, which increases the rate at which gas molecules collide with the surface of the liquid and dissolve. (c) As additional gas molecules dissolve at the higher pressure, the concentration of dissolved gas increases until a new dynamic equilibrium is established.*

The relationship between pressure and the solubility of a gas is described quantitatively by Henry's law, which is named for its discoverer, the English physician and chemist, William Henry (1775–1836):

$$C = kP$$

where C is the concentration of dissolved gas at equilibrium, P is the partial pressure of the gas, and k is the *Henry's law constant*, which must be determined experimentally for each combination of gas, solvent, and temperature. Although the gas concentration may be expressed in any convenient units, we will use molarity exclusively. The units of the Henry's law constant are therefore mol/(L·atm) = M/atm. Values of the Henry's law constants for solutions of several gases in water at 20°C are listed in Table 9.4.1 .

As the data in Table 9.4.1 demonstrate, the concentration of a dissolved gas in water at a given pressure depends strongly on its physical properties. For a series of related substances, London dispersion forces increase as molecular mass increases. Thus among the elements of group 18, the Henry's law constants increase smoothly from He to Ne to Ar. The table also shows that O_2 is almost

twice as soluble as N_2. Although London dispersion forces are too weak to explain such a large difference, O_2 is paramagnetic and hence more polarizable than N_2, which explains its high solubility.

Table 9.4.1 Henry's Law Constants for Selected Gases in Water at 20°C

Gas	Henry's Law Constant [mol/(L·atm)] × 10^{-4}
He	3.9
Ne	4.7
Ar	15
H_2	8.1
N_2	7.1
O_2	14
CO_2	392

Gases that react chemically with water, such as HCl and the other hydrogen halides, H_2S, and NH_3, do not obey Henry's law; all of these gases are much more soluble than predicted by Henry's law. For example, HCl reacts with water to give $H^+(aq)$ and $Cl^-(aq)$, *not* dissolved HCl molecules, and its dissociation into ions results in a much higher solubility than expected for a neutral molecule.

Note the Pattern

Gases that react with water do not obey Henry's law.

Henry's law has important applications. For example, bubbles of CO_2 form as soon as a carbonated beverage is opened because the drink was bottled under CO_2 at a pressure greater than 1 atm. When the bottle is opened, the pressure of CO_2 above the solution drops rapidly, and some of the dissolved gas escapes from the solution as bubbles. Henry's law also explains why scuba divers have to be careful to ascend to the surface slowly after a dive if they are breathing compressed air. At the higher pressures under water, more N_2 from the air dissolves in the diver's internal fluids. If the diver ascends too quickly, the rapid pressure change causes small bubbles of N_2 to form throughout the body, a condition known as "the bends." These bubbles can block the flow of blood through the small blood vessels, causing great pain and even proving fatal in some cases.

Due to the low Henry's law constant for O_2 in water, the levels of dissolved oxygen in water are too low to support the energy needs of multicellular organisms, including humans. To increase the O_2 concentration in internal fluids, organisms synthesize highly soluble carrier molecules that bind O_2 reversibly. For example, human red blood cells contain a protein called hemoglobin that specifically binds O_2 and facilitates its transport from the lungs to the tissues, where it is used to oxidize food molecules to provide energy. The concentration of hemoglobin in normal blood is about 2.2 mM, and each hemoglobin molecule can bind four O_2 molecules. Although the concentration of dissolved O_2 in blood serum at 37°C (normal body temperature) is only 0.010 mM, the total dissolved O_2 concentration is 8.8 mM, almost a thousand times greater than would be possible without hemoglobin. Synthetic oxygen carriers based on fluorinated alkanes have been developed for use as an emergency replacement for whole blood. Unlike donated blood, these "blood substitutes" do not require refrigeration and have a long shelf life. Their very high Henry's law constants for O_2 result in dissolved oxygen concentrations comparable to those in normal blood.

Example 9.4.1

The Henry's law constant for O_2 in water at 25°C is 1.27×10^{-3} M/atm, and the mole fraction of O_2 in the atmosphere is 0.21. Calculate the solubility of O_2 in water at 25°C at an atmospheric pressure of 1.00 atm.

Given: Henry's law constant, mole fraction of O_2, and pressure

Asked for: solubility

Strategy:

A Use Dalton's law of partial pressures to calculate the partial pressure of oxygen. (For more information about Dalton's law of partial pressures, see Section 6.5.)

B Use Henry's law to calculate the solubility, expressed as the concentration of dissolved gas.

Solution:

A According to Dalton's law, the partial pressure of O_2 is proportional to the mole fraction of O_2:

$P_A = X_A P_t = (0.21)(1.00\ \text{atm}) = 0.21\ \text{atm}$

B From Henry's law, the concentration of dissolved oxygen under these conditions is

$$C_{O_2} = kP_{O_2}\left(1.27 \times 10^{-3}\ M/\cancel{atm}\right)\left(0.21\ \cancel{atm}\right) = 2.7 \times 10^{-4}\ M \qquad \text{(Chapter 9.4.1)}$$

Exercise

To understand why soft drinks "fizz" and then go "flat" after being opened, calculate the concentration of dissolved CO_2 in a soft drink

1. bottled under a pressure of 5.0 atm of CO_2.
2. in equilibrium with the normal partial pressure of CO_2 in the atmosphere (approximately 3×10^{-4} atm).

The Henry's law constant for CO_2 in water at 25°C is 3.4×10^{-2} M/atm.

Answer:

1. 0.17 M
2. 1×10^{-5} M

Summary

The solubility of most substances depends strongly on the temperature and, in the case of gases, on the pressure. The solubility of most solid or liquid solutes increases with increasing temperature. The components of a mixture can often be separated using **fractional crystallization**, which separates compounds according to their solubilities. The solubility of a gas decreases with increasing temperature. **Henry's law** describes the relationship between the pressure and the solubility of a gas.

Key Takeaway

- The solubility of a solid may increase or decrease with increasing temperature, whereas the solubility of a gas decreases with an increase in temperature and a decrease in pressure.

Conceptual Problems

1. Use the kinetic molecular theory of gases discussed in Section 6.6 to explain why the solubility of virtually all gases in liquids decreases with increasing temperature.
2. An industrial plant uses water from a nearby stream to cool its reactor and returns the water to the stream after use. Over a period of time, dead fish start to appear downstream from the plant, but there is no evidence for any leaks of potentially toxic chemicals into the stream. What other factor might be causing the fish to die?
3. One manufacturer's instructions for setting up an aquarium specify that if boiled water is used, the water must be cooled to room temperature and allowed to stand overnight before fish are added. Why is it necessary for the water to stand?
4. Using a carbonated beverage as an example, discuss the effect of temperature on the "fizz." How does the "foaminess" of a carbonated beverage differ between Los Angeles, California, and Denver, Colorado?
5. A common laboratory technique for degassing a solvent is to place it in a flask that is sealed to the atmosphere and then evacuate the flask to remove any gases above the liquid. Why is this procedure effective? Why does the temperature of the solvent usually decrease substantially during this process?

Answers

1. When water is boiled, all of the dissolved oxygen and nitrogen are removed. When the water is cooled to room temperature, it initially contains very little dissolved oxygen. Allowing the water to stand overnight allows oxygen in the air to dissolve, so that the fish will not suffocate.

4.
5. Evacuating the flask to remove gases decreases the partial pressure of oxygen above the solution. According to Henry's law, the solubility of any gas decreases as its partial pressure above the solution decreases. Consequently, dissolved oxygen escapes from solution into the gas phase, where it is removed by the vacuum pump. Filling the flask with nitrogen gas and repeating this process several times effectively removes almost all of the dissolved oxygen. The temperature of the solvent decreases because some solvent evaporates as well during this process. The heat that is required to evaporate some of the liquid is initially removed from the rest of the solvent, decreasing its temperature.

Numerical Problems

1. The solubility of CO_2 in water at 0°C and 1 atm is 0.335 g/100 g of H_2O. At 20°C and 1 atm, the solubility of CO_2 in water is 0.169 g/100 g of H_2O.
    1. What volume of CO_2 would be released by warming 750 g of water saturated with CO_2 from 0°C to 20°C?
    2. What is the value of the Henry's law constant for CO_2 under each set of conditions?
2. The solubility of O_2 in 100 g of H_2O at varying temperatures and a pressure of 1 atm is given in the following table:

Solubility (g)	Temperature (°C)
0.0069	0
0.0054	10
0.0043	20

    1. What is the value of the Henry's law constant at each temperature?
    2. Does Henry's law constant increase or decrease with increasing temperature?
    3. At what partial pressure of O_2 would the concentration of O_2 in water at 0°C be the same as the concentration in water at 20°C at a partial pressure of 1 atm?
    4. Assuming that air is 20% O_2 by volume, at what atmospheric pressure would the O_2 concentration be the same at 20°C as it is at atmospheric pressure and 0°C?

Answer

1. 1. 0.678 L CO_2
    2. $k_{0°C} = 7.61 \times 10^{-2}$ M/atm, $k_{20°C} = 3.84 \times 10^{-2}$ M/atm
2.

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Chapter 9.5: Colligative Properties

Learning Objective

- To describe the relationship between solute concentration and the physical properties of a solution.

Many of the physical properties of solutions differ significantly from those of the pure substances discussed in earlier chapters, and these differences have important consequences. For example, the limited temperature range of liquid water (0°C–100°C) severely limits its use. Aqueous solutions have both a lower freezing point and a higher boiling point than pure water. Probably one of the most familiar applications of this phenomenon is the addition of ethylene glycol (“antifreeze”) to the water in an automobile radiator. This solute lowers the freezing point of the water, preventing the engine from cracking in very cold weather from the expansion of pure water on freezing. Antifreeze also enables the cooling system to operate at temperatures greater than 100°C without generating enough pressure to explode.

Changes in the freezing point and boiling point of a solution depend primarily on the *number* of solute particles present rather than the *kind* of particles. Such properties of solutions are called colligative propertiesA property of a solution that depends primarily on the *number* of solute particles rather than the *kind* of solute particles. (from the Latin *colligatus*, meaning “bound together” as in a quantity). As we will see, the vapor pressure and osmotic pressure of solutions are also colligative properties.

When we determine the number of particles in a solution, it is important to remember that not all solutions with the same molarity contain the same concentration of solute particles. Consider, for example, 0.01 M aqueous solutions of sucrose, NaCl, and $CaCl_2$. Because sucrose dissolves to give a solution of neutral molecules, the concentration of solute particles in a 0.01 M sucrose solution is 0.01 M. In contrast, both NaCl and $CaCl_2$ are ionic compounds that dissociate in water to yield solvated ions. As a result, a 0.01 M aqueous solution of NaCl contains 0.01 M Na^+ ions *and* 0.01 M Cl^- ions, for a total particle concentration of 0.02 M. Similarly, the $CaCl_2$ solution contains 0.01 M Ca^{2+} ions and 0.02 M Cl^- ions, for a total particle concentration of 0.03 M.These values are correct for dilute solutions, where the dissociation of the compounds to form separately solvated ions is complete. At higher concentrations (typically >1 M), especially with salts of small, highly charged ions (such as Mg^{2+} or Al^{3+}), or in solutions with less polar solvents, dissociation to give separate ions is often incomplete (see Figure 9.5.9 "Ion Pairs"). The sum of the concentrations of the dissolved solute particles dictates the physical properties of a solution. In the following discussion, we must therefore keep the chemical nature of the solute firmly in mind.

Vapor Pressure of Solutions and Raoult’s Law

Adding a nonvolatile solute, one whose vapor pressure is too low to measure readily, to a volatile solvent decreases the vapor pressure of the solvent. We can understand this phenomenon qualitatively by examining Figure 9.5.1, which is a schematic diagram of the surface of a solution of glucose in water. In an aqueous solution of glucose, a portion of the surface area is occupied by nonvolatile glucose molecules rather than by volatile water molecules. As a result, fewer water molecules can enter the vapor phase per unit time, even though the surface water molecules have the same kinetic energy distribution as they would in pure water. At the same time, the rate at which water molecules in the vapor phase collide with the surface and reenter the solution is unaffected. The net effect is to shift the dynamic equilibrium between water in the vapor and the liquid phases, decreasing the vapor pressure of the solution compared with the vapor pressure of the pure solvent.

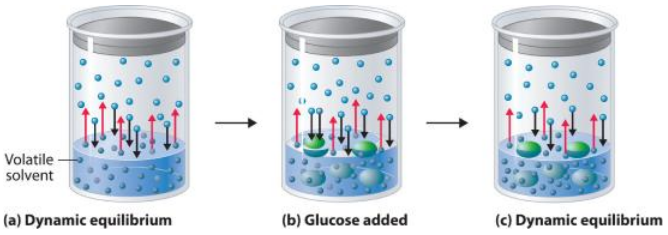


Figure 9.5.1 A Model Depicting Why the Vapor Pressure of a Solution of Glucose Is Less Than the Vapor Pressure of Pure Water (a) When water or any volatile solvent is in a closed container, water molecules move into and out of the liquid phase at the same rate in a dynamic equilibrium. (b) If a nonvolatile solute such as glucose is added, some fraction of the surface area is occupied by solvated solute molecules. As a result, the rate at which water molecules evaporate is decreased, although initially their

rate of condensation is unchanged. (c) When the glucose solution reaches equilibrium, the concentration of water molecules in the vapor phase, and hence the vapor pressure, is less than that of pure water.

Figure 9.5.2 shows two beakers, one containing pure water and one containing an aqueous glucose solution, in a sealed chamber. We can view the system as having two competing equilibria: water vapor will condense in both beakers at the same rate, but water molecules will evaporate more slowly from the glucose solution because fewer water molecules are at the surface. Eventually all of the water will evaporate from the beaker containing the liquid with the higher vapor pressure (pure water) and condense in the beaker containing the liquid with the lower vapor pressure (the glucose solution). If the system consisted of only a beaker of water inside a sealed container, equilibrium between the liquid and vapor would be achieved rather rapidly, and the amount of liquid water in the beaker would remain constant.

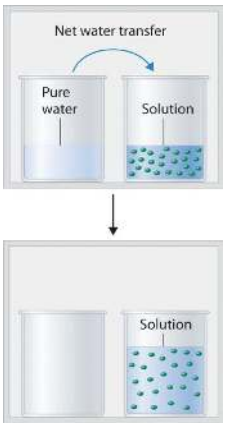


Figure 9.5.2 Transfer of Water to a Beaker Containing a Glucose Solution (top) One beaker contains an aqueous solution of glucose, and the other contains pure water. If they are placed in a sealed chamber, the lower vapor pressure of water in the glucose solution results in a net transfer of water from the beaker containing pure water to the beaker containing the glucose solution. (bottom) Eventually, all of the water is transferred to the beaker that has the glucose solution.

If the particles of a solute are essentially the same size as those of the solvent and both solute and solvent have roughly equal probabilities of being at the surface of the solution, then the effect of a solute on the vapor pressure of the solvent is proportional to the number of sites occupied by solute particles at the surface of the solution. Doubling the concentration of a given solute causes twice as many surface sites to be occupied by solute molecules, resulting in twice the decrease in vapor pressure. The relationship between solution composition and vapor pressure is therefore

$$P_A = X_A P_A^o$$

where P_A is the vapor pressure of component A of the solution (in this case the solvent), X_A is the mole fraction of A in solution, and P_A^0 is the vapor pressure of pure A. Equation 9.5.1 is known as Raoult's lawAn equation that quantifies the relationship between solution composition and vapor pressure: $P_A=X_AP_A^0$, after the French chemist who developed it. If the solution contains only a single nonvolatile solute (B), then $X_A + X_B = 1$, and we can substitute $X_A = 1 - X_B$ to obtain

$$P_A = (1 - X_B)\,P_A^o = P_A^o - X_B P_A^o$$

Rearranging and defining $\Delta P_A=P_A^o-P_A$ we obtain a relationship between the decrease in vapor pressure and the mole fraction of nonvolatile solute:

$$P_A^o - P_A = \Delta P_A = X_B P_A^o$$

We can solve vapor pressure problems in either of two ways: by using Equation 9.5.1 to calculate the actual vapor pressure above a solution of a nonvolatile solute, or by using Equation 9.5.3 to calculate the decrease in vapor pressure caused by a specified amount of a nonvolatile solute.

Example 9.5.1

Ethylene glycol ($HOCH_2CH_2OH$), the major ingredient in commercial automotive antifreeze, increases the boiling point of radiator fluid by lowering its vapor pressure. At 100°C, the vapor pressure of pure water is 760 mmHg. Calculate the vapor pressure of an

aqueous solution containing 30.2% ethylene glycol by mass, a concentration commonly used in climates that do not get extremely cold in winter.

Given: identity of solute, percentage by mass, and vapor pressure of pure solvent

Asked for: vapor pressure of solution

Strategy:

A Calculate the number of moles of ethylene glycol in an arbitrary quantity of water, and then calculate the mole fraction of water.

B Use Raoult's law to calculate the vapor pressure of the solution.

Solution:

A A 30.2% solution of ethylene glycol contains 302 g of ethylene glycol per kilogram of solution; the remainder (698 g) is water. To use Raoult's law to calculate the vapor pressure of the solution, we must know the mole fraction of water. Thus we must first calculate the number of moles of both ethylene glycol (EG) and water present:

$$moles\ EG = (302\ g)\frac{1\ mol}{62.07\ g} = 4.87\ mol\ EG$$

$$moles\ H_2O = (698\ g)\frac{1\ mol}{18.02\ g} = 38.7\ mol\ H_2O$$

The mole fraction of water is thus

$$X_{H_2O} = \frac{38.7\ mol\ H_2O}{38.7\ mol\ H_2O + 4.87\ mol\ EG} = 0.888$$

B From Raoult's law (Equation 9.5.1), the vapor pressure of the solution is

$$P_{H_2O} = X_{H_2O}P^o_{H_2O} = (0.888)\,(760\ Torr) = 675\ Torr$$

Alternatively, we could solve this problem by calculating the mole fraction of ethylene glycol and then using Equation 9.5.3 to calculate the resulting decrease in vapor pressure:

$$X_{EG} = \frac{4.87\ mol\ EG}{38.7\ mol\ H_2O + 4.87\ mol\ EG} = 0.112$$

$$\Delta P_{H_2O} = X_{EG}P^o_{H_2O} = (0.112)\,(760\ Torr) = 85.1\ Torr$$

$$P_{H_2O} = P^o_{H_2O} - \Delta P_{H_2O} = 760\ Torr - 85.1 = 675\ Torr$$

The same result is obtained using either method.

Exercise

Seawater is an approximately 3.0% aqueous solution of NaCl by mass with about 0.5% of other salts by mass. Calculate the decrease in the vapor pressure of water at 25°C caused by this concentration of NaCl, remembering that 1 mol of NaCl produces 2 mol of solute particles. The vapor pressure of pure water at 25°C is 23.8 mmHg.

Answer: 0.45 mmHg. This may seem like a small amount, but it constitutes about a 2% decrease in the vapor pressure of water and accounts in part for the higher humidity in the north-central United States near the Great Lakes, which are freshwater lakes. The decrease therefore has important implications for climate modeling.

Even when a solute is volatile, meaning that it has a measurable vapor pressure, we can still use Raoult's law. In this case, we calculate the vapor pressure of each component separately. The total vapor pressure of the solution (P_T) is the sum of the vapor pressures of the components:

$$P_T = P_A + P_B = X_AP^o_A + X_BP^o_B$$

Because $X_B = 1 - X_A$ for a two-component system,

$$P_T = X_AP^o_A + (1 - X_A)\,P^o_B$$

Thus we need to specify the mole fraction of only one of the components in a two-component system. Consider, for example, the vapor pressure of solutions of benzene and toluene of various compositions. At 20°C, the vapor pressures of pure benzene and toluene are 74.7 and 22.3 mmHg, respectively. The vapor pressure of benzene in a benzene–toluene solution is

$$P_{C_6H_6} = X_{C_6H_6} P^o_{C_6H_6}$$

and the vapor pressure of toluene in the solution is

$$P_{C_6H_5CH_3} = X_{C_6H_5CH_3} P^o_{C_6H_5CH_3}$$

Equation 9.5.6 and Equation 9.5.7 are both in the form of the equation for a straight line: $y = mx + b$, where $b = 0$. Plots of the vapor pressures of both components versus the mole fractions are therefore straight lines that pass through the origin, as shown in Figure 9.5.3. Furthermore, a plot of the total vapor pressure of the solution versus the mole fraction is a straight line that represents the sum of the vapor pressures of the pure components. Thus the vapor pressure of the solution is always greater than the vapor pressure of either component.

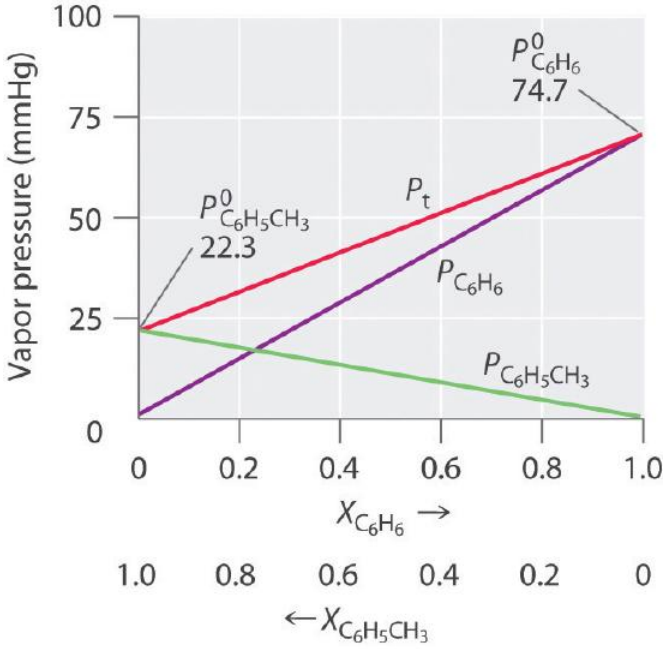


Figure 9.5.3 Vapor Pressures of Benzene–Toluene Solutions Plots of the vapor pressures of benzene (C_6H_6) and toluene ($C_6H_5CH_3$) versus the mole fractions at 20°C are straight lines. For a solution like this, which approximates an ideal solution, the total vapor pressure of the solution (P_t) is the sum of the vapor pressures of the components.

A solution of two volatile components that behaves like the solution in Figure 9.5.3 is an ideal solutionA solution that obeys Raoult's law., which is defined as a solution that obeys Raoult's law. Like an ideal gas, an ideal solution is a hypothetical system whose properties can be described in terms of a simple model. Mixtures of benzene and toluene approximate an ideal solution because the intermolecular forces in the two pure liquids are almost identical in both kind and magnitude. Consequently, the change in enthalpy on solution formation is essentially zero ($\Delta H_{soln} \approx 0$), which is one of the defining characteristics of an ideal solution.

Note the Pattern

Ideal solutions and ideal gases are both simple models that ignore intermolecular interactions.

Most real solutions, however, do not obey Raoult's law precisely, just as most real gases do not obey the ideal gas law exactly. Real solutions generally deviate from Raoult's law because the intermolecular interactions between the two components A and B differ. We can distinguish between two general kinds of behavior, depending on whether the intermolecular interactions between molecules A and B are stronger or weaker than the A–A and B–B interactions in the pure components. If the A–B interactions are *stronger* than the A–A and B–B interactions, each component of the solution exhibits a *lower* vapor pressure than expected for an ideal solution, as does the solution as a whole. The favorable A–B interactions effectively stabilize the solution compared with the vapor. This kind of behavior is called a *negative deviation from Raoult's law*. Systems stabilized by hydrogen bonding between two molecules, such as acetone and ethanol, exhibit negative deviations from Raoult's law. Conversely, if the A–B interactions are *weaker* than the A–A and B–B interactions yet the entropy increase is enough to allow the solution to form, both A and B have an increased tendency to escape from the solution into the vapor phase. The result is a *higher* vapor pressure than expected for an ideal

solution, producing a *positive deviation from Raoult's law.* In a solution of CCl_4 and methanol, for example, the nonpolar CCl_4 molecules interrupt the extensive hydrogen bonding network in methanol, and the lighter methanol molecules have weaker London dispersion forces than the heavier CCl_4 molecules. Consequently, solutions of CCl_4 and methanol exhibit positive deviations from Raoult's law.

Example 9.5.2

For each system, compare the intermolecular interactions in the pure liquids and in the solution to decide whether the vapor pressure will be greater than that predicted by Raoult's law (positive deviation), approximately equal to that predicted by Raoult's law (an ideal solution), or less than the pressure predicted by Raoult's law (negative deviation).

1. cyclohexane and ethanol
2. methanol and acetone
3. *n*-hexane and isooctane (2,2,4-trimethylpentane)

Given: identity of pure liquids

Asked for: predicted deviation from Raoult's law

Strategy:

Identify whether each liquid is polar or nonpolar, and then predict the type of intermolecular interactions that occur in solution.

Solution:

1. Liquid ethanol contains an extensive hydrogen bonding network, and cyclohexane is nonpolar. Because the cyclohexane molecules cannot interact favorably with the polar ethanol molecules, they will disrupt the hydrogen bonding. Hence the A–B interactions will be weaker than the A–A and B–B interactions, leading to a higher vapor pressure than predicted by Raoult's law (a positive deviation).
2. Methanol contains an extensive hydrogen bonding network, but in this case the polar acetone molecules create A–B interactions that are stronger than the A–A or B–B interactions, leading to a negative enthalpy of solution and a lower vapor pressure than predicted by Raoult's law (a negative deviation).
3. Hexane and isooctane are both nonpolar molecules (isooctane actually has a very small dipole moment, but it is so small that it can be ignored). Hence the predominant intermolecular forces in both liquids are London dispersion forces. We expect the A–B interactions to be comparable in strength to the A–A and B–B interactions, leading to a vapor pressure in good agreement with that predicted by Raoult's law (an ideal solution).

Exercise

For each system, compare the intermolecular interactions in the pure liquids with those in the solution to decide whether the vapor pressure will be greater than that predicted by Raoult's law (positive deviation), approximately equal to that predicted by Raoult's law (an ideal solution), or less than the pressure predicted by Raoult's law (negative deviation):

1. benzene and *n*-hexane
2. ethylene glycol and CCl_4
3. acetic acid and *n*-propanol

Answer:

1. approximately equal
2. positive deviation (vapor pressure greater than predicted)
3. negative deviation (vapor pressure less than predicted)

Boiling Point Elevation

Recall from Chapter 7 that the normal boiling point of a substance is the temperature at which the vapor pressure equals 1 atm. If a nonvolatile solute lowers the vapor pressure of a solvent, it must also affect the boiling point. Because the vapor pressure of the solution at a given temperature is *less* than the vapor pressure of the pure solvent, achieving a vapor pressure of 1 atm for the solution requires a *higher* temperature than the normal boiling point of the solvent. Thus *the boiling point of a solution is always greater than that of the pure solvent*. We can see why this must be true by comparing the phase diagram for an aqueous solution

with the phase diagram for pure water (Figure 9.5.4). The vapor pressure of the solution is less than that of pure water *at all temperatures*. Consequently, the liquid–vapor curve for the solution crosses the horizontal line corresponding to P = 1 atm at a higher temperature than does the curve for pure water.

Note the Pattern

The boiling point of a solution with a nonvolatile solute is always greater than the boiling point of the pure solvent.

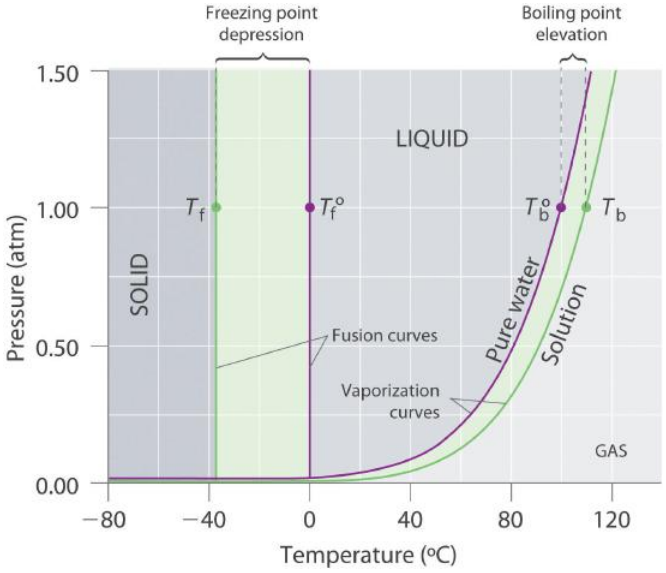


Figure 9.5.4 Phase Diagrams of Pure Water and an Aqueous Solution of a Nonvolatile Solute The vaporization curve for the solution lies below the curve for pure water at all temperatures, which results in an increase in the boiling point and a decrease in the freezing point of the solution.

The magnitude of the increase in the boiling point is related to the magnitude of the decrease in the vapor pressure. As we have just discussed, the decrease in the vapor pressure is proportional to the concentration of the solute in the solution. Hence the magnitude of the increase in the boiling point must also be proportional to the concentration of the solute (Figure 9.5.5). We can define the boiling point elevation (ΔT_b)The difference between the boiling point of a solution and the boiling point of the pure solvent. as the difference between the boiling points of the solution and the pure solvent:

$$\Delta T_b = T_b - T_b^o$$

where T_b is the boiling point of the solution and T_b^o is the boiling point of the pure solvent. We can express the relationship between ΔT_b and concentration as follows:

$$\Delta T_b = mK_b$$

where m is the concentration of the solute expressed in molality, and K_b is the *molal boiling point elevation constant* of the solvent, which has units of °C/m. Table 9.5.1 lists characteristic K_b values for several commonly used solvents.

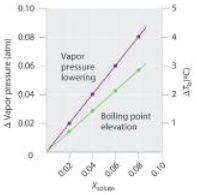
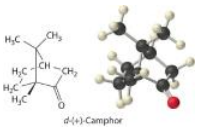


Figure 9.5.5 Vapor Pressure Decrease and Boiling Point Increase as Functions of the Mole Fraction of a Nonvolatile Solute For relatively dilute solutions, the magnitude of both properties is proportional to the solute concentration.

Table 9.5.1 Boiling Point Elevation Constants (K_b) and Freezing Point Depression Constants (K_f) for Some Solvents

Solvent	Boiling Point (°C)	K_b (°C/*m*)	Freezing Point (°C)	K_f (°C/*m*)
acetic acid	117.90	3.22	16.64	3.63
benzene	80.09	2.64	5.49	5.07
d-(+)-camphor	207.4	4.91	178.8	37.8
carbon disulfide	46.2	2.42	−112.1	3.74
carbon tetrachloride	76.8	5.26	−22.62	31.4
chloroform	61.17	3.80	−63.41	4.60
nitrobenzene	210.8	5.24	5.70	6.87
water	100.00	0.51	0.00	1.86



The concentration of the solute is typically expressed as molality rather than mole fraction or molarity for two reasons. First, because the density of a solution changes with temperature, the value of molarity also varies with temperature. If the boiling point depends on the solute concentration, then by definition the system is not maintained at a constant temperature. Second, molality and mole fraction are proportional for relatively dilute solutions, but molality has a larger numerical value (a mole fraction can be only between zero and one). Using molality allows us to eliminate nonsignificant zeros.

According to Table 9.5.1, the molal boiling point elevation constant for water is 0.51°C/*m*. Thus a 1.00 *m* aqueous solution of a nonvolatile molecular solute such as glucose or sucrose will have an increase in boiling point of 0.51°C, to give a boiling point of 100.51°C at 1.00 atm. The increase in the boiling point of a 1.00 *m* aqueous NaCl solution will be approximately twice as large as that of the glucose or sucrose solution because 1 mol of NaCl produces 2 mol of dissolved ions. Hence a 1.00 *m* NaCl solution will have a boiling point of about 101.02°C.

Example 9.5.3

In Example 8, we calculated that the vapor pressure of a 30.2% aqueous solution of ethylene glycol at 100°C is 85.1 mmHg less than the vapor pressure of pure water. We stated (without offering proof) that this should result in a higher boiling point for the solution compared with pure water. Now that we have seen why this assertion is correct, calculate the boiling point of the aqueous ethylene glycol solution.

Given: composition of solution

Asked for: boiling point

Strategy:

Calculate the molality of ethylene glycol in the 30.2% solution. Then use Equation 9.5.9 to calculate the increase in boiling point.

Solution:

From Example 8, we know that a 30.2% solution of ethylene glycol in water contains 302 g of ethylene glycol (4.87 mol) per 698 g of water. The molality of the solution is thus

$$molality\ of\ ethylene\ glycol = \frac{4.87\ mol}{698\ gH_2O}\frac{1000\ g}{1\ kg} = 6.98\ m$$

From Equation 9.5.9, the increase in boiling point is therefore

$$T_b = mK_b = (6.98\ m)\,(0.51\ °C/m) = 3.6\ °C$$

The boiling point of the solution is thus predicted to be 104°C. With a solute concentration of almost 7 *m*, however, the assumption of a dilute solution used to obtain Equation 9.5.9 may not be valid.

Exercise

Assume that a tablespoon (5.00 g) of NaCl is added to 2.00 L of water at 20.0°C, which is then brought to a boil to cook spaghetti. At what temperature will the water boil?

Answer: 100.04°C, or 100°C to three significant figures. (Recall that 1 mol of NaCl produces 2 mol of dissolved particles. The small increase in temperature means that adding salt to the water used to cook pasta has essentially no effect on the cooking time.)

Freezing Point Depression

The phase diagram in Figure 9.5.4 shows that dissolving a nonvolatile solute in water not only raises the boiling point of the water but also lowers its freezing point. The solid–liquid curve for the solution crosses the line corresponding to P = 1 atm at a *lower* temperature than the curve for pure water.

We can understand this result by imagining that we have a sample of water at the normal freezing point temperature, where there is a dynamic equilibrium between solid and liquid. Water molecules are continuously colliding with the ice surface and entering the solid phase at the same rate that water molecules are leaving the surface of the ice and entering the liquid phase. If we dissolve a nonvolatile solute such as glucose in the liquid, the dissolved glucose molecules will reduce the number of collisions per unit time between water molecules and the ice surface because some of the molecules colliding with the ice will be glucose. Glucose, though, has a very different structure than water, and it cannot fit into the ice lattice. Consequently, the presence of glucose molecules in the solution can only decrease the rate at which water molecules in the liquid collide with the ice surface and solidify. Meanwhile, the rate at which the water molecules leave the surface of the ice and enter the liquid phase is unchanged. The net effect is to cause the ice to melt. The only way to reestablish a dynamic equilibrium between solid and liquid water is to lower the temperature of the system, which decreases the rate at which water molecules leave the surface of the ice crystals until it equals the rate at which water molecules in the solution collide with the ice.

By analogy to our treatment of boiling point elevation, the freezing point depression (ΔT_f)The difference between the freezing point of a pure solvent and the freezing point of the solution. is defined as the difference between the freezing point of the pure solvent and the freezing point of the solution:

$$\Delta T_f = T_f - T_f^o$$

where T_f^o is the freezing point of the pure solvent and T_f is the freezing point of the solution. The order of the terms is reversed compared with Equation 13.18 to express the freezing point depression as a positive number. The relationship between ΔT_f and the solute concentration is given by an equation analogous to Equation 9.5.9:

$$\Delta T_f = mK_f$$

where m is the molality of the solution and K_f is the *molal freezing point depression constant* for the solvent (in units of °C/m). Like K_b, each solvent has a characteristic value of K_f (see Table 9.5.1). Freezing point depression depends on the total number of dissolved nonvolatile solute particles, just as with boiling point elevation. Thus an aqueous NaCl solution has twice as large a freezing point depression as a glucose solution of the same molality.

People who live in cold climates use freezing point depression to their advantage in many ways. For example, salt is used to melt ice and snow on roads and sidewalks, ethylene glycol is added to engine coolant water to prevent an automobile engine from being destroyed, and methanol is added to windshield washer fluid to prevent the fluid from freezing.

Note the Pattern

The decrease in vapor pressure, increase in boiling point, and decrease in freezing point of a solution versus a pure liquid all depend on the total number of dissolved nonvolatile solute particles.

Example 9.5.4

In colder regions of the United States, NaCl or $CaCl_2$ is often sprinkled on icy roads in winter to melt the ice and make driving safer. Use the data in Figure 9.4.1 "Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature" to estimate the concentrations of two saturated solutions at 0°C, one of NaCl and one of $CaCl_2$, and calculate the freezing points of both solutions to see which salt is likely to be more effective at melting ice.

Given: solubilities of two compounds

Asked for: concentrations and freezing points

Strategy:

A Estimate the solubility of each salt in 100 g of water from Figure 9.4.1. Determine the number of moles of each in 100 g and calculate the molalities.

B Determine the concentrations of the dissolved salts in the solutions. Substitute these values into Equation 9.5.9 to calculate the freezing point depressions of the solutions.

Solution:

A From Figure 9.5.1, we can estimate the solubilities of NaCl and $CaCl_2$ to be about 36 g and 60 g, respectively, per 100 g of water at 0°C. The corresponding concentrations in molality are

$$m\ NaCl = \left(\frac{36\ g\ NaCl}{100\ g\ H_2O}\right)\left(\frac{1\ mol\ NaCl}{58.44\ g\ NaCl}\right)\left(\frac{1000\ g}{1\ kg}\right) = 6.2\ m$$

$$m\ CaCl_2 = \left(\frac{60\ g\ CaCl_2}{100\ g\ H_2O}\right)\left(\frac{1\ mol\ CaCl_2}{110.98\ g\ CaCl_2}\right)\left(\frac{1000\ g}{1\ kg}\right) = 5.4\ m$$

The lower formula mass of NaCl more than compensates for its lower solubility, resulting in a saturated solution that has a slightly higher concentration than $CaCl_2$.

B Because these salts are ionic compounds that dissociate in water to yield two and three ions per formula unit of NaCl and $CaCl_2$, respectively, the actual concentrations of the dissolved species in the two saturated solutions are 2 × 6.2 *m* = 12 *m* for NaCl and 3 × 5.4 *m* = 16 *m* for $CaCl_2$. The resulting freezing point depressions can be calculated using Equation 9.5.11:

$$NaCl: \Delta T_f = mK_f = (12\ m)\,(1.86\ °C/m) = 22\ °C$$

$$CaCl_2: \Delta T_f = mK_f = (16\ m)\,(1.86\ °C/m) = 30\ °C$$

Because the freezing point of pure water is 0°C, the actual freezing points of the solutions are −22°C and −30°C, respectively. Note that $CaCl_2$ is substantially more effective at lowering the freezing point of water because its solutions contain three ions per formula unit. In fact, $CaCl_2$ is the salt usually sold for home use, and it is also often used on highways.

Because the solubilities of both salts decrease with decreasing temperature, the freezing point can be depressed by only a certain amount, regardless of how much salt is spread on an icy road. If the temperature is significantly below the minimum temperature at which one of these salts will cause ice to melt (say −35°C), there is no point in using salt until it gets warmer.

Exercise

Calculate the freezing point of the 30.2% solution of ethylene glycol in water whose vapor pressure and boiling point we calculated in Example 13.8 and Example 13.10.

Answer: −13.0°C

Example 9.5.5

Arrange these aqueous solutions in order of decreasing freezing points: 0.1 *m* KCl, 0.1 *m* glucose, 0.1 *m* $SrCl_2$, 0.1 *m* ethylene glycol, 0.1 *m* benzoic acid, and 0.1 *m* HCl.

Given: molalities of six solutions

Asked for: relative freezing points

Strategy:

A Identify each solute as a strong, weak, or nonelectrolyte, and use this information to determine the number of solute particles produced.

B Multiply this number by the concentration of the solution to obtain the effective concentration of solute particles. The solution with the highest effective concentration of solute particles has the largest freezing point depression.

Solution:

A Because the molal concentrations of all six solutions are the same, we must focus on which of the substances are strong electrolytes, which are weak electrolytes, and which are nonelectrolytes to determine the actual numbers of particles in solution. KCl, $SrCl_2$, and HCl are strong electrolytes, producing two, three, and two ions per formula unit, respectively. Benzoic acid is a weak electrolyte (approximately one particle per molecule), and glucose and ethylene glycol are both nonelectrolytes (one particle per molecule).

B The molalities of the solutions in terms of the total particles of solute are: KCl and HCl, 0.2 *m*; $SrCl_2$, 0.3 *m*; glucose and ethylene glycol, 0.1 *m*; and benzoic acid, 0.1–0.2 *m*. Because the magnitude of the decrease in freezing point is proportional to the concentration of dissolved particles, the order of freezing points of the solutions is: glucose and ethylene glycol (highest freezing point, smallest freezing point depression) > benzoic acid > HCl = KCl > $SrCl_2$.

Exercise

Arrange these aqueous solutions in order of increasing freezing points: 0.2 *m* NaCl, 0.3 *m* acetic acid, 0.1 *m* $CaCl_2$, and 0.2 *m* sucrose.

Answer: 0.2 *m* NaCl (lowest freezing point) < 0.3 *m* acetic acid ≈ 0.1 *m* $CaCl_2$ < 0.2 *m* sucrose (highest freezing point)

In biological systems, freezing plant and animal tissues produces ice crystals that rip cells apart, causing severe frostbite and degrading the quality of fish or meat. How, then, can living organisms survive in freezing climates, where we might expect that exposure to freezing temperatures would be fatal? Many organisms that live in cold climates are able to survive at temperatures well below freezing by synthesizing their own chemical antifreeze in concentrations that prevent freezing. Such substances are typically small organic molecules with multiple –OH groups analogous to ethylene glycol.

Colligative properties can also be used to determine the molar mass of an unknown compound. One method that can be carried out in the laboratory with minimal equipment is to measure the freezing point of a solution with a known mass of solute. This method is accurate for dilute solutions (≤1% by mass) because changes in the freezing point are usually large enough to measure accurately and precisely. By comparing K_b and K_f values in Table 2.5.1, we see that changes in the boiling point are smaller than changes in the freezing point for a given solvent. Boiling point elevations are thus more difficult to measure precisely. For this reason, freezing point depression is more commonly used to determine molar mass than is boiling point elevation. Because of its very large value of K_f (37.8°C/*m*), *d*-(+)-camphor (Table 9.5.1) is often used to determine the molar mass of organic compounds by this method.

Example 9.5.6

A 7.08 g sample of elemental sulfur is dissolved in 75.0 g of CS_2 to create a solution whose freezing point is −113.5°C. Use these data to calculate the molar mass of elemental sulfur and thus the formula of the dissolved S*n* molecules (i.e., what is the value of *n*?).

Given: masses of solute and solvent and freezing point

Asked for: molar mass and number of S atoms per molecule

Strategy:

A Use Equation 9.5.10, the measured freezing point of the solution, and the freezing point of CS_2 from Table 9.5.1 to calculate the freezing point depression. Then use Equation 9.5.11 and the value of K_f from Table 9.5.1 to calculate the molality of the solution.

B From the calculated molality, determine the number of moles of solute present.

C Use the mass and number of moles of the solute to calculate the molar mass of sulfur in solution. Divide the result by the molar mass of atomic sulfur to obtain *n*, the number of sulfur atoms per mole of dissolved sulfur.

Solution:

A The first step is to calculate the freezing point depression using Equation 9.5.10:

$$\Delta T_f = T_f^o - T_f = -112.1\ ^oC\ -(-113.5\ ^oC) = 1.4\ ^oC$$

Then Equation 9.5.11 gives

$$m=\dfrac{\Delta T_{f}}{K_{f}} = \dfrac{1.4 \; ^{o}C}{3.74 \; ^{o}C/m} = 0.37 \; m$$

B The total number of moles of solute present in the solution is

$$moles\ solute = \frac{0.37\ mol/kg}{75\ g}\frac{1\ kg}{1000\ g} = 0.028\ mol$$

C We now know that 0.708 g of elemental sulfur corresponds to 0.028 mol of solute. The molar mass of dissolved sulfur is thus

$$molar\ mass = \frac{7.08\ g}{0.028\ mol} = 260\ g/mol$$

The molar mass of atomic sulfur is 32 g/mol, so there must be 260/32 = 8.1 sulfur atoms per mole, corresponding to a formula of S_8.

Exercise

One of the byproducts formed during the synthesis of C_{60} is a deep red solid containing only carbon. A solution of 205 mg of this compound in 10.0 g of CCl_4 has a freezing point of −23.38°C. What are the molar mass and most probable formula of the substance?

Answer: 847 g/mol; C_{70}

Osmotic Pressure

Osmotic pressure is a colligative property of solutions that is observed using a semipermeable membraneA barrier with pores small enough to allow solvent molecules to pass through but not solute molecules or ions., a barrier with pores small enough to allow solvent molecules to pass through but not solute molecules or ions. The net flow of solvent through a semipermeable membrane is called osmosisThe net flow of solvent through a semipermeable membrane. (from the Greek *osmós*, meaning “push”). The direction of net solvent flow is *always* from the side with the lower concentration of solute to the side with the higher concentration.

Osmosis can be demonstrated using a U-tube like the one shown in Figure 9.5.6, which contains pure water in the left arm and a dilute aqueous solution of glucose in the right arm. A net flow of water through the membrane occurs until the levels in the arms eventually stop changing, which indicates that equilibrium has been reached. The osmotic pressure (Π)The pressure difference between the two sides of a semipermeable membrane that separates a pure solvent from a solution prepared from the same solvent. of the glucose solution is the difference in the pressure between the two sides, in this case the heights of the two columns. Although the semipermeable membrane allows water molecules to flow through in either direction, the *rate* of flow is not the same in both directions because the concentration of water is not the same in the two arms. The net flow of water through the membrane can be prevented by applying a pressure to the right arm that is equal to the osmotic pressure of the glucose solution.

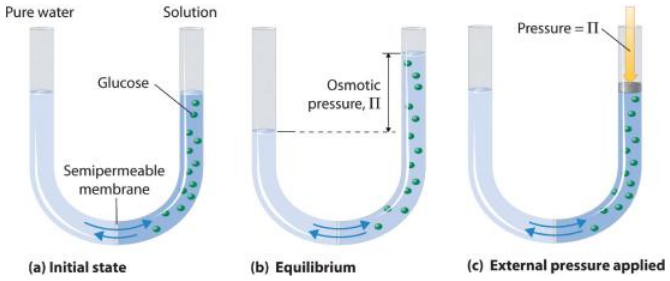


Figure 9.5.6 Osmotic Pressure (a) A dilute solution of glucose in water is placed in the right arm of a U-tube, and the left arm is filled to the same height with pure water; a semipermeable membrane separates the two arms. Because the flow of pure solvent through the membrane from left to right (from pure water to the solution) is greater than the flow of solvent in the reverse direction, the level of liquid in the right tube rises. (b) At equilibrium, the pressure differential, equal to the osmotic pressure of the solution (Π_{soln}), equalizes the flow rate of solvent in both directions. (c) Applying an external pressure equal to the osmotic pressure of the original glucose solution to the liquid in the right arm reverses the flow of solvent and restores the original situation.

Just as with any other colligative property, the osmotic pressure of a solution depends on the concentration of dissolved solute particles. Osmotic pressure obeys a law that resembles the ideal gas equation:

$$\Pi = \frac{nRT}{V} = MRT$$

where M is the number of moles of solute per unit volume of solution (i.e., the *molarity* of the solution), R is the ideal gas constant, and T is the absolute temperature. As shown in Example 14, osmotic pressures tend to be quite high, even for rather dilute solutions.

Example 9.5.7

When placed in a concentrated salt solution, certain yeasts are able to produce high internal concentrations of glycerol to counteract the osmotic pressure of the surrounding medium. Suppose that the yeast cells are placed in an aqueous solution containing 4.0% NaCl by mass; the solution density is 1.02 g/mL at 25°C.

1. Calculate the osmotic pressure of a 4.0% aqueous NaCl solution at 25°C.
2. If the normal osmotic pressure inside a yeast cell is 7.3 atm, corresponding to a total concentration of dissolved particles of 0.30 M, what concentration of glycerol must the cells synthesize to exactly balance the external osmotic pressure at 25°C?

Given: concentration, density, and temperature of NaCl solution; internal osmotic pressure of cell

Asked for: osmotic pressure of NaCl solution and concentration of glycerol needed

Strategy:

A Calculate the molarity of the NaCl solution using the formula mass of the solute and the density of the solution. Then calculate the total concentration of dissolved particles.

B Use Equation 9.5.12 to calculate the osmotic pressure of the solution.

C Subtract the normal osmotic pressure of the cells from the osmotic pressure of the salt solution to obtain the additional pressure needed to balance the two. Use Equation 9.5.12 to calculate the molarity of glycerol needed to create this osmotic pressure.

Solution:

1. **A** The solution contains 4.0 g of NaCl per 100 g of solution. Using the formula mass of NaCl (58.44 g/mol) and the density of the solution (1.02 g/mL), we can calculate the molarity:

   $$M\ NaCl = \frac{moles\ NaCl}{liter\ solution} = \left(\frac{4.0\ g\ NaCl}{58.44\ g/mol\ NaCl}\right)\left(\frac{1}{100\ g\ solution}\right)\left(\frac{1.02\ g\ solution}{1.00\ mL\ solution}\right)\left(\frac{1000\ mL}{1\ L}\right) = 0.70\ M\ NaCl$$

   Because 1 mol of NaCl produces 2 mol of particles in solution, the total concentration of dissolved particles in the solution is (2)(0.70 M) = 1.4 M.

   B Now we can use Equation 9.5.12 to calculate the osmotic pressure of the solution:

   $$\Pi = MRT = (1.4\ mol/L)\,(0.0821\ L \cdot atm/K \cdot mol)\,(298\ K) = 34\ atm$$

2. **C** If the yeast cells are to exactly balance the external osmotic pressure, they must produce enough glycerol to give an additional internal pressure of (34 atm − 7.3 atm) = 27 atm. Glycerol is a nonelectrolyte, so we can solve Equation 9.5.12 for the molarity corresponding to this osmotic pressure:

   $$M = \frac{\Pi}{RT} = \frac{27\ atm}{(0.0821\ L \cdot atm/K \cdot mol)\,(298\ K)} = 1.1\ M\ glycerol$$

   In solving this problem, we could also have recognized that the only way the osmotic pressures can be the same inside the cells and in the solution is if the concentrations of dissolved particles are the same. We are given that the normal concentration of dissolved particles in the cells is 0.3 M, and we have calculated that the NaCl solution is effectively 1.4 M in dissolved particles. The yeast cells must therefore synthesize enough glycerol to increase the internal concentration of dissolved particles from 0.3 M to 1.4 M—that is, an additional 1.1 M concentration of glycerol.

Exercise

Assume that the fluids inside a sausage are approximately 0.80 M in dissolved particles due to the salt and sodium nitrite used to prepare them. Calculate the osmotic pressure inside the sausage at 100°C to learn why experienced cooks pierce the semipermeable skin of sausages *before* boiling them.

Answer: 24 atm

Because of the large magnitude of osmotic pressures, osmosis is extraordinarily important in biochemistry, biology, and medicine. Virtually every barrier that separates an organism or cell from its environment acts like a semipermeable membrane, permitting the flow of water but not solutes. The same is true of the compartments inside an organism or cell. Some specialized barriers, such as those in your kidneys, are slightly more permeable and use a related process called dialysisA process that uses a semipermeable membrane with pores large enough to allow small solute molecules and solvent molecules to pass through but not large solute molecules., which permits both water and small molecules to pass through but not large molecules such as proteins.

The same principle has long been used to preserve fruits and their essential vitamins over the long winter. High concentrations of sugar are used in jams and jellies not for sweetness alone but because they greatly increase the osmotic pressure. Thus any bacteria not killed in the cooking process are dehydrated, which keeps them from multiplying in an otherwise rich medium for bacterial growth. A similar process using salt prevents bacteria from growing in ham, bacon, salt pork, salt cod, and other preserved meats. The effect of osmotic pressure is dramatically illustrated in Figure 9.5.7, which shows what happens when red blood cells are placed in a solution whose osmotic pressure is much lower or much higher than the internal pressure of the cells.

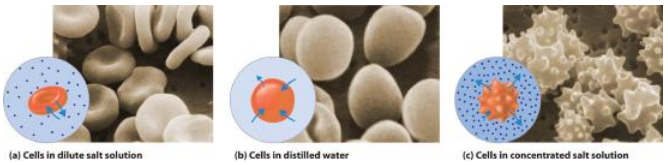


Figure 9.5.7 Effect on Red Blood Cells of the Surrounding Solution's Osmotic Pressure *(a) When red blood cells are placed in a dilute salt solution having the same osmotic pressure as the intracellular fluid, the rate of flow of water into and out of the cells is the same and their shape does not change. (b) When cells are placed in distilled water whose osmotic pressure is less than that of the intracellular fluid, the rate of flow of water into the cells is greater than the rate of flow out of the cells. The cells swell and eventually burst. (c) When cells are placed in a concentrated salt solution with an osmotic pressure greater than that of the intracellular fluid, the rate of flow of water out of the cells is greater than the rate of flow into the cells. The cells shrivel and become so deformed that they cannot function.*

In addition to capillary action, trees use osmotic pressure to transport water and other nutrients from the roots to the upper branches. (For more information about capillary action, see Section 7.3 .) Evaporation of water from the leaves results in a local increase in the salt concentration, which generates an osmotic pressure that pulls water up the trunk of the tree to the leaves.

Finally, a process called reverse osmosisA process that uses the application of an external pressure greater than the osmotic pressure of a solution to reverse the flow of solvent through the semipermeable membrane. can be used to produce pure water from seawater. As shown schematically in Figure 9.5.8, applying high pressure to seawater forces water molecules to flow through a semipermeable membrane that separates pure water from the solution, leaving the dissolved salt behind. Large-scale desalinization plants that can produce hundreds of thousands of gallons of freshwater per day are common in the desert lands of the Middle East, where they supply a large proportion of the freshwater needed by the population. Similar facilities are now being used to supply freshwater in southern California. Small, hand-operated reverse osmosis units can produce approximately 5 L of freshwater per hour, enough to keep 25 people alive, and are now standard equipment on US Navy lifeboats.

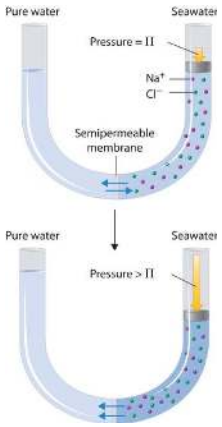


Figure 9.5.8 Desalinization of Seawater by Reverse Osmosis (top) When the pressure applied to seawater equals its osmotic pressure (Π_{soln}), there is no net flow of water across the semipermeable membrane. (bottom) The application of pressure greater than the osmotic pressure of seawater forces water molecules to flow through the membrane, leaving behind a concentrated salt solution. In desalinization plants, seawater is continuously introduced under pressure and pure water is collected, so the process continues indefinitely.

Colligative Properties of Electrolyte Solutions

Thus far we have assumed that we could simply multiply the molar concentration of a solute by the number of ions per formula unit to obtain the actual concentration of dissolved particles in an electrolyte solution. We have used this simple model to predict such properties as freezing points, melting points, vapor pressure, and osmotic pressure. If this model were perfectly correct, we would expect the freezing point depression of a 0.10 *m* solution of sodium chloride, with 2 mol of ions per mole of NaCl in solution, to be exactly twice that of a 0.10 *m* solution of glucose, with only 1 mol of molecules per mole of glucose in solution. In reality, this is not always the case. Instead, the observed change in freezing points for 0.10 *m* aqueous solutions of NaCl and KCl are significantly less than expected (−0.348°C and −0.344°C, respectively, rather than −0.372°C), which suggests that fewer particles than we expected are present in solution.

The relationship between the actual number of moles of solute added to form a solution and the apparent number as determined by colligative properties is called the van't Hoff factor(*i*)The ratio of the apparent number of particles in solution to the number predicted by the stoichiometry of the salt. and is defined as follows:Named for Jacobus Hendricus van't Hoff (1852–1911), a Dutch chemistry professor at the University of Amsterdam who won the first Nobel Prize in Chemistry (1901) for his work on thermodynamics and solutions.

$$i = \frac{\textit{apparent number of particles in solution}}{\textit{number of moles of solute dissolved}}$$

Note the Pattern

As the solute concentration increases the van't Hoff factor decreases.

The van't Hoff factor is therefore a measure of a deviation from ideal behavior. The lower the van't Hoff factor, the greater the deviation. As the data in Table 9.5.2 show, the van't Hoff factors for ionic compounds are somewhat lower than expected; that is, their solutions apparently contain fewer particles than predicted by the number of ions per formula unit. As the concentration of the solute increases, the van't Hoff factor decreases because ionic compounds generally do not totally dissociate in aqueous solution. Instead, some of the ions exist as ion pairsA cation and anion that are in intimate contact in solution rather than separated by solvent and that migrates in solution as a single unit., a cation and an anion that for a brief time are associated with each other without an intervening shell of water molecules (Figure 9.5.9). Each of these temporary units behaves like a single dissolved particle until it dissociates. Highly charged ions such as Mg^{2+}, Al^{3+}, SO_4^{2-}, and PO_4^{3-} have a greater tendency to form ion pairs because of their strong electrostatic interactions. The actual number of solvated ions present in a solution can be determined by measuring a colligative property at several solute concentrations.

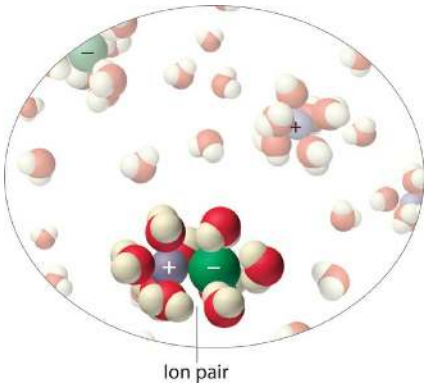


Figure 9.5.9 Ion Pairs *In concentrated solutions of electrolytes like NaCl, some of the ions form neutral ion pairs that are not separated by solvent and diffuse as single particles.*

Table 9.5.2 van't Hoff Factors for 0.0500 M Aqueous Solutions of Selected Compounds at 25°C

Compound	*i* (measured)	*i* (ideal)
glucose	1.0	1.0
sucrose	1.0	1.0
NaCl	1.9	2.0
HCl	1.9	2.0
$MgCl_2$	2.7	3.0
$FeCl_3$	3.4	4.0
$Ca(NO_3)_2$	2.5	3.0
$AlCl_3$	3.2	4.0
$MgSO_4$	1.4	2.0

Example 9.5.8

A 0.0500 M aqueous solution of $FeCl_3$ has an osmotic pressure of 4.15 atm at 25°C. Calculate the van't Hoff factor *i* for the solution.

Given: solute concentration, osmotic pressure, and temperature

Asked for: van't Hoff factor

Strategy:

A Use Equation 9.5.12 to calculate the expected osmotic pressure of the solution based on the effective concentration of dissolved particles in the solvent.

B Calculate the ratio of the observed osmotic pressure to the expected value. Multiply this number by the number of ions of solute per formula unit, and then use Equation 9.3.13 to calculate the van't Hoff factor.

Solution:

A If $FeCl_3$ dissociated completely in aqueous solution, it would produce four ions per formula unit [Fe^{3+}(aq) plus $3Cl^-$(aq)] for an effective concentration of dissolved particles of 4 × 0.0500 M = 0.200 M. The osmotic pressure would be

$$\Pi = MRT = (0.200\ mol\backslash L)\,(0.0821 L \cdot atm/K \cdot mol)\,(298\ K) = 4.89\ atm$$

B The observed osmotic pressure is only 4.15 atm, presumably due to ion pair formation. The ratio of the observed osmotic pressure to the calculated value is 4.15 atm/4.89 atm = 0.849, which indicates that the solution contains (0.849)(4) = 3.40 particles per mole of $FeCl_3$ dissolved. Alternatively, we can calculate the observed particle concentration from the osmotic pressure of 4.15 atm:

$$4.15\ atm = M\,(0.0821 L \cdot atm/K \cdot mol)\,(298\ K)$$

$$M = 0.170\ mol/L$$

The ratio of this value to the expected value of 0.200 M is 0.170 M/0.200 M = 0.850, which again gives us (0.850)(4) = 3.40 particles per mole of $FeCl_3$ dissolved. From Equation 13.23, the van't Hoff factor for the solution is

$$i = \frac{3.40\ particles\ observed}{formula\ uni\ FeCl_3} = 3.40$$

Exercise

Calculate the van't Hoff factor for a 0.050 *m* aqueous solution of $MgCl_2$ that has a measured freezing point of −0.25°C.

Answer: 2.7 (versus an ideal value of 3)

Summary

The **colligative properties** of a solution depend on only the total number of dissolved particles in solution, not on their chemical identity. Colligative properties include vapor pressure, boiling point, freezing point, and osmotic pressure. The addition of a *nonvolatile solute* (one without a measurable vapor pressure) decreases the vapor pressure of the solvent. The vapor pressure of the solution is proportional to the mole fraction of solvent in the solution, a relationship known as **Raoult's law**. Solutions that obey Raoult's law are called **ideal solutions**. Most real solutions exhibit positive or negative deviations from Raoult's law. The **boiling point elevation (ΔT_b)** and **freezing point depression (ΔT_f)** of a solution are defined as the differences between the boiling and freezing points, respectively, of the solution and the pure solvent. Both are proportional to the molality of the solute. When a solution and a pure solvent are separated by a **semipermeable membrane**, a barrier that allows solvent molecules but not solute molecules to pass through, the flow of solvent in opposing directions is unequal and produces an **osmotic pressure**, which is the difference in pressure between the two sides of the membrane. **Osmosis** is the net flow of solvent through such a membrane due to different solute concentrations. **Dialysis** uses a semipermeable membrane with pores that allow only small solute molecules and solvent molecules to pass through. In more concentrated solutions, or in solutions of salts with highly charged ions, the cations and anions can associate to form **ion pairs**, which decreases their effect on the colligative properties of the solution. The extent of ion pair formation is given by the **van't Hoff factor (*i*)**, the ratio of the apparent number of particles in solution to the number predicted by the stoichiometry of the salt.

Key Takeaway

- The total number of nonvolatile solute particles determines the decrease in vapor pressure, increase in boiling point, and decrease in freezing point of a solution versus the pure solvent.

Key Equations

Henry's law

Equation 9.4.2: $C = kP$

Raoult's law

Equation 9.5.1: $P_A = X_A P_A^o$

vapor pressure lowering

Equation 9..5.3: $P_A^o - P_A = \Delta P_A = X_B P_A^o$

vapor pressure of a system containing two volatile components

Equation 9.5.5: $P_T = X_A P_A^o + (1 - X_A) P_B^o$

boiling point elevation

Equation 9.5.9: $\Delta T_b = mK_b$

freezing point depression

Equation 9.5.11: $\Delta T_f = mK_f$

osmotic pressure

Equation 9.5.12: $\Pi = \frac{nRT}{V} = MRT$

van't Hoff factor

Equation 9.5.13: $i = \frac{apparent\ number\ of\ particles\ in\ solution}{number\ of\ moles\ of\ solute\ dissolved}$

Conceptual Problems

1. Why does the vapor pressure of a solvent decrease when adding a nonvolatile solute?
2. Does seawater boil at the same temperature as distilled water? If not, which has the higher boiling point? Explain your answer.

3. Which will be more soluble in benzene—O_2 or HCl? Will H_2S or HCl be more soluble in water? Explain your reasoning in each case.
4. Will the vapor pressure of a solution of hexane and heptane have an ideal vapor pressure curve (i.e., obey Raoult's law)? Explain your answer. What properties of two liquids determine whether a solution of the two will exhibit an ideal behavior?
5. Predict whether the following mixtures will exhibit negative, zero, or positive deviations from Raoult's law. Explain your reasoning in each case.
    1. carbon tetrachloride and heptane
    2. methanol and tetrahydrofuran (C_4H_8O)
    3. acetone [$(CH_3)_2C=CO$] and dichloromethane
    4. hexane and methanol
6. Why are deviations from the ideal behavior predicted by Raoult's law more common for solutions of liquids than are deviations from the ideal behavior predicted by the ideal gas law for solutions of gases?
7. Boiling point elevation is proportional to the molal concentration of the solute. Is it also proportional to the molar concentration of the solution? Why or why not?
8. Many packaged foods in sealed bags are cooked by placing the bag in boiling water. How could you reduce the time required to cook the contents of the bag using this cooking method?
9. If the costs per kilogram of ethylene glycol and of ethanol were the same, which would be the more cost-effective antifreeze?
10. Many people get thirsty after eating foods such as ice cream or potato chips that have a high sugar or salt content, respectively. Suggest an explanation for this phenomenon.
11. When two aqueous solutions with identical concentrations are separated by a semipermeable membrane, no net movement of water occurs. What happens when a solute that cannot penetrate the membrane is added to one of the solutions? Why?
12. A solution injected into blood vessels must have an electrolyte concentration nearly identical to that found in blood plasma. Why? What would happen if red blood cells were placed in distilled water? What would happen to red blood cells if they were placed in a solution that had twice the electrolyte concentration of blood plasma?
13. If you were stranded on a desert island, why would drinking seawater lead to an increased rate of dehydration, eventually causing you to die of thirst?
14. What is the relationship between the van't Hoff factor for a compound and its lattice energy?

Numerical Problems

1. Hemoglobin is the protein that is responsible for the red color of blood and for transporting oxygen from the lungs to the tissues. A solution with 11.2 mg of hemoglobin per mL has an osmotic pressure of 2.9 mmHg at 5°C. What is the molecular mass of hemoglobin?
2. To determine the molar mass of the antifreeze protein from the Arctic right-eye flounder, the osmotic pressure of a solution containing 13.2 mg of protein per mL was measured and found to be 21.2 mmHg at 10°C. What is the molar mass of the protein?
3. What is the osmotic pressure at 21.0°C of 13.5 mL of a solution with 1.77 g of sucrose ($C_{12}H_{22}O_{11}$)?
4. A solution of $NaNO_3$ is generated by dissolving 1.25 g of $NaNO_3$ in enough water to give a final volume of 25.0 mL. What is the osmotic pressure of this sample at 25.0°C?
5. Which would have the lower vapor pressure—an aqueous solution that is 0.12 M in glucose or one that is 0.12 M in $CaCl_2$? Why?
6. What is the total particle concentration expected for each aqueous solution? Which would produce the highest osmotic pressure?
    1. 0.35 M KBr

2. 0.11 M $MgSO_4$
3. 0.26 M $MgCl_2$
4. 0.24 M glucose ($C_6H_{12}O_6$)

7. The boiling point of an aqueous solution of sodium chloride is 100.37°C. What is the molality of the solution? How many grams of NaCl are present in 125 g of the solution?
8. Calculate the boiling point of a solution of sugar prepared by dissolving 8.4 g of glucose ($C_6H_{12}O_6$) in 250 g of water.
9. At 37°C, the vapor pressure of 300.0 g of water was reduced from 0.062 atm to 0.058 atm by the addition of NaBr. How many grams of NaBr were added?
10. How many grams of KCl must be added to reduce the vapor pressure of 500.0 g of H_2O from 17.5 mmHg to 16.0 mmHg at 20.0°C?
11. How much NaCl would you have to add to 2.0 L of water at a mountain lodge at an elevation of 7350 ft, where the pressure is 0.78 atm and the boiling point of water is 94°C, to get the water to boil at the same temperature as in New Orleans, Louisiana, where the pressure is 1.00 atm?
12. You have three solutions with the following compositions: 12.5 g of KCl in 250 mL of water, 12.5 g of glucose in 400 mL of water, and 12.5 g of $MgCl_2$ in 350 mL of water. Which will have the highest boiling point?
13. Assuming the price per kilogram is the same, which is a better salt to use for deicing wintry roads—NaCl or $MgCl_2$? Why? Would magnesium chloride be an effective deicer at a temperature of −8°C?
14. How many grams of KNO_3 must be added to water to produce the same boiling point elevation as a solution of 2.03 g of $MgCl_2$ in a total volume of 120.0 mL of solution, assuming complete dissociation? If the van't Hoff factor for $MgCl_2$ at this concentration is 2.73, how much KNO_3 would be needed?
15. Calculate the quantity of each compound that would need to be added to lower the freezing point of 500.0 mL of water by 1.0°C: KBr, ethylene glycol, $MgBr_2$, ethanol. Assume that the density of water is 1.00 g/cm^3.
16. The melting point depression of biphenyl (melting point = 69.0°C) can be used to determine the molecular mass of organic compounds. A mixture of 100.0 g of biphenyl and 2.67 g of naphthalene ($C_{10}H_8$) has a melting point of 68.50°C. If a mixture of 1.00 g of an unknown compound with 100.0 g of biphenyl has a melting point of 68.86°C, what is the molar mass of the unknown compound?
17. Four solutions of urea in water were prepared, with concentrations of 0.32 *m*, 0.55 *m*, 1.52 *m*, and 3.16 *m*. The freezing points of these solutions were found to be −0.595°C, −1.02°C, −2.72°C, and −5.71°C, respectively. Graphically determine the freezing point depression constant for water. A fifth solution made by dissolving 6.22 g of urea in 250.0 g of water has a freezing point of −0.75°C. Use these data to determine the molar mass of urea.
18. The term *osmolarity* has been used to describe the total solute concentration of a solution (generally water), where 1 osmole (Osm) is equal to 1 mol of an ideal, nonionizing molecule.
    1. What is the osmolarity of a 1.5 M solution of glucose? a 1.5 M solution of NaCl? a 1.5 M solution of $CaCl_2$?
    2. What is the relationship between osmolarity and the concentration of water?
    3. What would be the direction of flow of water through a semipermeable membrane separating a 0.1 M solution of NaCl and a 0.1 M solution of $CaCl_2$?
19. At 40°C, the vapor pressures of pure CCl_4 and cyclohexane are 0.2807 atm and 0.2429 atm, respectively. Assuming ideal behavior, what is the vapor pressure of a solution with a CCl_4 mole fraction of 0.475? What is the mole fraction of cyclohexane in the vapor phase? The boiling points of CCl_4 and cyclohexane are 76.8°C and 80.7°C, respectively.
20. A benzene/toluene solution with a mole fraction of benzene of 0.6589 boils at 88°C at 1 atm. The vapor pressures of pure benzene and toluene at this temperature are 1.259 atm and 0.4993 atm, respectively. What is the composition of the vapor above the boiling solution at this temperature?
21. Plot the vapor pressure of the solution versus composition for the system CCl_4–CH_3CN at 45°C, given the following

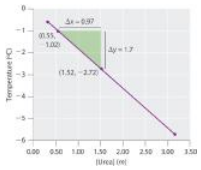
experimental data:

X_{CCl4} (liquid)	0.035	0.375	0.605	0.961
X_{CCl4} (vapor)	0.180	0.543	0.594	0.800
Total *P* (atm)	0.326	0.480	0.488	0.414

Source: Adapted from L. Brown and W. Foch, *Australian Journal of Chemistry*, 9 (1956): 180.

Does your diagram show behavior characteristic of an ideal solution? Explain your answer.

Answers

1. 6.7×10^4 amu
2.
3. 9.24 atm
4.
5. The $CaCl_2$ solution will have a lower vapor pressure, because it contains three times as many particles as the glucose solution.
6.
7. 0.36 *m* NaCl, 2.6 g NaCl
8.
9. 60 g NaBr
10.
11. 700 g NaCl
12.
13. $MgCl_2$ produces three particles in solution versus two for NaCl, so the same molal concentration of $MgCl_2$ will produce a 50% greater freezing point depression than for NaCl. Nonetheless, the molar mass of $MgCl_2$ is 95.3 g/mol versus 48.45 g/mol for NaCl. Consequently, a solution containing 1 g NaCl per 1000 g H_2O will produce a freezing point depression of 0.064°C versus 0.059°C for a solution containing 1 g $MgCl_2$ per 1000 g H_2O. Thus, given equal cost per gram, NaCl is more effective. Yes, $MgCl_2$ would be effective at −8°C; a 1.43 *m* solution (136 g per 1000 g H_2O) would be required.
14.
15.
16.
17. 
    k_f = 1.81(°C·kg)/mol, molecular mass of urea = 60.0 g/mol
18.
19.
20.
21.

Contributors

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Chapter 9.6: Aggregate Particles

Learning Objective

- To distinguish between true solutions and solutions with aggregate particles.

Suspensions and colloids are two common types of mixtures whose properties are in many ways intermediate between those of true solutions and heterogeneous mixtures. A suspensionA heterogeneous mixture of particles with diameters of about 1 µm that are distributed throughout a second phase and that separate from the dispersing phase on standing. is a heterogeneous mixture of particles with diameters of about 1 µm (1000 nm) that are distributed throughout a second phase. Common suspensions include paint, blood, and hot chocolate, which are solid particles in a liquid, and aerosol sprays, which are liquid particles in a gas. If the suspension is allowed to stand, the two phases will separate, which is why paints must be thoroughly stirred or shaken before use. A colloidA heterogeneous mixture of particles with diameters of about 2–500 nm that are distributed throughout a second phase and do not separate from the dispersing phase on standing. is also a heterogeneous mixture, but the particles of a colloid are typically smaller than those of a suspension, generally in the range of 2 to about 500 nm in diameter. Colloids include fog and clouds (liquid particles in a gas), milk (solid particles in a liquid), and butter (solid particles in a solid). Other colloids are used industrially as catalysts. Unlike in a suspension, the particles in a colloid do not separate into two phases on standing. The only combination of substances that cannot produce a suspension or a colloid is a mixture of two gases because their particles are so small that they always form true solutions. The properties of suspensions, colloids, and solutions are summarized in Table 9.6.1.

Table 9.6.1 Properties of Liquid Solutions, Colloids, and Suspensions

Type of Mixture	Approximate Size of Particles (nm)	Characteristic Properties	Examples
solution	< 2	not filterable; does not separate on standing; does not scatter visible light	air, white wine, gasoline, salt water
colloid	2–500	scatters visible light; translucent or opaque; not filterable; does not separate on standing	smoke, fog, ink, milk, butter, cheese
suspension	500–1000	cloudy or opaque; filterable; separates on standing	muddy water, hot cocoa, blood, paint

Colloids and Suspensions

Colloids were first characterized in about 1860 by Thomas Graham, who also gave us Graham's law of diffusion and effusion. Although some substances, such as starch, gelatin, and glue, appear to dissolve in water to produce solutions, Graham found that they diffuse very slowly or not at all compared with solutions of substances such as salt and sugar. Graham coined the word *colloid* (from the Greek *kólla*, meaning "glue") to describe these substances, as well as the words solA dispersion of solid particles in a liquid or solid. and gelA semisolid sol in which all of the liquid phase has been absorbed by the solid particles. to describe certain types of colloids in which all of the solvent has been absorbed by the solid particles, thus preventing the mixture from flowing readily, as we see in Jell-O. Two other important types of colloids are aerosolsA dispersion of solid or liquid particles in a gas., which are dispersions of solid or liquid particles in a gas, and emulsions, which are dispersions of one liquid in another liquid with which it is immiscible.

Colloids share many properties with solutions. For example, the particles in both are invisible without a powerful microscope, do not settle on standing, and pass through most filters. However, the particles in a colloid scatter a beam of visible light, a phenomenon known as the Tyndall effectThe phenomenon of scattering a beam of visible light.,The effect is named after its discoverer, John Tyndall, an English physicist (1820–1893). whereas the particles of a solution do not. The Tyndall effect is responsible for the way the beams from automobile headlights are clearly visible from the side on a foggy night but cannot be seen from the side on a clear night. It is also responsible for the colored rays of light seen in many sunsets, where the sun's light is scattered by water droplets and dust particles high in the atmosphere. An example of the Tyndall effect is shown in Figure 9.6.1



Figure 9.6.1 Tyndall Effect, the Scattering of Light by Colloids *The glass on the left has dilute colloidal silver, the one on the right tap water. The red laser pointer beam is scattered by the Tyndall effect in the glass on the left.*

Although colloids and suspensions can have particles similar in size, the two differ in stability: the particles of a colloid remain dispersed indefinitely unless the temperature or chemical composition of the dispersing medium is changed. The chemical explanation for the stability of colloids depends on whether the colloidal particles are hydrophilic or hydrophobic.

Most proteins, including those responsible for the properties of gelatin and glue, are hydrophilic because their exterior surface is largely covered with polar or charged groups. Starch, a long-branched polymer of glucose molecules, is also hydrophilic. A hydrophilic colloid particle interacts strongly with water, resulting in a shell of tightly bound water molecules that prevents the particles from aggregating when they collide. Heating such a colloid can cause aggregation because the particles collide with greater energy and disrupt the protective shell of solvent. Moreover, heat causes protein structures to unfold, exposing previously buried hydrophobic groups that can now interact with other hydrophobic groups and cause the particles to aggregate and precipitate from solution. When an egg is boiled, for example, the egg white, which is primarily a colloidal suspension of a protein called *albumin*, unfolds and exposes its hydrophobic groups, which aggregate and cause the albumin to precipitate as a white solid.



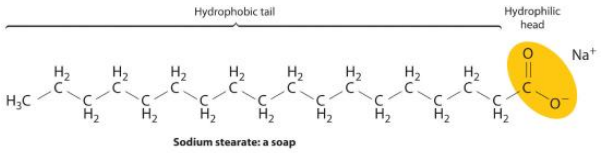
Figure 9.6.2 Formation of New Land by the Destabilization of a Colloid Suspension *This satellite photograph shows the Mississippi River delta from New Orleans (top) to the Gulf of Mexico (bottom). Where seawater mixes with freshwater from the Mississippi River, colloidal clay particles in the river water precipitate (tan area).*

Aggregation and precipitation can also result when the outer, charged layer of a particle is neutralized by ions with the opposite charge. In inland waterways, clay particles, which have a charged surface, form a colloidal suspension. High salt concentrations in seawater neutralize the charge on the particles, causing them to precipitate and form land at the mouths of large rivers, as seen in the satellite view in Figure 9.6.2. Charge neutralization is also an important strategy for precipitating solid particles from gaseous colloids such as smoke, and it is widely used to reduce particulate emissions from power plants that burn fossil fuels.

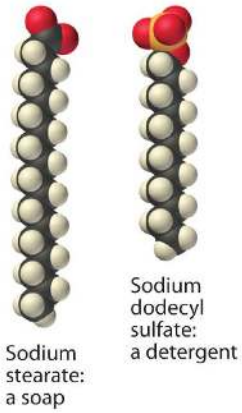
Emulsions

EmulsionsA dispersion of one liquid phase in another liquid with which it is immiscible. are colloids formed by the dispersion of a hydrophobic liquid in water, thereby bringing two mutually insoluble liquids, such as oil and water, in close contact. Various agents

have been developed to stabilize emulsions, the most successful being molecules that combine a relatively long hydrophobic "tail" with a hydrophilic "head":



Examples of such emulsifying agents include soaps, which are salts of long-chain carboxylic acids, such as sodium stearate [$CH_3(CH_2)_{16}CO_2^-Na^+$], and detergents, such as sodium dodecyl sulfate [$CH_3(CH_2)_{11}OSO_3^-Na^+$], whose structures are as follows:



When you wash your laundry, the hydrophobic tails of soaps and detergents interact with hydrophobic particles of dirt or grease through dispersion forces, dissolving in the interior of the hydrophobic particle. The hydrophilic group is then exposed at the surface of the particle, which enables it to interact with water through ion–dipole forces and hydrogen bonding. This causes the particles of dirt or grease to disperse in the wash water and allows them to be removed by rinsing. Similar agents are used in the food industry to stabilize emulsions such as mayonnaise.

A related mechanism allows us to absorb and digest the fats in buttered popcorn and French fries. To solubilize the fats so that they can be absorbed, the gall bladder secretes a fluid called *bile* into the small intestine. Bile contains a variety of *bile salts*, detergent-like molecules that emulsify the fats.

Micelles

Detergents and soaps are surprisingly soluble in water in spite of their hydrophobic tails. The reason for their solubility is that they do not, in fact, form simple solutions. Instead, above a certain concentration they spontaneously form micellesA spherical or cylindrical aggregate of detergents or soaps in water that minimizes contact between the hydrophobic tails of the detergents or soaps and water., which are spherical or cylindrical aggregates that minimize contact between the hydrophobic tails and water. In a micelle, only the hydrophilic heads are in direct contact with water, and the hydrophobic tails are in the interior of the aggregate (part (a) in Figure 9.6.3).

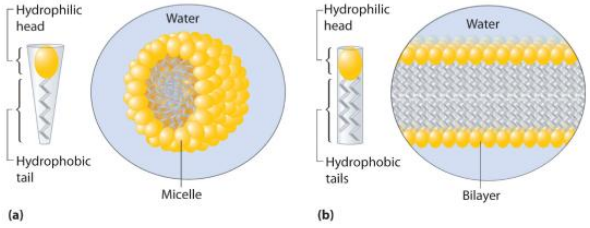
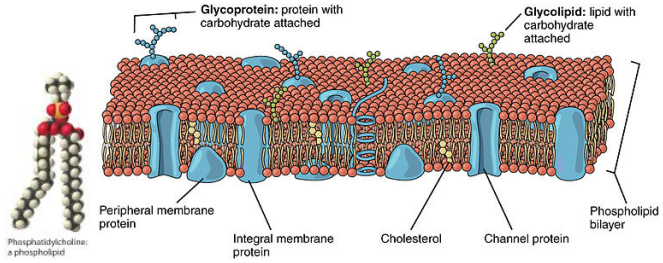


Figure 9.6.3 Micelles and a Phospholipid Bilayer *(a) Soaps and detergents, which contain a single hydrophobic tail on each molecule, form spherical micelles with the intertwined tails in the interior and the hydrophilic head groups on the exterior. (b) Phospholipids, which have two hydrophobic tails, tend to form extended double layers in which the hydrophobic tails are sandwiched between the hydrophilic head groups.*

A large class of biological molecules called phospholipidsA large class of biological, detergent-like molecules that have a hydrophilic head and two hydrophobic tails and that form bilayers. consists of detergent-like molecules with a hydrophilic head and *two* hydrophobic tails, as can be seen in the molecule of phosphatidylcholine. The additional tail results in a cylindrical shape that prevents phospholipids from forming a spherical micelle. Consequently, phospholipids form bilayersA two-dimensional sheet consisting of a double layer of phospholipid molecules arranged tail to tail., extended sheets consisting of a double layer of molecules. As shown in part (b) in Figure 9.6.3, the hydrophobic tails are in the center of the bilayer, where they are not in contact with water, and the hydrophilic heads are on the two surfaces, in contact with the surrounding aqueous solution.



A cell membraneA mixture of phospholipids that form a phospholipid bilayer around the cell. is essentially a mixture of phospholipids that form a phospholipid bilayer. One definition of a cellA collection of molecules, capable of reproducing itself, that is surrounded by a phospholipid bilayer. is a collection of molecules surrounded by a phospholipid bilayer that is capable of reproducing itself. The simplest cells are bacteria, which consist of only a single compartment surrounded by a single membrane. Animal and plant cells are much more complex, however, and contain many different kinds of compartments, each surrounded by a membrane and able to carry out specialized tasks.

Summary

A **suspension** is a heterogeneous mixture of particles of one substance distributed throughout a second phase; the dispersed particles separate from the dispersing phase on standing. In contrast, the particles in a **colloid** are smaller and do not separate on standing. A colloid can be classified as a **sol**, a dispersion of solid particles in a liquid or solid; a **gel**, a semisolid sol in which all of the liquid phase has been absorbed by the solid particles; an **aerosol**, a dispersion of solid or liquid particles in a gas; or an **emulsion**, a dispersion of one liquid phase in another. A colloid can be distinguished from a true solution by its ability to scatter a beam of light, known as the **Tyndall effect**. Hydrophilic colloids contain an outer shell of groups that interact favorably with water, whereas hydrophobic colloids have an outer surface with little affinity for water. **Emulsions** are prepared by dispersing a hydrophobic liquid in water. In the absence of a dispersed hydrophobic liquid phase, solutions of detergents in water form organized spherical aggregates called **micelles**. **Phospholipids** are a class of detergent-like molecules that have two hydrophobic tails attached to a hydrophilic head. A **bilayer** is a two-dimensional sheet consisting of a double layer of phospholipid molecules arranged tail to tail with a hydrophobic interior and a hydrophilic exterior. **Cells** are collections of molecules that are surrounded by a phospholipid bilayer called a **cell membrane** and are able to reproduce themselves.

Key Takeaway

- Colloids and suspensions are mixtures whose properties are in many ways intermediate between those of true solutions and heterogeneous mixtures.

Conceptual Problems

1. How does a colloid differ from a suspension? Which has a greater effect on solvent properties, such as vapor pressure?
2. Is homogenized milk a colloid or a suspension? Is human plasma a colloid or a suspension? Justify your answers.
3. How would you separate the components of an emulsion of fat dispersed in an aqueous solution of sodium chloride?

Contributors

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Chapter 9.7: End of Chapter Materials

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Problems

Problems marked with a ♦ involve multiple concepts.

1. ♦ Scuba divers utilize high-pressure gas in their tanks to allow them to breathe under water. At depths as shallow as 100 ft (30 m), the pressure exerted by water is 4.0 atm. At 25°C the values of Henry's law constants for N_2, O_2, and He in blood are as follows: $N_2 = 6.5 \times 10^{-4}$ mol/(L·atm), $O_2 = 1.28 \times 10^{-3}$ mol/(L·atm), and He = 3.7×10^{-4} mol/(L·atm).
   a. What would be the concentration of nitrogen and oxygen in blood at sea level where the air is 21% oxygen and 79% nitrogen?
   b. What would be the concentration of nitrogen and oxygen in blood at a depth of 30 m, assuming that the diver is breathing compressed air?
2. ♦ Many modern batteries take advantage of lithium ions dissolved in suitable electrolytes. Typical batteries have lithium concentrations of 0.10 M. Which aqueous solution has the higher concentration of ion pairs: 0.08 M LiCl or 1.4 M LiCl? Why? Does an increase in the number of ion pairs correspond to a higher or lower van't Hoff factor? Batteries rely on a high concentration of unpaired Li^+ ions. Why is using a more concentrated solution not an ideal strategy in this case?
3. Hydrogen sulfide, which is extremely toxic to humans, can be detected at a concentration of 2.0 ppb. At this level, headaches, dizziness, and nausea occur. At higher concentrations, however, the sense of smell is lost, and the lack of warning can result in coma and death can result. What is the concentration of H_2S in milligrams per liter at the detection level? The lethal dose of hydrogen sulfide by inhalation for rats is 7.13×10^{-4} g/L. What is this lethal dose in ppm? The density of air is 1.2929 g/L.
4. One class of antibiotics consists of cyclic polyethers that can bind alkali metal cations in aqueous solution. Given the following antibiotics and cation selectivities, what conclusion can you draw regarding the relative sizes of the cavities?

Antibiotic	Cation Selectivity
nigericin	$K^+ > Rb^+ > Na^+ > Cs^+ > Li^+$
lasalocid	$Ba^{2+} >> Cs^+ > Rb^+, K^+ > Na^+, Ca^{2+}, Mg^{2+}$

5. Phenylpropanolamine hydrochloride is a common nasal decongestant. An aqueous solution of phenylpropanolamine hydrochloride that is sold commercially as a children's decongestant has a concentration of 6.67×10^{-3} M. If a common dose is 1.0 mL/12 lb of body weight, how many moles of the decongestant should be given to a 26 lb child?
6. The "freeze-thaw" method is often used to remove dissolved oxygen from solvents in the laboratory. In this technique, a liquid is placed in a flask that is then sealed to the atmosphere, the liquid is frozen, and the flask is evacuated to remove any gas and solvent vapor in the flask. The connection to the vacuum pump is closed, the liquid is warmed to room temperature and then refrozen, and the process is repeated. Why is this technique effective for degassing a solvent?
7. Suppose that, on a planet in a galaxy far, far away, a species has evolved whose biological processes require even more oxygen than we do. The partial pressure of oxygen on this planet, however, is much less than that on Earth. The chemical composition of the "blood" of this species is also different. Do you expect their "blood" to have a higher or lower value of the Henry's law constant for oxygen at standard temperature and pressure? Justify your answer.
8. A car owner who had never taken general chemistry decided that he needed to put some ethylene glycol antifreeze in his car's radiator. After reading the directions on the container, however, he decided that "more must be better." Instead of using the recommended mixture (30% ethylene glycol/70% water), he decided to reverse the amounts and used a 70% ethylene glycol/30% water mixture instead. Serious engine problems developed. Why?
9. The ancient Greeks produced "Attic ware," pottery with a characteristic black and red glaze. To separate smaller clay particles from larger ones, the powdered clay was suspended in water and allowed to settle. This process yielded clay fractions with coarse, medium, and fine particles, and one of these fractions was used for painting. Which size of clay

particles forms a suspension, which forms a precipitate, and which forms a colloidal dispersion? Would the colloidal dispersion be better characterized as an emulsion? Why or why not? Which fraction of clay particles was used for painting?

10. The Tyndall effect is often observed in movie theaters, where it makes the beam of light from the projector clearly visible. What conclusions can you draw about the quality of the air in a movie theater where you observe a large Tyndall effect?
11. Aluminum sulfate is the active ingredient in styptic pencils, which can be used to stop bleeding from small cuts. The Al^{3+} ions induce aggregation of colloids in the blood, which facilitates formation of a blood clot. How can Al^{3+} ions induce aggregation of a colloid? What is the probable charge on the colloidal particles in blood?
12. ♦ The liver secretes bile, which is essential for the digestion of fats. Fats are biomolecules with long hydrocarbon chains. The globules of fat released by partial digestion of food particles in the stomach and lower intestine are too large to be absorbed by the intestine unless they are emulsified by bile salts, such as glycocholate. Explain why a molecule like glycocholate is effective at creating an aqueous dispersion of fats in the digestive tract.



Glycocholate (a bile salt)

ANSWERS

1. a. 1 atm: 2.7×10^{-4} M O_2 and 5.1×10^{-4} M N_2
   b. 4 atm: 1.1×10^{-3} M O_2 and 2.1×10^{-3} M N_2
2.
3. 2.6×10^{-6} mg/L, 550 ppm
4.
5. 1.4×10^{-5} mol
6.
7. To obtain the same concentration of dissolved oxygen in their “blood” at a lower partial pressure of oxygen, the value of the Henry’s law constant would have to be higher.
8.
9. The large, coarse particles would precipitate, the medium particles would form a suspension, and the fine ones would form a colloid. A colloid consists of solid particles in a liquid medium, so it is not an emulsion, which consists of small particles of one liquid suspended in another liquid. The finest particles would be used for painting.
10.
11.
12.

Contributors

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CHAPTER OVERVIEW

Chapter 10: Nomenclature

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Chapter 10.0: Introduction

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Chapter 1 introduced some of the fundamental concepts of chemistry, with particular attention to the basic properties of atoms and elements. These entities are the building blocks of all substances we encounter, yet most common substances do not consist of only pure elements or individual atoms. Instead, nearly all substances are chemical compounds or mixtures of chemical compounds. Although there are only about 115 elements (of which about 86 occur naturally), millions of chemical compounds are known, with a tremendous range of physical and chemical properties. Consequently, the emphasis of modern chemistry (and this text) is on understanding the relationship between the structures and properties of chemical compounds.

Antoine Lavoisier expressed the need for a systematic chemical nomenclature in the Preface to his Elements of Chemistry

> The impossibility of separating the nomenclature of a science from the science itself, is owing to this, that every branch of physical science must consist of three things; the series of facts which are the objects of the science, the ideas which represent these facts, and the words by which these ideas are expressed. Like three impressions of the same seal, the word ought to produce the idea, and the idea to be a picture of the fact. And, as ideas are preserved and communicated by means of words, it necessarily follows that we cannot improve the language of any science without at the same time improving the science itself; neither can we, on the other hand, improve a science, without improving the language or nomenclature which belongs to it. However certain the facts of any science may be, and, however just the ideas we may have formed of these facts, we can only communicate false impressions to others, while we want words by which these may be properly expressed

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

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Chapter 10.1: Molecular Representations and Formula

Learning Objective

- To review the differences between covalent and ionic bonding.

Unit 2 discussed chemical bonding. This chapter uses what we learned about chemical bonding to construct consistent nomenclatures. Chemical bonds are generally divided into two fundamentally different kinds: ionic and covalent. The structural differences between these two types of bonds make it necessary to use different naming conventions for each. Further, the ability of carbon atoms to facily hybridize yielding a rich and complex chemistry makes it necessary to have a separate nomenclature for organic molecules.

Pictorial representations are symbolic labels. We begin by reviewing such structures and their links to molecular formulas starting with covalent compounds.

Note the Pattern

Ionic compounds consist of ions of opposite charges held together by strong electrostatic forces, whereas pairs of electrons are shared between bonded atoms in covalent compounds.

Covalent Molecules and Compounds

Just as an atom is the simplest unit that has the fundamental chemical properties of an element, a molecule is the simplest unit that has the fundamental chemical properties of a covalent compound. Some pure elements exist as covalent molecules. Hydrogen, nitrogen, oxygen, and the halogens occur naturally as the *diatomic* ("two atoms") *molecules* H_2, N_2, O_2, F_2, Cl_2, Br_2, and I_2 (part (a) in Figure 10.1.1). Similarly, a few pure elements are polyatomicMolecules that contain more than two atoms. ("many atoms") *molecules*, such as elemental phosphorus and sulfur, which occur as P_4 and S_8 (part (b) in Figure 10.1.1).

Each covalent compound is represented by a molecular formulaA representation of a covalent compound that consists of the atomic symbol for each component element (in a prescribed order) accompanied by a subscript indicating the number of atoms of that element in the molecule. The subscript is written only if the number is greater than 1., which gives the atomic symbol for each component element, in a prescribed order, accompanied by a subscript indicating the number of atoms of that element in the molecule. The subscript is written only if the number of atoms is greater than 1. For example, water, with two hydrogen atoms and one oxygen atom per molecule, is written as H_2O. Similarly, carbon dioxide, which contains one carbon atom and two oxygen atoms in each molecule, is written as CO_2.

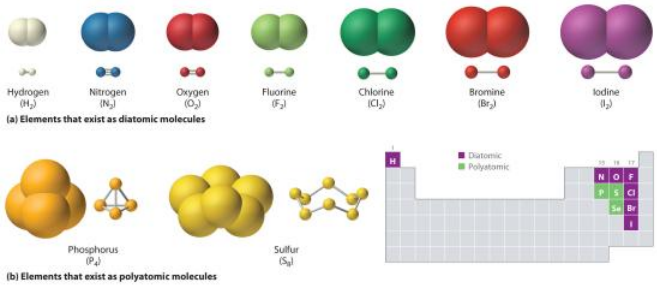


Figure 10.1.1 Elements That Exist as Covalent Molecules *(a) Several elements naturally exist as diatomic molecules, in which two atoms (E) are joined by one or more covalent bonds to form a molecule with the general formula E_2. (b) A few elements naturally exist as polyatomic molecules, which contain more than two atoms. For example, phosphorus exists as P_4 tetrahedra—regular polyhedra with four triangular sides—with a phosphorus atom at each vertex. Elemental sulfur consists of a puckered ring of eight sulfur atoms connected by single bonds. Selenium is not shown due to the complexity of its structure.*

Covalent compounds that contain predominantly carbon and hydrogen are called organic compoundsA covalent compound that contains predominantly carbon and hydrogen.. One convention for representing the formulas of organic compounds is to write carbon first, followed by hydrogen and then any other elements in alphabetical order (e.g., CH_4O is methyl alcohol, a fuel). Another convention better represents the molecular structure as a structural formula, as, for example, writing the formula for methyl alcohol as CH_3OH, where CH_3 is the methyl group and OH the hydroxyl. Compounds that consist primarily of elements

other than carbon and hydrogen are called inorganic compoundsAn ionic or covalent compound that consists primarily of elements other than carbon and hydrogen.; they include both covalent and ionic compounds. In inorganic compounds, the component elements are listed beginning with the one farthest to the left in the periodic table, such as we see in CO_2 or SF_6. Those in the same group are listed beginning with the element lower in the periodic table and working up, as in ClF. By convention, however, when an inorganic compound contains both hydrogen and an element from groups 13–15, the hydrogen is usually listed last in the formula. Examples are ammonia (NH_3) and silane (SiH_4). Some compounds such as water, whose compositions were established long before this convention was adopted, are always written with hydrogen first: Water is always written as H_2O, not OH_2. The conventions for inorganic acids, such as hydrochloric acid (HCl) and sulfuric acid (H_2SO_4), are described in Section 10.5 .

Note the Pattern

For organic compounds: write C first, then H, and then the other elements in alphabetical order. For molecular inorganic compounds: start with the element at far left in the periodic table; list elements in same group beginning with the lower element and working up.

Example 10.1.1

Write the molecular formula of each compound.

1. The phosphorus-sulfur compound that is responsible for the ignition of so-called strike anywhere matches has 4 phosphorus atoms and 3 sulfur atoms per molecule.
2. Ethyl alcohol, the alcohol of alcoholic beverages, has 1 oxygen atom, 2 carbon atoms, and 6 hydrogen atoms per molecule.
3. Freon-11, once widely used in automobile air conditioners and implicated in damage to the ozone layer, has 1 carbon atom, 3 chlorine atoms, and 1 fluorine atom per molecule.

Given: identity of elements present and number of atoms of each

Asked for: molecular formula

Strategy:

A Identify the symbol for each element in the molecule. Then identify the substance as either an organic compound or an inorganic compound.

B If the substance is an organic compound, arrange the elements in order beginning with carbon and hydrogen and then list the other elements alphabetically. If it is an inorganic compound, list the elements beginning with the one farthest left in the periodic table. List elements in the same group starting with the lower element and working up.

C From the information given, add a subscript for each kind of atom to write the molecular formula.

Solution:

1. **A** The molecule has 4 phosphorus atoms and 3 sulfur atoms. Because the compound does not contain mostly carbon and hydrogen, it is inorganic. **B** Phosphorus is in group 15, and sulfur is in group 16. Because phosphorus is to the left of sulfur, it is written first. **C** Writing the number of each kind of atom as a right-hand subscript gives P_4S_3 as the molecular formula.
2. **A** Ethyl alcohol contains predominantly carbon and hydrogen, so it is an organic compound. **B** The formula for an organic compound is written with the number of carbon atoms first, the number of hydrogen atoms next, and the other atoms in alphabetical order: CHO. **C** Adding subscripts gives the molecular formula C_2H_6O. To convey more structural information we could write this as C_2H_5OH. Draw the Lewis structure using this information
3. **A** Freon-11 contains carbon, chlorine, and fluorine. It can be viewed as either an inorganic compound or an organic compound (in which fluorine has replaced hydrogen). The formula for Freon-11 can therefore be written using either of the two conventions.

   B According to the convention for inorganic compounds, carbon is written first because it is farther left in the periodic table. Fluorine and chlorine are in the same group, so they are listed beginning with the lower element and working up: CClF. Adding subscripts gives the molecular formula CCl_3F.

   C We obtain the same formula for Freon-11 using the convention for organic compounds. The number of carbon atoms is written first, followed by the number of hydrogen atoms (zero) and then the other elements in alphabetical order, also giving

CCl_3F.

Exercise

Write the molecular formula for each compound.

1. Nitrous oxide, also called “laughing gas,” has 2 nitrogen atoms and 1 oxygen atom per molecule. Nitrous oxide is used as a mild anesthetic for minor surgery and as the propellant in cans of whipped cream.
2. Sucrose, also known as cane sugar, has 12 carbon atoms, 11 oxygen atoms, and 22 hydrogen atoms.
3. Sulfur hexafluoride, a gas used to pressurize “unpressurized” tennis balls and as a coolant in nuclear reactors, has 6 fluorine atoms and 1 sulfur atom per molecule.

Answer:

1. N_2O
2. $C_{12}H_{22}O_{11}$
3. SF_6

Representations of Molecular Structures

Molecular formulas give only the elemental composition of molecules. In contrast, structural formulasA representation of a molecule that shows which atoms are bonded to one another and, in some cases, the approximate arrangement of atoms in space. show which atoms are bonded to one another and, in some cases, the approximate arrangement of the atoms in space. These are the Lewis structures we learned about. Knowing the structural formula of a compound enables chemists to create a three-dimensional model, which provides information about how that compound will behave physically and chemically.

The structural formula for H_2 can be drawn as H–H and that for I_2 as I–I, where the line indicates a single pair of shared electrons, a single bondA chemical bond formed when two atoms share a single pair of electrons.. Two pairs of electrons are shared in a double bondA chemical bond formed when two atoms share two pairs of electrons., which is indicated by two lines— for example, O_2 is O=O. Three electron pairs are shared in a triple bondA chemical bond formed when two atoms share three pairs of electrons., which is indicated by three lines—for example, N_2 is N≡N (see Figure 10.1.2). Carbon is unique in the extent to which it forms single, double, and triple bonds to itself and other elements. The number of bonds formed by an atom in its covalent compounds is *not* arbitrary. As we have learned in Chapter 4, hydrogen, oxygen, nitrogen, and carbon have a very strong tendency to form substances in which they have one, two, three, and four bonds to other atoms, respectively (Figure 10.1.2).

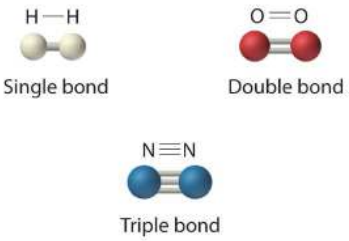


Figure 10.1.2 Molecules That Contain Single, Double, and Triple Bonds *Hydrogen (H_2) has a single bond between atoms. Oxygen (O_2) has a double bond between atoms, indicated by two lines (=). Nitrogen (N_2) has a triple bond between atoms, indicated by three lines (≡). Each bond represents an electron pair.*

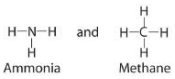
Table 10.1.1 The Number of Bonds That Selected Atoms Commonly Form to Other Atoms

Atom	Number of Bonds
H (group 1)	1
O (group 16)	2
N (group 15)	3
C (group 14)	4

The structural formula for water can be drawn as follows, but including the two lone pairs on the oxygen provides more information:



Because as we learned from VSEPR, the latter approximates the experimentally determined shape of the water molecule, it is more informative. Similarly, ammonia (NH_3) and methane (CH_4) are often written as planar molecules but at least for ammonia, it would be more informative to include the lone pair on the nitrogen atom:



As shown in Figure 10.1.3, however, we know that the the actual three-dimensional structure of NH_3 looks like a pyramid with a triangular base of three hydrogen atoms. Again using VSEPR, or what we know about sp3 orbitals on the central atom in all three molecules the structure of CH_4, with four hydrogen atoms arranged around a central carbon atom as shown in Figure 10.1.3 , is *tetrahedral*. That is, the hydrogen atoms are positioned at every other vertex of a cube. Many compounds—carbon compounds, in particular—have four bonded atoms arranged around a central atom to form a tetrahedron.

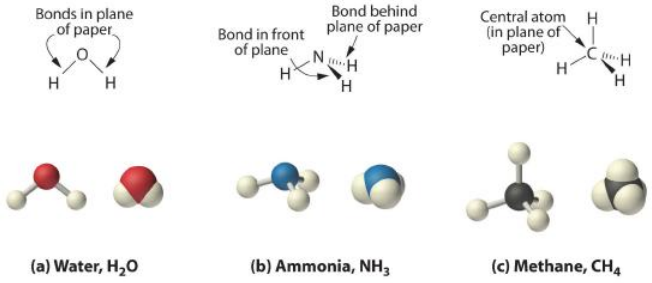
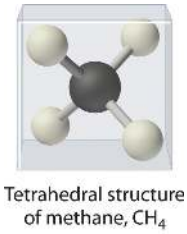


Figure 10.1.3 The Three-Dimensional Structures of Water, Ammonia, and Methane *(a) Water is a V-shaped molecule, in which all three atoms lie in a plane. (b) In contrast, ammonia has a pyramidal structure, in which the three hydrogen atoms form the base of the pyramid and the nitrogen atom is at the vertex. (c) The four hydrogen atoms of methane form a tetrahedron; the carbon atom lies in the center.*



CH_4. *Methane has a three-dimensional, tetrahedral structure.*

Figure 10.1.1 , and Figure 10.1.3 illustrate different ways to represent the structures of molecules. It should be clear that there is no single “best” way to draw the structure of a molecule; the method you use depends on which aspect of the structure you want to emphasize and how much time and effort you want to spend. Figure 10.1.4 shows some of the different ways to portray the structure of a slightly more complex molecule: methanol. These representations differ greatly in their information content. For example, the molecular formula for methanol (part (a) in Figure 10.1.4) gives only the number of each kind of atom; writing methanol as CH_4O tells nothing about its structure. In contrast, the structural formula (part (b) in Figure 10.1.4) indicates how the atoms are connected, but it makes methanol look as if it is planar (which it is not). Both the ball-and-stick model (part (c) in Figure 10.1.4) and the perspective drawing (part (d) in Figure 10.1.4) show the three-dimensional structure of the molecule. The latter (also called a *wedge-and-dash* representation) is the easiest way to sketch the structure of a molecule in three dimensions. It shows which atoms are above and below the plane of the paper by using wedges and dashes, respectively; the central atom is always assumed to be in the plane of the paper. The space-filling model (part (e) in Figure 10.1.4) illustrates the approximate relative sizes

of the atoms in the molecule, but it does not show the bonds between the atoms. Also, in a space-filling model, atoms at the "front" of the molecule may obscure atoms at the "back."

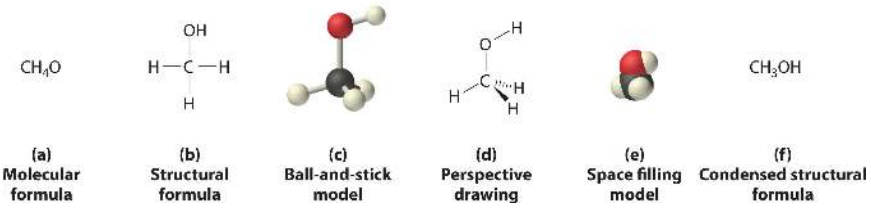


Figure 10.1.4 Different Ways of Representing the Structure of a Molecule *(a) The molecular formula for methanol gives only the number of each kind of atom present. (b) The structural formula shows which atoms are connected. (c) The ball-and-stick model shows the atoms as spheres and the bonds as sticks. (d) A perspective drawing (also called a wedge-and-dash representation) attempts to show the three-dimensional structure of the molecule. (e) The space-filling model shows the atoms in the molecule but not the bonds. (f) The condensed structural formula is by far the easiest and most common way to represent a molecule.*

Although a structural formula, a ball-and-stick model, a perspective drawing, and a space-filling model provide a significant amount of information about the structure of a molecule, each requires time and effort. Consequently, chemists often use a *condensed structural formula* (part (f) in Figure 10.1.4), which omits the lines representing bonds between atoms and simply lists the atoms bonded to a given atom next to it. Multiple groups attached to the same atom are shown in parentheses, followed by a subscript that indicates the number of such groups. For example, the condensed structural formula for methanol is CH_3OH, which tells us that the molecule contains a CH_3 unit that looks like a fragment of methane (CH_4). Methanol can therefore be viewed either as a methane molecule in which one hydrogen atom has been replaced by an –OH group or as a water molecule in which one hydrogen atom has been replaced by a $–CH_3$ fragment. Because of their ease of use and information content, we use condensed structural formulas for molecules throughout this text. Ball-and-stick models are used when needed to illustrate the three-dimensional structure of molecules, and space-filling models are used only when it is necessary to visualize the relative sizes of atoms or molecules to understand an important point.

Example 10.1.2

Write the molecular formula for each compound. The condensed structural formula is given.

1. Sulfur monochloride (also called disulfur dichloride) is a vile-smelling, corrosive yellow liquid used in the production of synthetic rubber. Its condensed structural formula is ClSSCl.
2. Ethylene glycol is the major ingredient in antifreeze. Its condensed structural formula is $HOCH_2CH_2OH$.
3. Trimethylamine is one of the substances responsible for the smell of spoiled fish. Its condensed structural formula is $(CH_3)_3N$.

Given: condensed structural formula

Asked for: molecular formula

Strategy:

A Identify every element in the condensed structural formula and then determine whether the compound is organic or inorganic.

B As appropriate, use either organic or inorganic convention to list the elements. Then add appropriate subscripts to indicate the number of atoms of each element present in the molecular formula.

Solution:

The molecular formula lists the elements in the molecule and the number of atoms of each.

1. **A** Each molecule of sulfur monochloride has two sulfur atoms and two chlorine atoms. Because it does not contain mostly carbon and hydrogen, it is an inorganic compound. **B** Sulfur lies to the left of chlorine in the periodic table, so it is written first in the formula. Adding subscripts gives the molecular formula S_2Cl_2.
2. **A** Counting the atoms in ethylene glycol, we get six hydrogen atoms, two carbon atoms, and two oxygen atoms per molecule. The compound consists mostly of carbon and hydrogen atoms, so it is organic. **B** As with all organic compounds, C and H are

written first in the molecular formula. Adding appropriate subscripts gives the molecular formula $C_2H_6O_2$.

3. **A** The condensed structural formula shows that trimethylamine contains three CH_3 units, so we have one nitrogen atom, three carbon atoms, and nine hydrogen atoms per molecule. Because trimethylamine contains mostly carbon and hydrogen, it is an organic compound. **B** According to the convention for organic compounds, C and H are written first, giving the molecular formula C_3H_9N.

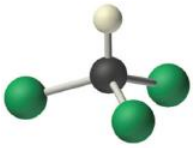


Trimethylamine

Exercise

Write the molecular formula for each molecule.

1. Chloroform, which was one of the first anesthetics and was used in many cough syrups until recently, contains one carbon atom, one hydrogen atom, and three chlorine atoms. Its condensed structural formula is $CHCl_3$.
2. Hydrazine is used as a propellant in the attitude jets of the space shuttle. Its condensed structural formula is H_2NNH_2.
3. Putrescine is a pungent-smelling compound first isolated from extracts of rotting meat. Its condensed structural formula is $H_2NCH_2CH_2CH_2CH_2NH_2$. This is often written as $H_2N(CH_2)_4NH_2$ to indicate that there are four CH_2 fragments linked together.



Chloroform

Answer:

1. $CHCl_3$
2. N_2H_4
3. $C_4H_{12}N_2$

Ionic Compounds

The substances described in the preceding discussion are composed of molecules that are electrically neutral; that is, the number of positively charged protons in the nucleus is equal to the number of negatively charged electrons. In contrast, *ions* are atoms or assemblies of atoms that have a net electrical charge. Ions that contain fewer electrons than protons have a net positive charge and are called cationsAn ion that has fewer electrons than protons, resulting in a net positive charge.. Conversely, ions that contain more electrons than protons have a net negative charge and are called anionsAn ion that has fewer protons than electrons, resulting in a net negative charge.. *Ionic compounds* contain both cations and anions in a ratio that results in no net electrical charge.

Note the Pattern

Ionic compounds contain both cations and anions in a ratio that results in zero electrical charge.

In covalent compounds, electrons are shared between bonded atoms and are simultaneously attracted to more than one nucleus. In contrast, ionic compounds contain cations and anions rather than discrete neutral molecules. Ionic compounds are held together by the attractive electrostatic interactions between cations and anions. In an ionic compound, the cations and anions are arranged in space to form an extended three-dimensional array that maximizes the number of attractive electrostatic interactions and minimizes the number of repulsive electrostatic interactions (Figure 10.1.5). As shown in Equation 10.1.1, the electrostatic energy of the interaction between two charged particles is proportional to the product of the charges on the particles and inversely proportional to the distance between them:

$$\textit{electrostatic energy} = \frac{Q_1 Q_2}{r}$$

where Q_1 and Q_2 are the electrical charges on particles 1 and 2, and r is the distance between them. When Q_1 and Q_2 are both positive, corresponding to the charges on cations, the cations repel each other and the electrostatic energy is positive. When Q_1 and Q_2 are both negative, corresponding to the charges on anions, the anions repel each other and the electrostatic energy is again positive. The electrostatic energy is negative only when the charges have opposite signs; that is, positively charged species are attracted to negatively charged species and vice versa. As shown in Figure 10.1.6 , the strength of the interaction is proportional to the *magnitude* of the charges and decreases as the *distance* between the particles increases as we have seen previously

Note the Pattern

If the electrostatic energy is positive, the particles repel each other; if the electrostatic energy is negative, the particles are attracted to each other.

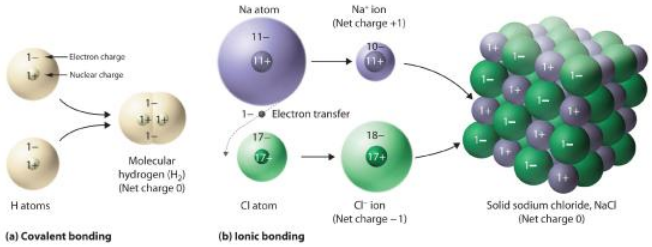


Figure 10.1.5 Covalent and Ionic Bonding *(a) In molecular hydrogen (H_2), two hydrogen atoms share two electrons to form a covalent bond. (b) The ionic compound NaCl forms when electrons from sodium atoms are transferred to chlorine atoms. The resulting Na^+ and Cl^- ions form a three-dimensional solid that is held together by attractive electrostatic interactions.*

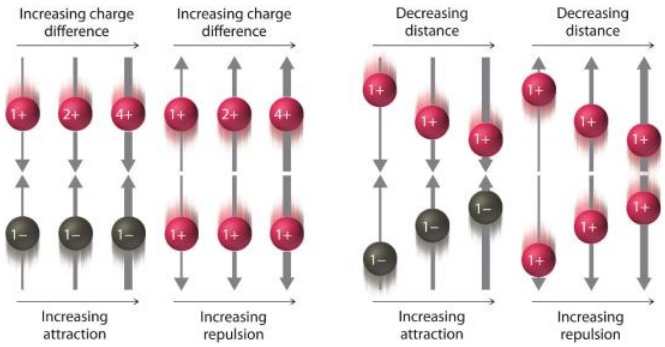


Figure1 10.1.6 The Effect of Charge and Distance on the Strength of Electrostatic Interactions *As the charge on ions increases or the distance between ions decreases, so does the strength of the attractive (−…+) or repulsive (−…− or +…+) interactions. The strength of these interactions is represented by the thickness of the arrows.*

One example we have studied of an ionic compound is sodium chloride (NaCl; Figure 10.1.7), formed from sodium and chlorine. In forming chemical compounds, many elements have a tendency to gain or lose enough electrons to attain the same number of electrons as the noble gas closest to them in the periodic table. When sodium and chlorine come into contact, each sodium atom gives up an electron to become a Na^+ ion, with 11 protons in its nucleus but only 10 electrons (like neon), and each chlorine atom gains an electron to become a Cl^- ion, with 17 protons in its nucleus and 18 electrons (like argon), as shown in part (b) in Figure 10.1.5 . Solid sodium chloride contains equal numbers of cations (Na^+) and anions (Cl^-), thus maintaining electrical neutrality. Each Na^+ ion is surrounded by 6 Cl^- ions, and each Cl^- ion is surrounded by 6 Na^+ ions. Because of the large number of attractive Na^+Cl^- interactions, the total attractive electrostatic energy in NaCl is great.

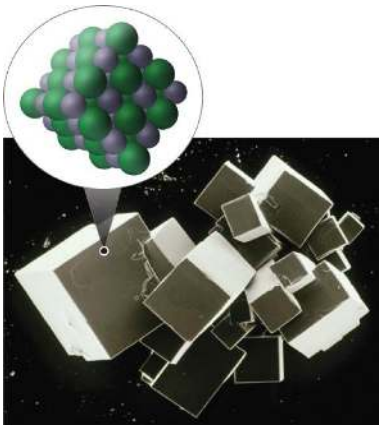


Figure 10.1.7Sodium Chloride: an Ionic Solid *The planes of an NaCl crystal reflect the regular three-dimensional arrangement of its Na^+ (purple) and Cl^- (green) ions.*

Consistent with a tendency to have the same number of electrons as the nearest noble gas, when forming ions, elements in groups 1, 2, and 3 tend to *lose* one, two, and three electrons, respectively, to form cations, such as Na^+ and Mg^{2+}. They then have the same number of electrons as the nearest noble gas: neon. Similarly, K^+, Ca^{2+}, and Sc^{3+} have 18 electrons each, like the nearest noble gas: argon. In addition, the elements in group 13 *lose* three electrons to form cations, such as Al^{3+}, again attaining the same number of electrons as the noble gas closest to them in the periodic table. Because the lanthanides and actinides formally belong to group 3, the most common ion formed by these elements is M^{3+}, where M represents the metal. Conversely, elements in groups 17, 16, and 15 often react to *gain* one, two, and three electrons, respectively, to form ions such as Cl^-, S^{2-}, and P^{3-}. Ions such as these, which contain only a single atom, are called monatomic ionsAn ion with only a single atom.. **The names of the single atom cations are simply the name of the metal from which they are derived. The names of the single atom anions add the suffix -ide to the first syllable of the atom, for example oxide, chloride, nitride, etc.**

The charges of the monotomic ions in Groups 1-3 and 15-17 are easily predicted either from your knowledge of atomic structure as discussed in Chapter 3. It can also be predicted simply by looking at the periodic table and counting how many columns an element lies from the extreme left or right. For example, you can predict that barium (in group 2) will form Ba^{2+} to have the same number of electrons as its nearest noble gas, xenon. Of course this also is what you would find based on the fact that the valence electrons are $6s^2$. Similarly oxygen (in group 16) will form O^{2-} to have the same number of electrons as neon, the valence electrons being $2s^22p^4$. Cesium (in group 1) will form Cs^+ to also have the same number of electrons as xenon as it only has a single 6s electron in the valence shell. This method does not usually work as well for the transition metals for reasons given in Section 2.4 . Some common monatomic ions are shown in Table 10.1.2 .

Note the Pattern

Elements in groups 1, 2, and 3 tend to form 1+, 2+, and 3+ ions, respectively; elements in groups 15, 16, and 17 tend to form 3−, 2−, and 1− ions, respectively.

Table 10.1.2 Some Common Monatomic Ions and Their Names

Group 1	Group 2	Group 3	Group 13	Group 15	Group 16	Group 17
Li^+ lithium	Be^{2+} beryllium			N^{3-} nitride (azide)	O^{2-} oxide	F^- fluoride
Na^+ sodium	Mg^{2+} magnesium		Al^{3+} aluminum	P^{3-} phosphide	S^{2-} sulfide	Cl^- chloride
K^+ potassium	Ca^{2+} calcium	Sc^{3+} scandium	Ga^{3+} gallium	As^{3-} arsenide	Se^{2-} selenide	Br^- bromide
Rb^+ rubidium	Sr^{2+} strontium	Y^{3+} yttrium	In^{3+} indium		Te^{2-} telluride	I^- iodide
Cs^+ cesium	Ba^{2+} barium	La^{3+} lanthanum				

Example 10.1.3

Predict the charge on the most common monatomic ion formed by each element.

1. aluminum, used in the quantum logic clock, the world's most precise clock
2. selenium, used to make ruby-colored glass
3. yttrium, used to make high-performance spark plugs

Given: element

Asked for: ionic charge

Strategy:

A Identify the group in the periodic table to which the element belongs. Based on its location in the periodic table, decide whether the element is a metal, which tends to lose electrons; a nonmetal, which tends to gain electrons; or a semimetal, which can do either.

B After locating the noble gas that is closest to the element, determine the number of electrons the element must gain or lose to have the same number of electrons as the nearest noble gas.

Solution:

1. **A** Aluminum is a metal in group 13; consequently, it will tend to lose electrons. **B** The nearest noble gas to aluminum is neon. Aluminum will lose three electrons to form the Al^{3+} ion, which has the same number of electrons as neon.
2. **A** Selenium is a nonmetal in group 16, so it will tend to gain electrons. **B** The nearest noble gas is krypton, so we predict that selenium will gain two electrons to form the Se^{2-} ion, which has the same number of electrons as krypton.
3. **A** Yttrium is in group 3, and elements in this group are metals that tend to lose electrons. **B** The nearest noble gas to yttrium is krypton, so yttrium is predicted to lose three electrons to form Y^{3+}, which has the same number of electrons as krypton.

Exercise

Predict the charge on the most common monatomic ion formed by each element.

1. calcium, used to prevent osteoporosis
2. iodine, required for the synthesis of thyroid hormones
3. zirconium, widely used in nuclear reactors

Answer:

1. Ca^{2+}
2. I^-

3. Zr^{4+}

Physical Properties of Ionic and Covalent Compounds

In general, ionic and covalent compounds have different physical properties. As we have discussed, ionic compounds usually form hard crystalline solids that melt at rather high temperatures and are *very* resistant to evaporation. These properties stem from the characteristic internal structure of an ionic solid, illustrated schematically in part (a) in Figure 10.1.8 , which shows the three-dimensional array of alternating positive and negative ions held together by strong electrostatic attractions. In contrast, as shown in part (b) in Figure 10.1.8 , most covalent compounds consist of discrete molecules held together by comparatively weak *intermolecular* forces (the forces between molecules), even though the atoms within each molecule are held together by strong *intramolecular* covalent bonds (the forces within the molecule). Covalent substances can be gases, liquids, or solids at room temperature and pressure, depending on the strength of the intermolecular interactions. Covalent molecular solids tend to form soft crystals that melt at rather low temperatures and evaporate relatively easily. Some covalent substances, however, are not molecular but consist of infinite three-dimensional arrays of covalently bonded atoms and include some of the hardest materials known, such as diamond. The covalent bonds that hold the atoms together in the molecules are unaffected when covalent substances melt or evaporate, so a liquid or vapor of discrete, independent molecules is formed. For example, at room temperature, methane, the major constituent of natural gas, is a gas that is composed of discrete CH_4 molecules. A comparison of the different physical properties of ionic compounds and covalent molecular substances is given in Table 10.1.3.

Ionic Compounds	Covalent Molecular Substances
hard solids	gases, liquids, or soft solids
high melting points	low melting points
nonvolatile	volatile

Figure 10.1.8 Interactions in Ionic and Covalent Solids

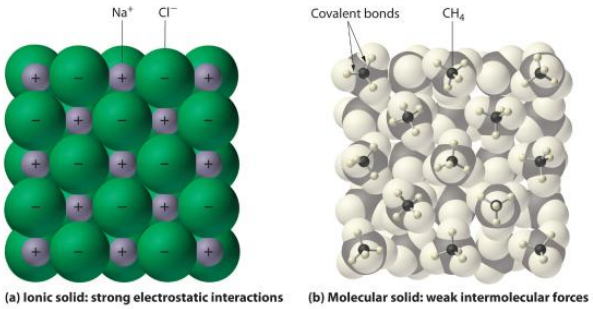


Table 10.1.3 The Physical Properties of Typical Ionic Compounds and Covalent Molecular Substances *(a) The positively and negatively charged ions in an ionic solid such as sodium chloride (NaCl) are held together by strong electrostatic interactions. (b) In this representation of the packing of methane (CH_4) molecules in solid methane, a prototypical molecular solid, the methane molecules are held together in the solid only by relatively weak intermolecular forces, even though the atoms within each methane molecule are held together by strong covalent bonds.*

Summary

The atoms in chemical compounds are held together by attractive electrostatic interactions known as **chemical bonds**. **Ionic compounds** contain positively and negatively charged ions in a ratio that results in an overall charge of zero. The ions are held together in a regular spatial arrangement by electrostatic forces. Most **covalent compounds** consist of **molecules**, groups of atoms in which one or more pairs of electrons are shared by at least two atoms to form a covalent bond. The atoms in molecules are held together by the **electrostatic attraction** between the positively charged nuclei of the bonded atoms and the negatively charged electrons shared by the nuclei. The **molecular formula** of a covalent compound gives the types and numbers of atoms present. Compounds that contain predominantly carbon and hydrogen are called **organic compounds**, whereas compounds that consist primarily of elements other than carbon and hydrogen are **inorganic compounds**. *Diatomic molecules* contain two atoms, and

polyatomic molecules contain more than two. A **structural formula** indicates the composition and approximate structure and shape of a molecule. **Single bonds, double bonds**, and **triple bonds** are covalent bonds in which one, two, and three pairs of electrons, respectively, are shared between two bonded atoms. Atoms or groups of atoms that possess a net electrical charge are called *ions*; they can have either a positive charge (**cations**) or a negative charge (**anions**). Ions can consist of one atom (**monatomic ions**) or several (*polyatomic ions*). The charges on monatomic ions of most main group elements can be predicted from the location of the element in the periodic table. Ionic compounds usually form hard crystalline solids with high melting points. Covalent molecular compounds, in contrast, consist of discrete molecules held together by weak intermolecular forces and can be gases, liquids, or solids at room temperature and pressure.

Key Takeaway

- There are two fundamentally different kinds of chemical bonds (covalent and ionic) that cause substances to have very different properties.

Conceptual Problems

1. Ionic and covalent compounds are held together by electrostatic attractions between oppositely charged particles. Describe the differences in the nature of the attractions in ionic and covalent compounds. Which class of compounds contains pairs of electrons shared between bonded atoms?
2. Which contains fewer electrons than the neutral atom—the corresponding cation or the anion?
3. What is the difference between an organic compound and an inorganic compound?
4. What is the advantage of writing a structural formula as a condensed formula?
5. The majority of elements that exist as diatomic molecules are found in one group of the periodic table. Identify the group.
6. Discuss the differences between covalent and ionic compounds with regard to
   1. the forces that hold the atoms together.
   2. melting points.
   3. physical states at room temperature and pressure.
7. Why do covalent compounds generally tend to have lower melting points than ionic compounds?

Answer

1. Covalent compounds generally melt at lower temperatures than ionic compounds because the intermolecular interactions that hold the molecules together in a molecular solid are weaker than the electrostatic attractions that hold oppositely charged ions together in an ionic solid.

Numerical Problems

1. The structural formula for chloroform ($CHCl_3$) was shown in Example 2. Based on this information, draw the structural formula of dichloromethane (CH_2Cl_2).
2. What is the total number of electrons present in each ion?
   1. F^-
   2. Rb^+
   3. Ce^{3+}
   4. Zr^{4+}
   5. Zn^{2+}
   6. Kr^{2+}
   7. B^{3+}
3. What is the total number of electrons present in each ion?
   1. Ca^{2+}
   2. Se^{2-}
   3. In^{3+}
   4. Sr^{2+}
   5. As^{3+}
   6. N^{3-}

7. Tl^{+}

4. Predict how many electrons are in each ion.

    1. an oxygen ion with a −2 charge
    2. a beryllium ion with a +2 charge
    3. a silver ion with a +1 charge
    4. a selenium ion with a +4 charge
    5. an iron ion with a +2 charge
    6. a chlorine ion with a −1 charge

5. Predict how many electrons are in each ion.

    1. a copper ion with a +2 charge
    2. a molybdenum ion with a +4 charge
    3. an iodine ion with a −1 charge
    4. a gallium ion with a +3 charge
    5. an ytterbium ion with a +3 charge
    6. a scandium ion with a +3 charge

6. Predict the charge on the most common monatomic ion formed by each element.

    1. chlorine
    2. phosphorus
    3. scandium
    4. magnesium
    5. arsenic
    6. oxygen

7. Predict the charge on the most common monatomic ion formed by each element.

    1. sodium
    2. selenium
    3. barium
    4. rubidium
    5. nitrogen
    6. aluminum

8. For each representation of a monatomic ion, identify the parent atom, write the formula of the ion using an appropriate superscript, and indicate the period and group of the periodic table in which the element is found.

    1. $^{9}_{4}X_{2+}$
    2. $^{1}_{1}X_{-}$
    3. $^{16}_{8}X_{2-}$

9. For each representation of a monatomic ion, identify the parent atom, write the formula of the ion using an appropriate superscript, and indicate the period and group of the periodic table in which the element is found.

    1. $^{7}_{3}X_{+}$
    2. $^{19}_{9}X_{-}$
    3. $^{27}_{13}X_{3+}$

5. 1. 27
4. 2. 28
3. 3. 54

Answers

1. 5. 67
    6. 18
6.
7.

8.
9. 1. Li, Li^+, 2nd period, group 1
   2. F, F^-, 2nd period, group 17
   3. Al, Al^{3+}, 3nd period, group 13

Contributors

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Chapter 10.2: Chemical Formulas

Learning Objective

- To describe the composition of a chemical compound.

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

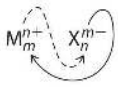
Because ionic compounds do not contain discrete molecules, empirical formulas are used to indicate their compositions. All compounds, whether ionic or covalent, must be electrically neutral. Consequently, the positive and negative charges in a formula unit must exactly cancel each other. If the cation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

Note the Pattern

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

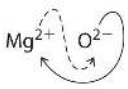
Binary Ionic Compounds

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



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

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



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

Example 10.2.1

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

1. Ga^{3+} and As^{3-}

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

Given: ions or elements

Asked for: empirical formula for binary ionic compound

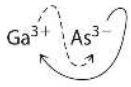
Strategy:

A If not given, determine the ionic charges based on the location of the elements in the periodic table.

B Use the absolute value of the charge on each ion as the subscript for the other ion. Reduce the subscripts to the lowest numbers to write the empirical formula. Check to make sure the empirical formula is electrically neutral.

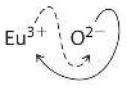
Solution:

1. **B** Using the absolute values of the charges on the ions as the subscripts gives Ga_3As_3:



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

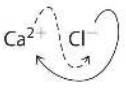
2. **B** Because Eu^{3+} has a charge of +3 and O^{2-} has a charge of −2, a 1:1 compound would have a net charge of +1. We must therefore find multiples of the charges that cancel. We cross charges, using the absolute value of the charge on one ion as the subscript for the other ion:



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

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

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



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

Exercise

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

1. Li^+ and N^{3-}
2. Al^{3+} and O^{2-}

3. lithium and oxygen

Answer:

1. Li_3N
2. Al_2O_3
3. Li_2O

Polyatomic Ions

Polyatomic ionsA group of two or more atoms that has a net electrical charge. are groups of atoms that bear a net electrical charge, although the atoms in a polyatomic ion are held together by the same covalent bonds that hold atoms together in molecules. Just as there are many more kinds of molecules than simple elements, there are many more kinds of polyatomic ions than monatomic ions. Two examples of polyatomic cations are the ammonium (NH_4^+) and the methylammonium ($CH_3NH_3^+$) ions. These are formed by adding a proton (the hydrogen nucleus) to the lone pair in ammonia and methylammonia. Polyatomic anions are much more numerous than polyatomic cations; some common examples are in Table 10.2.1 .

Table 10.2.1 Common Polyatomic Ions and Their Names

Formula	Name of Ion
NH_4^+	ammonium
$CH_3NH_3^+$	methylammonium
OH^-	hydroxide
O_2^{2-}	peroxide
CN^-	cyanide
SCN^-	thiocyanate
NO_2^-	nitrite
NO_3^-	nitrate
CO_3^{2-}	carbonate
HCO_3^-	hydrogen carbonate, or bicarbonate
SO_3^{2-}	sulfite
SO_4^{2-}	sulfate
HSO_4^-	hydrogen sulfate, or bisulfate
PO_4^{3-}	phosphate
HPO_4^{2-}	hydrogen phosphate
$H_2PO_4^-$	dihydrogen phosphate
ClO^-	hypochlorite
ClO_2^-	chlorite
ClO_3^-	chlorate
ClO_4^-	perchlorate
MnO_4^-	permanganate
CrO_4^{2-}	chromate
$Cr_2O_7^{2-}$	dichromate
$C_2O_4^{2-}$	oxalate
HCO_2^-	formate
$CH_3CO_2^-$	acetate
$C_6H_5CO_2^-$	benzoate

The method we used to predict the empirical formulas for ionic compounds that contain monatomic ions can also be used for compounds that contain polyatomic ions. The overall charge on the cations must balance the overall charge on the anions in the formula unit. Thus K^+ and NO_3^- ions combine in a 1:1 ratio to form KNO_3 (potassium nitrate or saltpeter), a major ingredient in black gunpowder. Similarly, Ca^{2+} and SO_4^{2-} form $CaSO_4$ (calcium sulfate), which combines with varying amounts of water to form gypsum and plaster of Paris. The polyatomic ions NH_4^+ and NO_3^- form NH_4NO_3 (ammonium nitrate), which is a widely used fertilizer and, in the wrong hands, an explosive. One example of a compound in which the ions have charges of different

magnitudes is calcium phosphate, which is composed of Ca^{2+} and PO_4^{3-} ions; it is a major component of bones. The compound is electrically neutral because the ions combine in a ratio of three Ca^{2+} ions [3(+2) = +6] for every two ions [2(−3) = −6], giving an empirical formula of $Ca_3(PO_4)_2$; the parentheses around PO_4 in the empirical formula indicate that it is a polyatomic ion. Writing the formula for calcium phosphate as $Ca_3P_2O_8$ gives the correct number of each atom in the formula unit, but it obscures the fact that the compound contains readily identifiable PO_4^{3-} ions.

Example 10.2.2

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

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

Given: ions

Asked for: empirical formula for ionic compound

Strategy:

A If it is not given, determine the charge on a monatomic ion from its location in the periodic table. Use Table 10.2.1 to find the charge on a polyatomic ion.

B Use the absolute value of the charge on each ion as the subscript for the other ion. Reduce the subscripts to the smallest whole numbers when writing the empirical formula.

Solution:

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

Exercise

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

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

Answer:

1. $Ca(H_2PO_4)_2$: calcium dihydrogen phosphate is one of the ingredients in baking powder.
2. $NaHCO_3$: sodium bicarbonate is found in antacids and baking powder; in pure form, it is sold as baking soda.
3. $(NH_4)_2SO_4$: ammonium sulfate is a common source of nitrogen in fertilizers.

Hydrates

Many ionic compounds occur as hydratesA compound that contains specific ratios of loosely bound water molecules, called waters of hydration., compounds that contain specific ratios of loosely bound water molecules, called waters of hydrationThe loosely bound water molecules in hydrate compounds. These waters of hydration can often be removed by simply heating the compound.. Waters of hydration can often be removed simply by heating. For example, calcium dihydrogen phosphate can form a solid that contains one molecule of water per $Ca(H_2PO_4)_2$ unit and is used as a leavening agent in the food industry to cause baked goods to

rise. The empirical formula for the solid is $Ca(H_2PO_4)_2 \cdot H_2O$. In contrast, copper sulfate usually forms a blue solid that contains *five* waters of hydration per formula unit, with the empirical formula $CuSO_4 \cdot 5H_2O$. When heated, all five water molecules are lost, giving a white solid with the empirical formula $CuSO_4$ (Figure 10.2.1).



Figure 10.2.1 Loss of Water from a Hydrate with Heating *When blue $CuSO_4 \cdot 5H_2O$ is heated, two molecules of water are lost at 30°C, two more at 110°C, and the last at 250°C to give white $CuSO_4$.*

Compounds that differ only in the numbers of waters of hydration can have very different properties. For example, $CaSO_4 \cdot ½H_2O$ is plaster of Paris, which was often used to make sturdy casts for broken arms or legs, whereas $CaSO_4 \cdot 2H_2O$ is the less dense, flakier gypsum, a mineral used in drywall panels for home construction. When a cast would set, a mixture of plaster of Paris and water crystallized to give solid $CaSO_4 \cdot 2H_2O$. Similar processes are used in the setting of cement and concrete.

Summary

An **empirical formula** gives the *relative* numbers of atoms of the elements in a compound, reduced to the lowest whole numbers. The **formula unit** is the *absolute* grouping represented by the empirical formula of a compound, either ionic or covalent. Empirical formulas are particularly useful for describing the composition of ionic compounds, which do not contain readily identifiable molecules. Some ionic compounds occur as **hydrates**, which contain specific ratios of loosely bound water molecules called **waters of hydration**.

Key Takeaway

- The composition of a compound is represented by an empirical or molecular formula, each consisting of at least one formula unit.

Conceptual Problems

1. What are the differences and similarities between a polyatomic ion and a molecule?
2. Classify each compound as ionic or covalent.
    1. $Zn_3(PO_4)_2$
    2. $C_6H_5CO_2H$
    3. $K_2Cr_2O_7$
    4. CH_3CH_2SH
    5. NH_4Br
    6. CCl_2F_2
3. Classify each compound as ionic or covalent. Which are organic compounds and which are inorganic compounds?
    1. $CH_3CH_2CO_2H$
    2. $CaCl_2$
    3. $Y(NO_3)_3$
    4. H_2S
    5. $NaC_2H_3O_2$
4. Generally, one cannot determine the molecular formula directly from an empirical formula. What other information is needed?
5. Give two pieces of information that we obtain from a structural formula that we cannot obtain from an empirical formula.
6. The formulas of alcohols are often written as ROH rather than as empirical formulas. For example, methanol is generally written as CH_3OH rather than CH_4O. Explain why the ROH notation is preferred.
7. The compound dimethyl sulfide has the empirical formula C_2H_6S and the structural formula CH_3SCH_3. What information do we obtain from the structural formula that we do not get from the empirical formula? Write the condensed structural formula for the compound.
8. What is the correct formula for magnesium hydroxide—$MgOH_2$ or $Mg(OH)_2$? Why?
9. Magnesium cyanide is written as $Mg(CN)_2$, not $MgCN_2$. Why?
10. Does a given hydrate always contain the same number of waters of hydration?

Answer

1.
2.
3.
4.
5.
6.
7. The structural formula gives us the connectivity of the atoms in the molecule or ion, as well as a schematic representation of their arrangement in space. Empirical formulas tell us only the ratios of the atoms present. The condensed structural formula of dimethylsulfide is $(CH_3)_2S$.
8.
9.
10.

Numerical Problems

1. Write the formula for each compound.
    1. magnesium sulfate, which has 1 magnesium atom, 4 oxygen atoms, and 1 sulfur atom
    2. ethylene glycol (antifreeze), which has 6 hydrogen atoms, 2 carbon atoms, and 2 oxygen atoms
    3. acetic acid, which has 2 oxygen atoms, 2 carbon atoms, and 4 hydrogen atoms
    4. potassium chlorate, which has 1 chlorine atom, 1 potassium atom, and 3 oxygen atoms
    5. sodium hypochlorite pentahydrate, which has 1 chlorine atom, 1 sodium atom, 6 oxygen atoms, and 10 hydrogen atoms
2. Write the formula for each compound.
    1. cadmium acetate, which has 1 cadmium atom, 4 oxygen atoms, 4 carbon atoms, and 6 hydrogen atoms
    2. barium cyanide, which has 1 barium atom, 2 carbon atoms, and 2 nitrogen atoms
    3. iron(III) phosphate dihydrate, which has 1 iron atom, 1 phosphorus atom, 6 oxygen atoms, and 4 hydrogen atoms
    4. manganese(II) nitrate hexahydrate, which has 1 manganese atom, 12 hydrogen atoms, 12 oxygen atoms, and 2 nitrogen atoms
    5. silver phosphate, which has 1 phosphorus atom, 3 silver atoms, and 4 oxygen atoms
3. Complete the following table by filling in the formula for the ionic compound formed by each cation-anion pair.

Ion	K^+	Fe^{3+}	NH_4^+	Ba^{2+}
Cl^-	KCl			
SO_4^{2-}				
PO_4^{3-}				
NO_3^-				
OH^-				

4. Write the empirical formula for the binary compound formed by the most common monatomic ions formed by each pair of elements.
    1. zinc and sulfur
    2. barium and iodine
    3. magnesium and chlorine
    4. silicon and oxygen
    5. sodium and sulfur
5. Write the empirical formula for the binary compound formed by the most common monatomic ions formed by each pair of elements.
    1. lithium and nitrogen
    2. cesium and chlorine
    3. germanium and oxygen
    4. rubidium and sulfur
    5. arsenic and sodium
6. Write the empirical formula for each compound.
    1. $Na_2S_2O_4$
    2. B_2H_6
    3. $C_6H_{12}O_6$
    4. P_4O_{10}
    5. $KMnO_4$

7. Write the empirical formula for each compound.
    1. Al_2Cl_6
    2. $K_2Cr_2O_7$
    3. C_2H_4
    4. $(NH_2)_2CNH$
    5. CH_3COOH
8. Draw the Lewis structures for
    a. OH^-
    b. CN^-
    c. NO_3^-
    d. SO_4^{2-}

b.

Answers

1. 1. $MgSO_4$
    2. $C_2H_6O_2$
    3. $C_2H_4O_2$
    4. $KClO_3$
    5. $NaOCl{\cdot}5H_2O$
2.
3.

Ion	**K^+**	**Fe^{3+}**	**NH_4^+**	**Ba^{2+}**
Cl^-	**KCl**	$FeCl_3$	NH_4Cl	$BaCl_2$
SO_4^{2-}	K_2SO_4	$Fe_2(SO_4)_3$	$(NH_4)_2SO_4$	$BaSO_4$
PO_4^{3-}	K_3PO_4	$FePO_4$	$(NH_4)_3PO_4$	$Ba_3(PO_4)_2$
NO_3^-	KNO_3	$Fe(NO_3)_3$	NH_4NO_3	$Ba(NO_3)_2$
OH^-	KOH	$Fe(OH)_3$	NH_4OH	$Ba(OH)_2$

4.
5. 1. Li_3N
    2. CsCl
    3. GeO_2
    4. Rb_2S
    5. Na_3As
6.
7. 1. $AlCl_3$
    2. $K_2Cr_2O_7$
    3. CH_2
    4. CH_5N_3
    5. CH_2O

Contributors

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Copper sulfate heating video from Dr. Mark Foreman @ YouTube

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Chapter 10.3: Naming Ionic Compounds

Learning Objective

- To name ionic compounds.

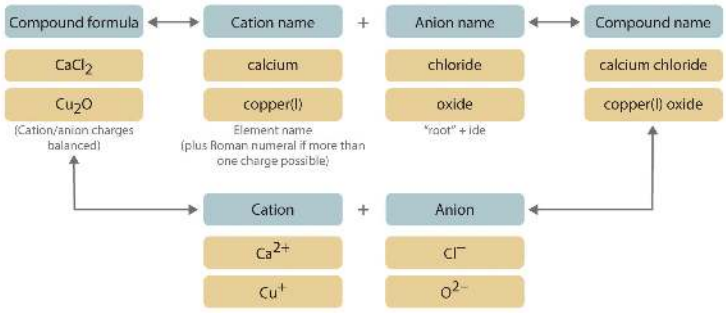
The empirical and molecular formulas discussed in the preceding section are precise and highly informative, but they have some disadvantages. First, they are inconvenient for routine verbal communication. For example, saying “C-A-three-P-O-four-two” for $Ca_3(PO_4)_2$ is much more difficult than saying “calcium phosphate.” In addition, many compounds, especially organic compounds, have the same empirical and molecular formulas but different arrangements of atoms, which result in very different chemical and physical properties. In such cases, it is necessary for the compounds to have different names that distinguish among the possible arrangements.

Many compounds, particularly those that have been known for a relatively long time, have more than one name: a *common* name (sometimes more than one) and a *systematic* name, which is the name assigned by adhering to specific rules. Like the names of most elements, the common names of chemical compounds generally have historical origins, although they often appear to be unrelated to the compounds of interest. For example, the systematic name for KNO_3 is potassium nitrate, but its common name is saltpeter.

In this text, we use a systematic nomenclature to assign meaningful names to the millions of known substances. Unfortunately, some chemicals that are widely used in commerce and industry are still known almost exclusively by their common names; in such cases, you must be familiar with the common name as well as the systematic one. The objective of this and the next two sections is to teach you to write the formula for a simple inorganic compound from its name—and vice versa—and introduce you to some of the more frequently encountered common names.

We begin with *binary ionic compounds*, which contain only two elements. The procedure for naming such compounds is outlined in Figure 10.3.1 and uses the following steps:

Figure 10.3.1 Naming an Ionic Compound



1. Place the ions in their proper order: cation and then anion.
2. Name the cation.
    1. **Metals that form only one cation.** As noted in Section 3.3 , these metals are usually in groups 1–3, 12, and 13. The name of the cation of a metal that forms only one cation is the same as the name of the metal (with the word *ion* added if the cation is by itself). For example, Na^+ is the sodium ion, Ca^{2+} is the calcium ion, and Al^{3+} is the aluminum ion.
    2. **Metals that form more than one cation.** As shown in Figure 10.3.2, many metals can form more than one cation. This behavior is observed for most transition metals, many actinides, and the heaviest elements of groups 13–15. We have discussed the reasons for this. In particular, transition metals tend to lose electrons in the ns orbitals before they lose electrons in the (n-1)d orbitals. In such cases, the positive charge on the metal is indicated by a roman numeral in parentheses immediately following the name of the metal. Thus Cu^+ is copper(I) (read as “copper one”), Fe^{2+} is iron(II), Fe^{3+} is iron(III), Sn^{2+} is tin(II), and Sn^{4+} is tin(IV).

        An older system of nomenclature for such cations is still widely used, however. The name of the cation with the *higher* charge is formed from the root of the element’s Latin name with the suffix *-ic* attached, and the name of the cation with the

lower charge has the same root with the suffix *-ous*. The names of Fe^{3+}, Fe^{2+}, Sn^{4+}, and Sn^{2+} are therefore ferric, ferrous, stannic, and stannous, respectively. Even though this text uses the systematic names with roman numerals, you should be able to recognize these common names because they are still often used. For example, on the label of your dentist's fluoride rinse, the compound chemists call tin(II) fluoride is usually listed as stannous fluoride.

Some examples of metals that form more than one cation are in Table 10.3.1 along with the names of the ions. Note that the simple Hg^{+} cation does not occur in chemical compounds. Instead, all compounds of mercury(I) contain a *dimeric* cation, Hg_2^{2+}, in which the two Hg atoms are bonded together.

Table 10.3.1 Common Cations of Metals That Form More Than One Ion

Cation	Systematic Name	Common Name	Cation	Systematic Name	Common Name
Cr^{2+}	chromium(II)	chromous	Cu^{2+}	copper(II)	cupric
Cr^{3+}	chromium(III)	chromic	Cu^{+}	copper(I)	cuprous
Mn^{2+}	manganese(II)	manganous*	Hg^{2+}	mercury(II)	mercuric
Mn^{3+}	manganese(III)	manganic*	Hg_2^{2+}	mercury(I)	mercurous†
Fe^{2+}	iron(II)	ferrous	Sn^{4+}	tin(IV)	stannic
Fe^{3+}	iron(III)	ferric	Sn^{2+}	tin(II)	stannous
Co^{2+}	cobalt(II)	cobaltous*	Pb^{4+}	lead(IV)	plumbic*
Co^{3+}	cobalt(III)	cobaltic*	Pb^{2+}	lead(II)	plumbous*

* Not widely used.

†The isolated mercury(I) ion exists only as the gaseous ion.

3. **Polyatomic cations.** The names of the common polyatomic cations that are relatively important in ionic compounds (such as, the ammonium ion) are in Table 10.2.1

3. Name the anion.

1. **Monatomic anions.** Monatomic anions are named by adding the suffix *-ide* to the root of the name of the parent element; thus, Cl^{-} is chloride, O^{2-} is oxide, P^{3-} is phosphide, N^{3-} is nitride (also called azide), and C^{4-} is carbide. Because the charges on these ions can be predicted from their position in the periodic table, it is *not* necessary to specify the charge in the name. Examples of monatomic anions are in Table 10.1.2.

2. **Polyatomic anions.** Polyatomic anions typically have common names that you must learn; some examples are in Table 10.2.1 . Polyatomic anions that contain a single metal or nonmetal atom plus one or more oxygen atoms are called *oxoanions (or oxyanions)*. In cases where only two oxoanions are known for an element, the name of the oxoanion with more oxygen atoms ends in *-ate*, and the name of the oxoanion with fewer oxygen atoms ends in *-ite*. For example, NO_{3-} is nitrate and NO_{2-} is nitrite.

   The halogens and some of the transition metals form more extensive series of oxoanions with as many as four members. In the names of these oxoanions, the prefix *per-* is used to identify the oxoanion with the most oxygen (so that ClO_4^{-} is perchlorate and ClO_3^{-} is chlorate), and the prefix *hypo-* is used to identify the anion with the fewest oxygen (ClO_2^{-} is chlorite and ClO^{-} is hypochlorite). The relationship between the names of oxoanions and the number of oxygen atoms present is diagrammed in Figure 10.3.3. Differentiating the oxoanions in such a series is no trivial matter. For example, the hypochlorite ion is the active ingredient in laundry bleach and swimming pool disinfectant, but compounds that contain the perchlorate ion can explode if they come into contact with organic substances.

4. Write the name of the compound as the name of the cation followed by the name of the anion.

It is *not* necessary to indicate the number of cations or anions present per formula unit in the name of an ionic compound because this information is implied by the charges on the ions. You must consider the charge of the ions when writing the formula for an ionic compound from its name, however. Because the charge on the chloride ion is −1 and the charge on the calcium ion is +2, for example, consistent with their positions in the periodic table, simple arithmetic tells you that calcium chloride must contain twice as many chloride ions as calcium ions to maintain electrical neutrality. Thus the formula is $CaCl_2$. Similarly, calcium phosphate must be $Ca_3(PO_4)_2$ because the cation and the anion have charges of +2 and −3, respectively. The best way to learn how to name ionic compounds is to work through a few examples, referring to Figure 10.3.1, Table 10.1.2, Table 10.2.1, and Table 10.3.1 as needed.

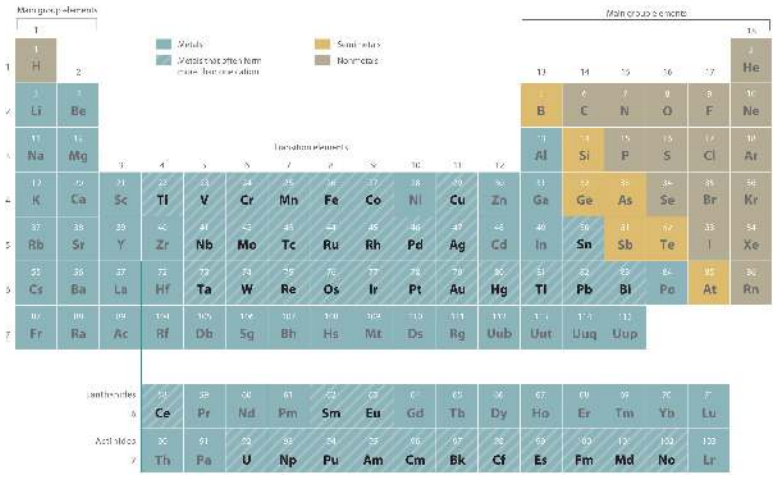


Figure 10.3.2 Metals That Form More Than One Cation and Their Locations in the Periodic Table *With only a few exceptions, these metals are usually transition metals or actinides.*

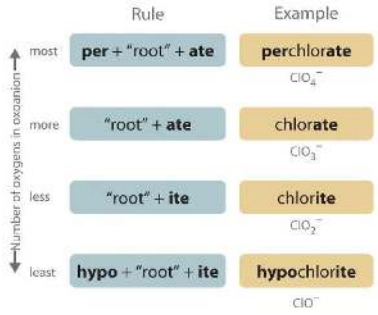


Figure 10.3.3 The Relationship between the Names of Oxoanions and the Number of Oxygen Atoms Present

Note the Pattern

Cations are always named before anions.

Most transition metals, many actinides, and the heaviest elements of groups 13–15 can form more than one cation.

Example 10.3.1

Write the systematic name (and the common name if applicable) for each ionic compound.

1. LiCl
2. $MgSO_4$
3. $(NH_4)_3PO_4$
4. Cu_2O

Given: empirical formula

Asked for: name

Strategy:

A If only one charge is possible for the cation, give its name, consulting Table 10.1.2 or Table 10.2.1 if necessary. If the cation can have more than one charge (Table 10.3.1), specify the charge using roman numerals.

B If the anion does not contain oxygen, name it according to step 3a, using Table 10.1.2 and Table 10.3.1 if necessary. For polyatomic anions that contain oxygen, use Table 10.2.1 and the appropriate prefix and suffix listed in step 3b.

C Beginning with the cation, write the name of the compound.

Solution:

1. **A B** Lithium is in group 1, so we know that it forms only the Li^+ cation, which is the lithium ion. Similarly, chlorine is in group 7, so it forms the Cl^- anion, which is the chloride ion. **C** Because we begin with the name of the cation, the name of this compound is lithium chloride, which is used medically as an antidepressant drug.
2. **A B** The cation is the magnesium ion, and the anion, which contains oxygen, is sulfate. **C** Because we list the cation first, the name of this compound is magnesium sulfate. A hydrated form of magnesium sulfate ($MgSO_4·7H_2O$) is sold in drugstores as Epsom salts, a harsh but effective laxative.
3. **A B** The cation is the ammonium ion (from Table 10.2.1), and the anion is phosphate. **C** The compound is therefore ammonium phosphate, which is widely used as a fertilizer. It is not necessary to specify that the formula unit contains three ammonium ions because three are required to balance the negative charge on phosphate.
4. **A B** The cation is a transition metal that often forms more than one cation (Table 10.3.1). We must therefore specify the positive charge on the cation in the name: copper(I) or, according to the older system, cuprous. The anion is oxide. **C** The name of this compound is copper(I) oxide or, in the older system, cuprous oxide. Copper(I) oxide is used as a red glaze on ceramics and in antifouling paints to prevent organisms from growing on the bottoms of boats.



Cu_2O. The bottom of a boat is protected with a red antifouling paint containing copper(I) oxide, Cu_2O.

Exercise

Write the systematic name (and the common name if applicable) for each ionic compound.

1. $CuCl_2$
2. $MgCO_3$
3. $FePO_4$

Answer:

1. copper(II) chloride (or cupric chloride)
2. magnesium carbonate
3. iron(III) phosphate (or ferric phosphate)

Example 10.3.2

Write the formula for each compound.

1. calcium dihydrogen phosphate
2. aluminum sulfate
3. chromium(III) oxide

Given: systematic name

Asked for: formula

Strategy:

A Identify the cation and its charge using the location of the element in the periodic table and Table 10.1.2 Table 10.2.1 , and Table 10.3.1. If the cation is derived from a metal that can form cations with different charges, use the appropriate roman numeral or suffix to indicate its charge.

B Identify the anion using Table 10.1.2 and Table 10.2.1 Beginning with the cation, write the compound's formula and then determine the number of cations and anions needed to achieve electrical neutrality.

Solution:

1. **A** Calcium is in group 2, so it forms only the Ca^{2+} ion. **B** Dihydrogen phosphate is the $H_2PO_4^-$ ion (Table 10.2.1). Two $H_2PO_4^-$ ions are needed to balance the positive charge on Ca^{2+}, to give $Ca(H_2PO_4)_2$. A hydrate of calcium dihydrogen phosphate, $Ca(H_2PO_4)_2{\cdot}H_2O$, is the active ingredient in baking powder.
2. **A** Aluminum, near the top of group 13 in the periodic table, forms only one cation, Al^{3+} (Figure 10.3.2). **B** Sulfate is SO_4^{2-} (Table 10.2.1). To balance the electrical charges, we need two Al^{3+} cations and three SO_4^{2-} anions, giving $Al_2(SO_4)_3$. Aluminum sulfate is used to tan leather and purify drinking water.
3. **A** Because chromium is a transition metal, it can form cations with different charges. The roman numeral tells us that the positive charge in this case is +3, so the cation is Cr^{3+}. **B** Oxide is O^{2-}. Thus two cations (Cr^{3+}) and three anions (O^{2-}) are required to give an electrically neutral compound, Cr_2O_3. This compound is a common green pigment that has many uses, including camouflage coatings.



Chromium(III) oxide (Cr_2O_3) is a common pigment in dark green paints, such as camouflage paint. Figure used with permission from Wikipedia

Exercise

Write the formula for each compound.

1. barium chloride
2. sodium carbonate
3. iron(III) hydroxide

Answer:

1. $BaCl_2$
2. Na_2CO_3
3. $Fe(OH)_3$

Summary

Ionic compounds are named according to systematic procedures, although common names are widely used. Systematic nomenclature enables us to write the structure of any compound from its name and vice versa. Ionic compounds are named by writing the cation first, followed by the anion. If a metal can form cations with more than one charge, the charge is indicated by roman numerals in parentheses following the name of the metal. **Oxoanions** are polyatomic anions that contain a single metal or nonmetal atom and one or more oxygen atoms.

Key Takeaway

- There is a systematic method used to name ionic compounds.

Conceptual Problems

1. Name each cation.
    1. K^+
    2. Al^{3+}
    3. NH_4^+
    4. Mg^{2+}
    5. Li^+
2. Name each anion.
    1. Br^-
    2. CO_3^{2-}
    3. S^{2-}
    4. NO_3^-
    5. HCO_2^-
    6. F^-
    7. ClO^-
    8. $C_2O_4^{2-}$
3. Name each anion.
    1. PO_4^{3-}
    2. Cl^-
    3. SO_3^{2-}
    4. $CH_3CO_2^-$
    5. HSO_4^-
    6. ClO_4^-
    7. NO_2^-
    8. O^{2-}
4. Name each anion.
    1. SO_4^{2-}
    2. CN^-
    3. $Cr_2O_7^{2-}$
    4. N^{3-}
    5. OH^-
    6. I^-
    7. O_2^{2-}
5. Name each compound.
    1. $MgBr_2$
    2. NH_4CN

3. CaO
4. $KClO_3$
5. K_3PO_4
6. NH_4NO_2
7. NaN_3

6. Name each compound.

1. $NaNO_3$
2. $Cu_3(PO_4)_2$
3. NaOH
4. Li_4C
5. CaF_2
6. NH_4Br
7. $MgCO_3$

7. Name each compound.

1. RbBr
2. $Mn_2(SO_4)_3$
3. NaClO
4. $(NH_4)_2SO_4$
5. NaBr
6. KIO_3
7. Na_2CrO_4

8. Name each compound.

1. NH_4ClO_4
2. $SnCl_4$
3. $Fe(OH)_2$
4. Na_2O
5. $MgCl_2$
6. K_2SO_4
7. $RaCl_2$

9. Name each compound.

1. KCN
2. LiOH
3. $CaCl_2$
4. $NiSO_4$
5. NH_4IO_2
6. ZrO_4
7. $La(CN)_3$

7. sodium bromide
6. manganese(III) sulfate
5. sodium hypochlorite
4. ammonium sulfate
3. sodium bromide
2. potassium iodate
1. sodium chromate

Answer

1.
8.
9.

Numerical Problems

1. For each ionic compound, name the cation and the anion and give the charge on each ion.

1. BeO

2. $Pb(OH)_2$
3. BaS
4. $Na_2Cr_2O_7$
5. $ZnSO_4$
6. KClO
7. NaH_2PO_4

2. For each ionic compound, name the cation and the anion and give the charge on each ion.

1. $Zn(NO_3)_2$
2. CoS
3. $BeCO_3$
4. Na_2SO_4
5. $K_2C_2O_4$
6. NaCN
7. $FeCl_2$

3. Write the formula for each compound.

1. magnesium carbonate
2. aluminum sulfate
3. potassium phosphate
4. lead(IV) oxide
5. silicon nitride
6. sodium hypochlorite
7. titanium(IV) chloride
8. disodium ammonium phosphate

4. Write the formula for each compound.

1. lead(II) nitrate
2. ammonium phosphate
3. silver sulfide
4. barium sulfate
5. cesium iodide
6. sodium bicarbonate
7. potassium dichromate
8. sodium hypochlorite

5. Write the formula for each compound.

1. zinc cyanide
2. silver chromate
3. lead(II) iodide
4. benzene
5. copper(II) perchlorate

6. Write the formula for each compound.

1. calcium fluoride
2. sodium nitrate
3. iron(III) oxide
4. copper(II) acetate
5. sodium nitrite

7. Write the formula for each compound.

1. sodium hydroxide
2. calcium cyanide
3. magnesium phosphate
4. sodium sulfate
5. nickel(II) bromide
6. calcium chlorite
7. titanium(IV) bromide

8. Write the formula for each compound.
    1. sodium chlorite
    2. potassium nitrite
    3. sodium nitride (also called sodium azide)
    4. calcium phosphide
    5. tin(II) chloride
    6. calcium hydrogen phosphate
    7. iron(II) chloride dihydrate

9. Write the formula for each compound.
    1. potassium carbonate
    2. chromium(III) sulfite
    3. cobalt(II) phosphate
    4. magnesium hypochlorite
    5. nickel(II) nitrate hexahydrate

Contributors

- Anonymous

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Chapter 10.4: Naming Covalent Compounds

Learning Objective

- To name covalent compounds that contain up to three elements.
- To name simple organic compounds

As with ionic compounds, the system that chemists have devised for naming covalent compounds enables us to write the molecular formula from the name and vice versa. In this and the following section, we describe the rules for naming simple covalent compounds. We begin with inorganic compounds and then turn to simple organic compounds that contain only carbon and hydrogen.

Binary Inorganic Compounds

Binary covalent compounds—that is, covalent compounds that contain only two elements—are named using a procedure similar to that used to name simple ionic compounds, but prefixes are added as needed to indicate the number of atoms of each kind. The procedure, diagrammed in Figure 10.4.1, uses the following steps:

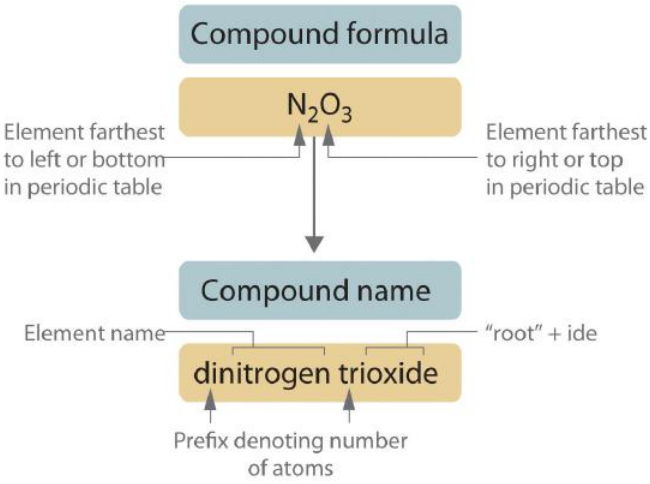


Figure 10.4.1 Naming a Covalent Inorganic Compound

1. Place the elements in their proper order.
    1. The element farthest to the left in the periodic table is usually named first. If both elements are in the same group, the element closer to the bottom of the column is named first.
    2. The second element is named as if it were a monatomic anion in an ionic compound (even though it is not), with the suffix -*ide* attached to the root of the element name.

The reason for this is that we know that the less electronegative elements are to the left and bottom of the periodic table. The more electronegative elements attract electrons from the less electronegative ones and behave more like anions than the less electronegative ones that behave like cations. However, unlike binary inorganic compounds electron transfer is not complete and the binary organic compounds do not form crystal lattices,

2. Identify the number of each type of atom present.

1. 1. Prefixes derived from Greek stems are used to indicate the number of each type of atom in the formula unit (Table 10.4.1). The prefix *mono-* ("one") is used only when absolutely necessary to avoid confusion, just as we omit the subscript 1 when writing molecular formulas.

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

Prefix	Number
mono-	1
di-	2
tri-	3
tetra-	4
penta-	5
hexa-	6
hepta-	7
octa-	8
nona-	9
deca-	10
undeca-	11
dodeca-	12

Table 10.4.1 Prefixes for Indicating the Number of Atoms in Chemical Names

2. If a molecule contains more than one atom of both elements, then prefixes are used for both. Thus N_2O_3 is *di*nitrogen *tri*oxide, as shown in Figure 10.4.1.
3. In some names, the final *a* or *o* of the prefix is dropped to avoid awkward pronunciation. Thus OsO_4 is osmium tetroxide rather than osmium tetraoxide.

2. Write the name of the compound.

    1. Binary compounds of the elements with oxygen are generally named as “element oxide,” with prefixes that indicate the number of atoms of each element per formula unit. For example, CO is carbon monoxide. The only exception is binary compounds of oxygen with fluorine, which are named as oxygen fluorides following the rules for the most electronegative element being treated as the anion for naming purposes.
    2. Certain compounds are *always* called by the common names that were assigned long ago when names rather than formulas were used. For example, H_2O is water (not dihydrogen oxide); NH_3 is ammonia; PH_3 is phosphine; SiH_4 is silane; and B_2H_6, a *dimer* of BH_3, is diborane. For many compounds, the systematic name and the common name are both used frequently, so you must be familiar with them. For example, the systematic name for NO is nitrogen monoxide, but it is much more commonly called nitric oxide. Similarly, N_2O is usually called nitrous oxide rather than dinitrogen monoxide. Notice that the suffixes *-ic* and *-ous* are the same ones used for ionic compounds.

Note the Pattern

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

Example 10.4.1

Write the name of each binary covalent compound.

1. SF_6
2. N_2O_4
3. ClO_2

Given: molecular formula

Asked for: name of compound

Strategy:

A List the elements in order according to their positions in the periodic table. Identify the number of each type of atom in the chemical formula and then use Table 10.4.1 to determine the prefixes needed.

B If the compound contains oxygen, follow step 3a. If not, decide whether to use the common name or the systematic name.

Solution:

1. **A** Because sulfur is to the left of fluorine in the periodic table, sulfur is named first. Because there is only one sulfur atom in the formula, no prefix is needed. **B** There are, however, six fluorine atoms, so we use the prefix for six: *hexa-* (Table 10.4.1). The compound is sulfur hexafluoride.
2. **A** Because nitrogen is to the left of oxygen in the periodic table, nitrogen is named first. Because more than one atom of each element is present, prefixes are needed to indicate the number of atoms of each. According to Table 10.4.1, the prefix for two is *di-*, and the prefix for four is *tetra-*. **B** The compound is dinitrogen tetroxide (omitting the *a* in *tetra-* according to step 2c) and is used as a component of some rocket fuels.
3. **A** Although oxygen lies to the left of chlorine in the periodic table, it is not named first because ClO_2 is an oxide of an element other than fluorine (step 3a). Consequently, chlorine is named first, but a prefix is not necessary because each molecule has only one atom of chlorine. **B** Because there are two oxygen atoms, the compound is a dioxide. Thus the compound is chlorine dioxide. It is widely used as a substitute for chlorine in municipal water treatment plants because, unlike chlorine, it does not react with organic compounds in water to produce potentially toxic chlorinated compounds.

Exercise

Write the name of each binary covalent compound.

1. IF_7
2. N_2O_5
3. OF_2

Answer:

1. iodine heptafluoride
2. dinitrogen pentoxide
3. oxygen difluoride

Example 10.4.2

Write the formula for each binary covalent compound.

1. sulfur trioxide
2. diiodine pentoxide

Given: name of compound

Asked for: formula

Strategy:

List the elements in the same order as in the formula, use Table 10.4.1 to identify the number of each type of atom present, and then indicate this quantity as a subscript to the right of that element when writing the formula.

Solution:

1. Sulfur has no prefix, which means that each molecule has only one sulfur atom. The prefix *tri-* indicates that there are three oxygen atoms. The formula is therefore SO_3. Sulfur trioxide is produced industrially in huge amounts as an intermediate in the synthesis of sulfuric acid.

2. The prefix *di-* tells you that each molecule has two iodine atoms, and the prefix *penta-* indicates that there are five oxygen atoms. The formula is thus I_2O_5, a compound used to remove carbon monoxide from air in respirators.

Exercise

Write the formula for each binary covalent compound.

1. silicon tetrachloride
2. disulfur decafluoride

Answer:

1. $SiCl_4$
2. S_2F_{10}

The structures of some of the compounds in Example 8 and Example 9 are shown in Figure 10.4.2 ", along with the location of the "central atom" of each compound in the periodic table. The compositions and structures of such compounds can be deduced from the rules for covalent bonding, Lewis structures, hybridization, expanded octets and VSEPR discussed in Chapters 4, 5 and 6. and but this is not true.

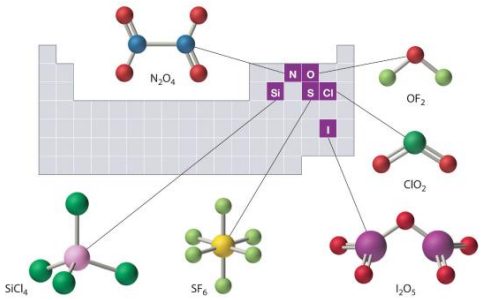


Figure 10.4.2 The Structures of Some Covalent Inorganic Compounds and the Locations of the "Central Atoms" in the Periodic Table

The compositions and structures of covalent inorganic compounds are not random. As you learned in Chapter 4 "The Periodic Table and Periodic Trends" and Chapter 5"Chemical Bonding", they can be predicted from the locations of the component atoms in the periodic table.

Hydrocarbons

Approximately one-third of the compounds produced industrially are organic compounds. All living organisms are composed of organic compounds, as is most of the food you consume, the medicines you take, the fibers in the clothes you wear, and the plastics in the materials you use. Section 10.1 introduced two organic compounds: methane (CH_4) and methanol (CH_3OH). These and other organic compounds appear frequently in discussions and examples throughout this text.

The detection of organic compounds is useful in many fields. In one recently developed application, scientists have devised a new method called "material degradomics" to make it possible to monitor the degradation of old books and historical documents. As paper ages, it produces a familiar "old book smell" from the release of organic compounds in gaseous form. The composition of the gas depends on the original type of paper used, a book's binding, and the applied media. By analyzing these organic gases and isolating the individual components, preservationists are better able to determine the condition of an object and those books and documents most in need of immediate protection.

The simplest class of organic compounds is the hydrocarbonsThe simplest class of organic molecules, consisting of only carbon and hydrogen., which consist entirely of carbon and hydrogen. Petroleum and natural gas are complex, naturally occurring mixtures of many different hydrocarbons that furnish raw materials for the chemical industry. The four major classes of hydrocarbons are the alkanesA saturated hydrocarbon with only carbon–hydrogen and carbon–carbon single bonds., which contain only carbon–hydrogen and carbon–carbon single bonds; the alkenesAn unsaturated hydrocarbon with at least one carbon–carbon double bond., which contain at least one carbon–carbon double bond; the alkynesAn unsaturated hydrocarbon with at least one carbon–carbon triple bond., which contain at least one carbon–carbon triple bond; and the aromatic hydrocarbonsAn unsaturated hydrocarbon

consisting of a ring of six carbon atoms with alternating single and double bonds., which usually contain rings of six carbon atoms that can be drawn with alternating single and double bonds. Alkanes are also called *saturated* hydrocarbons, whereas hydrocarbons that contain multiple bonds (alkenes, alkynes, and aromatics) are *unsaturated*.

Alkanes

The simplest alkane is methane (CH_4), a colorless, odorless gas that is the major component of natural gas. In larger alkanes whose carbon atoms are joined in an unbranched chain (*straight-chain alkanes*), each carbon atom is bonded to at most two other carbon atoms. The structures of two simple alkanes are shown in Figure 10.4.3 , and the names and condensed structural formulas for the first 10 straight-chain alkanes are in Table 10.4.2. The names of all alkanes end in *-ane*, and their boiling points increase as the number of carbon atoms increases.

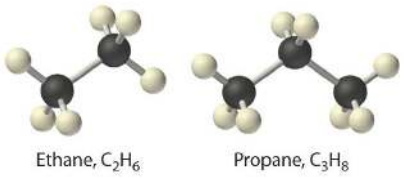
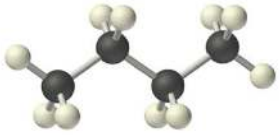


Figure 10.4.3 Straight-Chain Alkanes with Two and Three Carbon Atoms

Table 10.4.2 The First 10 Straight-Chain Alkanes

Name	Number of Carbon Atoms	Molecular Formula	Condensed Structural Formula	Boiling Point (°C)	Uses
methane	1	CH_4	CH_4	−162	natural gas constituent
ethane	2	C_2H_6	CH_3CH_3	−89	natural gas constituent
propane	3	C_3H_8	$CH_3CH_2CH_3$	−42	bottled gas
butane	4	C_4H_{10}	$CH_3CH_2CH_2CH_3$ or $CH_3(CH_2)_2CH_3$	0	lighters, bottled gas
pentane	5	C_5H_{12}	$CH_3(CH_2)_3CH_3$	36	solvent, gasoline
hexane	6	C_6H_{14}	$CH_3(CH_2)_4CH_3$	69	solvent, gasoline
heptane	7	C_7H_{16}	$CH_3(CH_2)_5CH_3$	98	solvent, gasoline
octane	8	C_8H_{18}	$CH_3(CH_2)_6CH_3$	126	gasoline
nonane	9	C_9H_{20}	$CH_3(CH_2)_7CH_3$	151	gasoline
decane	10	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	174	kerosene

Alkanes with four or more carbon atoms can have more than one arrangement of atoms. The carbon atoms can form a single unbranched chain, or the primary chain of carbon atoms can have one or more shorter chains that form branches. For example, butane (C_4H_{10}) has two possible structures. *Normal* butane (usually called *n*-butane) is $CH_3CH_2CH_2CH_3$, in which the carbon atoms form a single unbranched chain. In contrast, the condensed structural formula for *isobutane* is $(CH_3)_2CHCH_3$, in which the primary chain of three carbon atoms has a one-carbon chain branching at the central carbon. Three-dimensional representations of both structures are as follows:

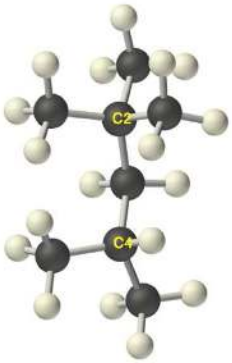


n-Butane, C_4H_{10}



Isobutane (2-methylpropane), C_4H_{10}

The systematic names for branched hydrocarbons use the lowest possible number to indicate the position of the branch along the longest straight carbon chain in the structure. Thus the systematic name for isobutane is 2-methylpropane, which indicates that a methyl group (a branch consisting of $–CH_3$) is attached to the second carbon of a propane molecule. Similarly, one of the major components of gasoline is commonly called isooctane; its structure is as follows:



Isooctane (2,2,4-trimethylpentane)

As you can see, the longest chain in this compound has five carbon atoms, so it is a derivative of pentane. There are two methyl group branches at one carbon atom and one methyl group at another. Using the lowest possible numbers for the branches gives 2,2,4-trimethylpentane for the systematic name of this compound.

Alkenes

The simplest alkenes are *ethylene*, C_2H_4 or $CH_2{=}CH_2$, and *propylene*, C_3H_6 or $CH_3CH{=}CH_2$ (part (a) in Figure 10.4.4). The names of alkenes that have more than three carbon atoms use the same stems as the names of the alkanes (Table 10.4.2) but end in *-ene* instead of *-ane*.

Once again, more than one structure is possible for alkenes with four or more carbon atoms. For example, an alkene with four carbon atoms has three possible structures. One is $CH_2{=}CHCH_2CH_3$ (1-butene), which has the double bond between the first and second carbon atoms in the chain. The other two structures have the double bond between the second and third carbon atoms and are forms of $CH_3CH{=}CHCH_3$ (2-butene). All four carbon atoms in 2-butene lie in the same plane, so there are two possible structures (part (a) in Figure 10.4.4). If the two methyl groups are on the same side of the double bond, the compound is *cis*-2-butene (from the Latin *cis*, meaning “on the same side”). If the two methyl groups are on opposite sides of the double bond, the compound is *trans*-2-butene (from the Latin *trans*, meaning “across”). These are distinctly different molecules: *cis*-2-butene melts at −138.9°C, whereas *trans*-2-butene melts at −105.5°C.

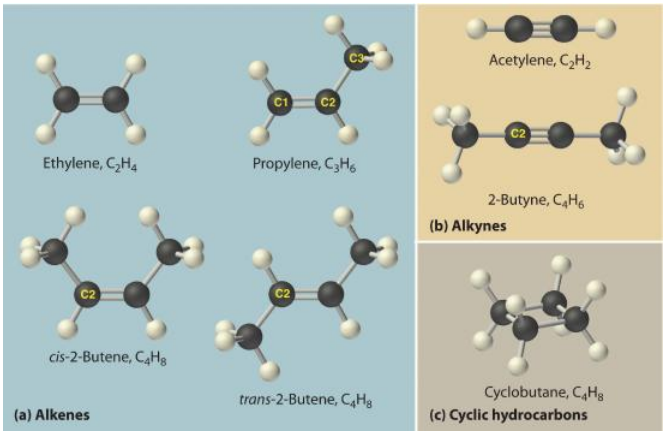
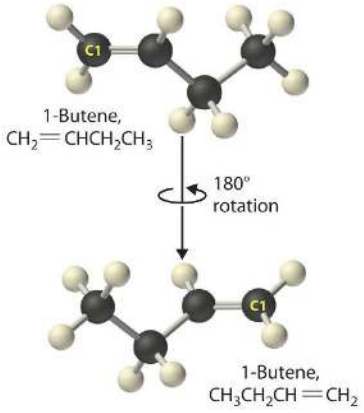


Figure 10.4.4 Some Simple (a) Alkenes, (b) Alkynes, and (c) Cyclic Hydrocarbons *The positions of the carbon atoms in the chain are indicated by C1 or C2.*

Just as a number indicates the positions of branches in an alkane, the number in the name of an alkene specifies the position of the *first* carbon atom of the double bond. The name is based on the lowest possible number starting from *either end* of the carbon chain, so $CH_3CH_2CH{=}CH_2$ is called 1-butene, *not* 3-butene. Note that $CH_2{=}CHCH_2CH_3$ and $CH_3CH_2CH{=}CH_2$ are different ways of writing the *same molecule* (1-butene) in two different orientations.



The name of a compound does *not* depend on its orientation. As illustrated for 1-butene, both condensed structural formulas and molecular models show different orientations of the same molecule. Don't let orientation fool you; you must be able to recognize the same structure no matter what its orientation.

Note the Pattern

The positions of groups or multiple bonds are always indicated by the lowest number possible.

Alkynes

The simplest alkyne is *acetylene*, C_2H_2 or HC≡CH (part (b) in Figure 10.4.4). Because a mixture of acetylene and oxygen burns with a flame that is hot enough (>3000°C) to cut metals such as hardened steel, acetylene is widely used in cutting and welding torches. The names of other alkynes are similar to those of the corresponding alkanes but end in *-yne*. For example, $HC{\equiv}CCH_3$ is *propyne*, and $CH_3C{\equiv}CCH_3$ is *2-butyne* because the multiple bond begins on the second carbon atom.

Note the Pattern

The number of bonds between carbon atoms in a hydrocarbon is indicated in the suffix:

- alk*ane*: only carbon–carbon single bonds
- alk*ene*: at least one carbon–carbon double bond
- alk*yne*: at least one carbon–carbon triple bond

Cyclic Hydrocarbons

In a cyclic hydrocarbonA hydrocarbon in which the ends of the carbon chain are connected to form a ring of covalently bonded carbon atoms., the ends of a hydrocarbon chain are connected to form a ring of covalently bonded carbon atoms. Cyclic hydrocarbons are named by attaching the prefix *cyclo-* to the name of the alkane, the alkene, or the alkyne. The simplest cyclic alkanes are *cyclopropane* (C_3H_6) a flammable gas that is also a powerful anesthetic, and *cyclobutane* (C_4H_8) (part (c) in Figure 10.4.4). The most common way to draw the structures of cyclic alkanes is to sketch a polygon with the same number of vertices as there are carbon atoms in the ring; each vertex represents a CH_2 unit. The structures of the cycloalkanes that contain three to six carbon atoms are shown schematically in Figure 10.4.5.

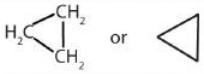
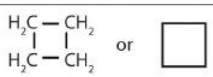
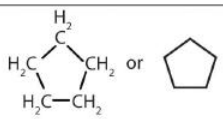
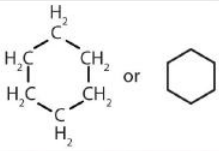
Name	Molecular Formula	Structural Formula
cyclopropane	C_3H_6	
cyclobutane	C_4H_8	
cyclopentane	C_5H_{10}	
cyclohexane	C_6H_{12}	

Figure 10.4.5 The Simple Cycloalkanes

Aromatic Hydrocarbons

Alkanes, alkenes, alkynes, and cyclic hydrocarbons are generally called aliphatic hydrocarbonsAlkanes, alkenes, alkynes, and cyclic hydrocarbons (hydrocarbons that are not aromatic).. The name comes from the Greek *aleiphar*, meaning “oil,” because the first examples were extracted from animal fats. In contrast, the first examples of **aromatic hydrocarbons**, also called *arenes*, were obtained by the distillation and degradation of highly scented (thus *aromatic*) resins from tropical trees.

The simplest aromatic hydrocarbon is *benzene* (C_6H_6), which was first obtained from a coal distillate. The word *aromatic* now refers to benzene and structurally similar compounds. As shown in part (a) in Figure 10.4.6, it is possible to draw the structure of benzene in two different but equivalent ways, depending on which carbon atoms are connected by double bonds or single bonds. We learned that this is a consequence of the p orbitals on each carbon forming a bonding molecular π orbital which extends over the planar carbon chain. *Toluene* is similar to benzene, except that one hydrogen atom is replaced by a $–CH_3$ group; it has the formula C_7H_8 (part (b) in Figure 10.4.6). As you will soon learn, the chemical behavior of aromatic compounds differs from the behavior of aliphatic compounds. Benzene and toluene are found in gasoline, and benzene is the starting material for preparing substances as diverse as aspirin and nylon.

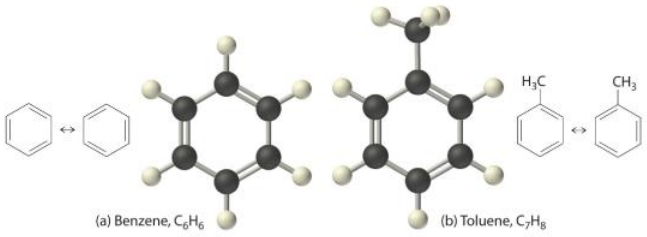


Figure 10.4.6 Two Aromatic Hydrocarbons: (a) Benzene and (b) Toluene

Figure 10.4.7 illustrates two of the molecular structures possible for hydrocarbons that have six carbon atoms. As you can see, compounds with the same molecular formula can have very different structures.

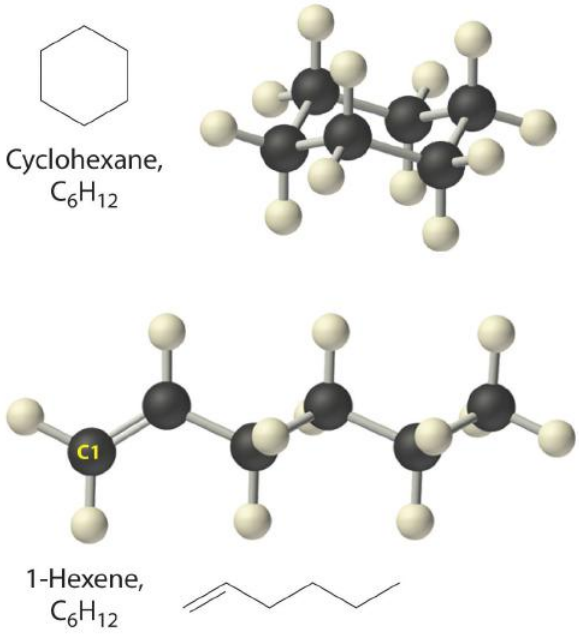


Figure 10.4.7 Two Hydrocarbons with the Molecular Formula C_6H_{12}

Example 10.4.3

Write the condensed structural formula for each hydrocarbon.

1. *n*-heptane
2. 2-pentene
3. 2-butyne
4. cyclooctene

Given: name of hydrocarbon

Asked for: condensed structural formula

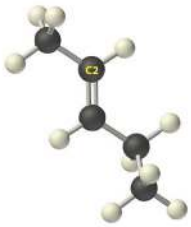
Strategy:

A Use the prefix to determine the number of carbon atoms in the molecule and whether it is cyclic. From the suffix, determine whether multiple bonds are present.

B Identify the position of any multiple bonds from the number(s) in the name and then write the condensed structural formula.

Solution:

1. **A** The prefix *hept-* tells us that this hydrocarbon has seven carbon atoms, and *n-* indicates that the carbon atoms form a straight chain. The suffix *-ane* tells that it is an alkane, with no carbon–carbon double or triple bonds. **B** The condensed structural formula is $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$, which can also be written as $CH_3(CH_2)_5CH_3$.
2. **A** The prefix *pent-* tells us that this hydrocarbon has five carbon atoms, and the suffix *-ene* indicates that it is an alkene, with a carbon–carbon double bond. **B** The 2- tells us that the double bond begins on the second carbon of the five-carbon atom chain. The condensed structural formula of the compound is therefore $CH_3CH{=}CHCH_2CH_3$.



2-Pentene



2-Butyne

3. **A** The prefix *but-* tells us that the compound has a chain of four carbon atoms, and the suffix *-yne* indicates that it has a carbon–carbon triple bond. **B** The 2- tells us that the triple bond begins on the second carbon of the four-carbon atom chain. So the condensed structural formula for the compound is $CH_3C{\equiv}CCH_3$.
4. **A** The prefix *cyclo-* tells us that this hydrocarbon has a ring structure, and *oct-* indicates that it contains eight carbon atoms, which we can draw as



The suffix *-ene* tells us that the compound contains a carbon–carbon double bond, but where in the ring do we place the double bond? **B** Because all eight carbon atoms are identical, it doesn't matter. We can draw the structure of cyclooctene as



Exercise

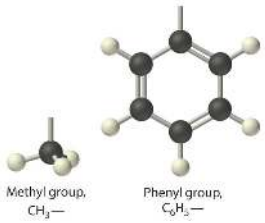
Write the condensed structural formula for each hydrocarbon.

1. *n*-octane
2. 2-hexene
3. 1-heptyne
4. cyclopentane

Answer:

1. $CH_3(CH_2)_6CH_3$
2. $CH_3CH{=}CHCH_2CH_2CH_3$
3. $HC{\equiv}C(CH_2)_4CH_3$
4. 

The general name for a group of atoms derived from an alkane is an *alkyl group*. The name of an alkyl group is derived from the name of the alkane by adding the suffix *-yl*. Thus the $–CH_3$ fragment is a *methyl* group, the $–CH_2CH_3$ fragment is an *ethyl* group, and so forth, where the dash represents a single bond to some other atom or group. Similarly, groups of atoms derived from aromatic hydrocarbons are *aryl groups*, which sometimes have unexpected names. For example, the $–C_6H_5$ fragment is derived from benzene, but it is called a *phenyl* group. In general formulas and structures, alkyl and aryl groups are often abbreviated as RThe abbreviation used for alkyl groups and aryl groups in general formulas and structures..



Structures of alkyl and aryl groups. *The methyl group is an example of an alkyl group, and the phenyl group is an example of an aryl group.*

Alcohols

Replacing one or more hydrogen atoms of a hydrocarbon with an –OH group gives an alcoholA class of organic compounds obtained by replacing one or more of the hydrogen atoms of a hydrocarbon with an −OH group., represented as ROH. The simplest alcohol (CH_3OH) is called either *methanol* (its systematic name) or *methyl alcohol* (its common name) (see Figure 10.1.4). Methanol is the antifreeze in automobile windshield washer fluids, and it is also used as an efficient fuel for racing cars, most notably in the Indianapolis 500. Ethanol (or ethyl alcohol, CH_3CH_2OH) is familiar as the alcohol in fermented or distilled beverages, such as beer, wine, and whiskey; it is also used as a gasoline additive. The simplest alcohol derived from an aromatic hydrocarbon is C_6H_5OH, *phenol* (shortened from *phenyl* alcohol), a potent disinfectant used in some sore throat medications and mouthwashes.



Ethanol, which is easy to obtain from fermentation processes, has successfully been used as an alternative fuel for several decades. Although it is a “green” fuel when derived from plants, it is an imperfect substitute for fossil fuels because it is less efficient than gasoline. Moreover, because ethanol absorbs water from the atmosphere, it can corrode an engine’s seals. Thus other types of processes are being developed that use bacteria to create more complex alcohols, such as octanol, that are more energy efficient and that have a lower tendency to absorb water. As scientists attempt to reduce mankind’s dependence on fossil fuels, the development of these so-called *biofuels* is a particularly active area of research.

Summary

Covalent inorganic compounds are named by a procedure similar to that used for ionic compounds, using prefixes to indicate the numbers of atoms in the molecular formula. The simplest organic compounds are the **hydrocarbons**, which contain *only* carbon and hydrogen. **Alkanes** contain only carbon–hydrogen and carbon–carbon single bonds, **alkenes** contain at least one carbon–carbon double bond, and **alkynes** contain one or more carbon–carbon triple bonds. Hydrocarbons can also be **cyclic**, with the ends of the chain connected to form a ring. Collectively, alkanes, alkenes, and alkynes are called **aliphatic hydrocarbons**. **Aromatic hydrocarbons**, or *arenes*, are another important class of hydrocarbons that contain rings of carbon atoms related to the structure of benzene (C_6H_6). A derivative of an alkane or an arene from which one hydrogen atom has been removed is called an *alkyl group* or an *aryl group*, respectively. **Alcohols** are another common class of organic compound, which contain an –OH group covalently bonded to either an alkyl group or an aryl group (often abbreviated **R**).

Key Takeaway

- Covalent inorganic compounds are named using a procedure similar to that used for ionic compounds, whereas hydrocarbons use a system based on the number of bonds between carbon atoms.

Conceptual Problems

1. Benzene (C_6H_6) is an organic compound, and KCl is an ionic compound. The sum of the masses of the atoms in each empirical formula is approximately the same. How would you expect the two to compare with regard to each of the following? What species are present in benzene vapor?
    1. melting point
    2. type of bonding
    3. rate of evaporation
    4. structure
2. Can an inorganic compound be classified as a hydrocarbon? Why or why not?
3. Is the compound $NaHCO_3$ a hydrocarbon? Why or why not?
4. Name each compound.
    1. NiO
    2. TiO_2
    3. N_2O
    4. CS_2
    5. SO_3
    6. NF_3
    7. SF_6
5. Name each compound.
    1. $HgCl_2$
    2. IF_5
    3. N_2O_5
    4. Cl_2O
    5. HgS
    6. PCl_5
6. For each structural formula, write the condensed formula and the name of the compound.
    1. 
    2. 
    3. 
    4. 
    5. 
7. For each structural formula, write the condensed formula and the name of the compound.

1. 
2. 
3. 
4. 

8. Would you expect PCl_3 to be an ionic compound or a covalent compound? Explain your reasoning.
9. What distinguishes an aromatic hydrocarbon from an aliphatic hydrocarbon?
10. The following general formulas represent specific classes of hydrocarbons. Refer to Table 10.4.2 and Figure 10.4.4 and identify the classes.
    1. C_nH_{2n+2}
    2. C_nH_{2n}
    3. C_nH_{2n-2}
11. Using R to represent an alkyl or aryl group, show the general structure of an
    1. alcohol.
    2. phenol.

Answer

1.
2.
3.
4.
5.
6.
7.
8.
9.
10.
11. 1. ROH (where R is an alkyl group)
    2. ROH (where R is an aryl group)

Numerical Problems

1. Write the formula for each compound.
    1. dinitrogen monoxide
    2. silicon tetrafluoride
    3. boron trichloride
    4. nitrogen trifluoride
    5. phosphorus tribromide
2. Write the formula for each compound.
    1. dinitrogen trioxide
    2. iodine pentafluoride
    3. boron tribromide

4. oxygen difluoride
5. arsenic trichloride

3. Write the formula for each compound.

1. thallium(I) selenide
2. neptunium(IV) oxide
3. iron(II) sulfide
4. copper(I) cyanide
5. nitrogen trichloride

4. Name each compound.

1. RuO_4
2. PbO_2
3. MoF_6
4. $Hg_2(NO_3)_2 \cdot 2H_2O$
5. WCl_4

5. Name each compound.

1. NbO_2
2. MoS_2
3. P_4S_{10}
4. Cu_2O
5. ReF_5

6. Draw the structure of each compound.

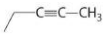
1. propyne
2. ethanol
3. *n*-hexane
4. cyclopropane
5. benzene

7. Draw the structure of each compound.

1. 1-butene
2. 2-pentyne
3. cycloheptane
4. toluene
5. phenol

Answers

1. 1. N_2O
   2. SiF_4
   3. BCl_3
   4. NF_3
   5. PBr_3
2.
3. 1. Tl_2Se
   2. NpO_2
   3. FeS
   4. CuCN
   5. NCl_3
4.

5. 1. niobium (IV) oxide
   2. molybdenum (IV) sulfide
   3. tetraphosphorus decasulfide
   4. copper(I) oxide
   5. rhenium(V) fluoride
6.
7. 1. 
   2. 
   3. 
   4. 
   5. 

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Chapter 10.5: Acids and Bases

Learning Objective

- To identify and name some common acids and bases.

For our purposes at this point in the text, we can define an acidA substance with at least one hydrogen atom that can dissociate to form an anion and an H^+ ion (a proton) in aqueous solution, thereby foming an acidic solution. as a substance with at least one hydrogen atom that can dissociate to form an anion and an H^+ ion (a proton) in aqueous solution, thereby forming an *acidic solution*. We can define basesA substance that produces one or more hydroxide ions OH^- and a cation when dissolved in aqueous solution, thereby forming a basic solution. as compounds that produce hydroxide ions (OH^-) and a cation when dissolved in water, thus forming a *basic solution*. Solutions that are neither basic nor acidic are *neutral*. We will discuss the chemistry of acids and bases in more detail in Section 12.5, but in this section we describe the nomenclature of common acids and identify some important bases so that you can recognize them in future discussions. Pure acids and bases and their concentrated aqueous solutions are commonly encountered in the laboratory. They are usually highly corrosive, so they must be handled with care.

Acids

The names of acids differentiate between (1) acids in which the H^+ ion is attached to an oxygen atom of a polyatomic anion (these are called oxoacidsAn acid in which the dissociable H^+ ion is attached to an oxygen atom of a polyatomic anion., or occasionally **oxyacids**) and (2) acids in which the H^+ ion is attached to some other element. In the latter case, the name of the acid begins with *hydro-* and ends in *-ic*, with the root of the name of the other element or ion in between. Recall that the name of the anion derived from this kind of acid always ends in *-ide*. Thus hydrogen chloride (HCl) gas dissolves in water to form hydrochloric acid (which contains H^+ and Cl^- ions), hydrogen cyanide (HCN) gas forms hydrocyanic acid (which contains H^+ and CN^- ions), and so forth (Table 10.5.1). Examples of this kind of acid are commonly encountered and very important. For instance, your stomach contains a dilute solution of hydrochloric acid to help digest food. When the mechanisms that prevent the stomach from digesting itself malfunction, the acid destroys the lining of the stomach and an ulcer forms.

Note the Pattern

Acids are distinguished by whether the H^+ ion is attached to an oxygen atom of a polyatomic anion or some other element.

Table 10.5.1 Some Common Acids That Do Not Contain Oxygen

Formula	Name in Aqueous Solution	Name of Gaseous Species
HF	hydrofluoric acid	hydrogen fluoride
HCl	hydrochloric acid	hydrogen chloride
HBr	hydrobromic acid	hydrogen bromide
HI	hydroiodic acid	hydrogen iodide
HCN	hydrocyanic acid	hydrogen cyanide
H_2S	hydrosulfuric acid	hydrogen sulfide

If an acid contains one or more H^+ ions attached to oxygen, it is a derivative of one of the common oxoanions, such as sulfate (SO_4^{2-}) or nitrate (NO_3^-). These acids contain as many H^+ ions as are necessary to balance the negative charge on the anion, resulting in a neutral species such as H_2SO_4 and HNO_3.

The names of acids are derived from the names of anions according to the following rules:

1. **If the name of the anion ends in *-ate*, then the name of the acid ends in *-ic*.** For example, because NO_3^- is the nitrate ion, HNO_3 is nitric acid. Similarly, ClO_4^- is the perchlorate ion, so $HClO_4$ is perchloric acid. Two important acids are sulfuric acid (H_2SO_4) from the sulfate ion (SO_4^{2-}) and phosphoric acid (H_3PO_4) from the phosphate ion (PO_4^{3-}). These two names use a slight variant of the root of the anion name: *sulf*ate becomes *sulfur*ic and *phosph*ate becomes *phosphor*ic.

2. **If the name of the anion ends in *-ite*, then the name of the acid ends in *-ous*.** For example, OCl^- is the hypochlorite ion, and HOCl is hypochlorous acid; NO_2^- is the nitrite ion, and HNO_2 is nitrous acid; and SO_3^{2-} is the sulfite ion, and H_2SO_3 is sulfurous acid. The same roots are used whether the acid name ends in *-ic* or *-ous*; thus, *sulfite* becomes *sulfurous*.

The relationship between the names of the oxoacids and the parent oxoanions is illustrated in Figure 10.5.1 , and some common oxoacids are in Table 10.5.1.

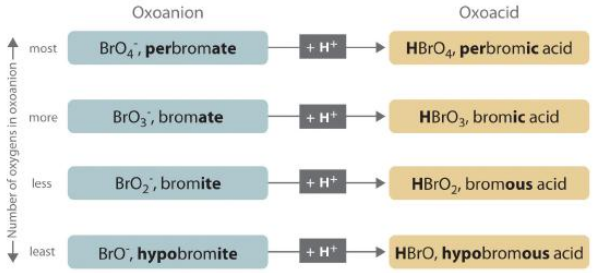


Figure 10.5.1 The Relationship between the Names of the Oxoacids and the Names of the Parent Oxoanions

Table 10.5.2 Some Common Oxoacids

Formula	Name
HNO_2	nitrous acid
HNO_3	nitric acid
H_2SO_3	sulfurous acid
H_2SO_4	sulfuric acid
H_3PO_4	phosphoric acid
H_2CO_3	carbonic acid
HClO	hypochlorous acid
$HClO_2$	chlorous acid
$HClO_3$	chloric acid
$HClO_4$	perchloric acid

Example 10.5.1

Name and give the formula for each acid.

1. the acid formed by adding a proton to the hypobromite ion (OBr^-)
2. the acid formed by adding two protons to the selenate ion (SeO_4^{2-})

Given: anion

Asked for: parent acid

Strategy:

Refer to Table 10.5.1 and Table 10.5.2 to find the name of the acid. If the acid is not listed, use the guidelines given previously.

Solution:

Neither species is listed in Table 10.5.1 or Table 10.5.2 so we must use the information given previously to derive the name of the acid from the name of the polyatomic anion.

1. The anion name, *hypobromite*, ends in *-ite*, so the name of the parent acid ends in *-ous*. The acid is therefore hypobromous acid (HOBr).
2. *Selenate* ends in *-ate*, so the name of the parent acid ends in *-ic*. The acid is therefore selenic acid (H_2SeO_4).

Exercise

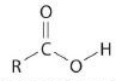
Name and give the formula for each acid.

1. the acid formed by adding a proton to the perbromate ion (BrO_4^-)
2. the acid formed by adding three protons to the arsenite ion (AsO_3^{3-})

Answer:

1. perbromic acid; $HBrO_4$
2. arsenous acid; H_3AsO_3

Many organic compounds contain the carbonyl groupA carbon atom double-bonded to an oxygen atom. It is a characteristic feature of many organic compounds, including carboxylic acids., in which there is a carbon–oxygen double bond. In carboxylic acidsAn organic compound that contains an −OH group covalently bonded to the carbon atom of a carbonyl group. The general formula of a carboxylic acid is RCO_2H. In water a carboxylic acid dissociates to produce an acidic solution., an –OH group is covalently bonded to the carbon atom of the carbonyl group. Their general formula is RCO_2H, sometimes written as RCOOH:



Carboxylic acid

where R can be an alkyl group, an aryl group, or a hydrogen atom. The simplest example, HCO_2H, is *formic acid*, so called because it is found in the secretions of stinging ants (from the Latin *formica*, meaning “ant”). Another example is *acetic acid* (CH_3CO_2H), which is found in vinegar. Like many acids, carboxylic acids tend to have sharp odors. For example, butyric acid ($CH_3CH_2CH_2CO_2H$), is responsible for the smell of rancid butter, and the characteristic odor of sour milk and vomit is due to lactic acid [$CH_3CH(OH)CO_2H$]. Some common carboxylic acids are shown in Figure 10.5.2.


Lactic acid, $CH_3CH(OH)CO_2H$

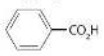
Formula (Structure)	Name	Uses
HCO_2H	formic acid	tanning, dyeing
CH_3CO_2H	acetic acid	vinegar, food preservative
$CH_3CH_2CO_2H$	propionic acid	food preservative
$CH_3CH_2CH_2CO_2H$	butyric acid	varnishes
$C_6H_5CO_2H$ 	benzoic acid	food preservative, dyeing

Figure 10.5.2 Some Common Carboxylic Acids

Although carboxylic acids are covalent compounds, when they dissolve in water, they dissociate to produce H^+ ions (just like any other acid) and RCO_2^- ions. Note that *only the hydrogen attached to the oxygen atom of the CO_2 group dissociates to form an H^+ ion*. In contrast, the hydrogen atom attached to the oxygen atom of an alcohol does *not* dissociate to form an H^+ ion when an alcohol is dissolved in water.

Note the Pattern

Only the hydrogen attached to the oxygen atom of the CO_2 group dissociates to form an H^+ ion.

Bases

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



Methylamine

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

Note the Pattern

Metal hydroxides (MOH) yield OH^- ions and are bases, alcohols (ROH) do not yield OH^- or H^+ ions and are neutral, and carboxylic acids (RCO_2H) yield H^+ ions and are acids.

Summary

Common **acids** and the polyatomic anions derived from them have their own names and rules for nomenclature. The nomenclature of acids differentiates between **oxoacids**, in which the H^+ ion is attached to an oxygen atom of a polyatomic ion, and acids in which the H^+ ion is attached to another element. **Carboxylic acids** are an important class of organic acids. Ammonia is an important **base**, as are its organic derivatives, the **amines**.

Key Takeaway

- Common acids and polyatomic anions derived from them have their own names and rules for nomenclature.

Conceptual Problems

1. Name each acid.
    1. HCl
    2. $HBrO_3$
    3. HNO_3
    4. H_2SO_4
    5. HIO_3
2. Name each acid.
    1. HBr
    2. H_2SO_3
    3. $HClO_3$

4. HCN
5. H_3PO_4

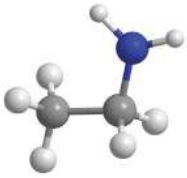
3. Name the aqueous acid that corresponds to each gaseous species.

1. hydrogen bromide
2. hydrogen cyanide
3. hydrogen iodide

4. For each structural formula, write the condensed formula and the name of the compound.

1. 
2. 

5. For each structural formula, write the condensed formula and the name of the compound.

1. 
2. 

6. When each compound is added to water, is the resulting solution acidic, neutral, or basic?

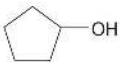
1. CH_3CH_2OH
2. $Mg(OH)_2$
3. $C_6H_5CO_2H$
4. LiOH
5. $C_3H_7CO_2H$
6. H_2SO_4

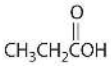
7. Draw the structure of the simplest example of each type of compound.

1. alkane
2. alkene
3. alkyne
4. aromatic hydrocarbon
5. alcohol
6. carboxylic acid
7. amine
8. cycloalkane

8. Identify the class of organic compound represented by each compound.

1. 
2. CH_3CH_2OH
3. HC≡CH

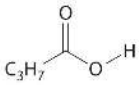
4. 
5. $C_3H_7NH_2$
6. $CH_3CH{=}CHCH_2CH_3$
7. 

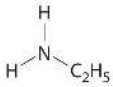
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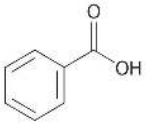
9. Identify the class of organic compound represented by each compound.

1. 

2. 

3. 
4. 
5. 

6. $CH_3C{\equiv}CH$
7. 

8. 

Numerical Problems

1. Write the formula for each compound.
    1. hypochlorous acid
    2. perbromic acid
    3. hydrobromic acid
    4. sulfurous acid
    5. sodium perbromate
2. Write the formula for each compound.
    1. hydroiodic acid
    2. hydrogen sulfide
    3. phosphorous acid
    4. perchloric acid
    5. calcium hypobromite
3. Name each compound.
    1. HBr

2. H_2SO_3
3. HCN
4. $HClO_4$
5. $NaHSO_4$

4. Name each compound.

1. H_2SO_4
2. HNO_2
3. K_2HPO_4
4. H_3PO_3
5. $Ca(H_2PO_4)_2 \cdot H_2O$

Contributors

- Anonymous

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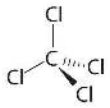
Chapter 10.6: End of Chapter Material

Application Problems

Problems marked with a ♦ involve multiple concepts.

1. Carbon tetrachloride (CCl_4) was used as a dry cleaning solvent until it was found to cause liver cancer. Based on the structure of chloroform given in Section 10.1, draw the structure of carbon tetrachloride.
2. Ammonium nitrate and ammonium sulfate are used in fertilizers as a source of nitrogen. The ammonium cation is tetrahedral. Refer to Section 10.1 to draw the structure of the ammonium ion.
3. The white light in fireworks displays is produced by burning magnesium in air, which contains oxygen. What compound is formed?
4. Sodium hydrogen sulfite, which is used for bleaching and swelling leather and to preserve flavor in almost all commercial wines, is made from sulfur dioxide. What are the formulas for these two sulfur-containing compounds?
5. Carbonic acid is used in carbonated drinks. When combined with lithium hydroxide, it produces lithium carbonate, a compound used to increase the brightness of pottery glazes and as a primary treatment for depression and bipolar disorder. Write the formula for both of these carbon-containing compounds.
6. Vinegar is a dilute solution of acetic acid, an organic acid, in water. What grouping of atoms would you expect to find in the structural formula for acetic acid?
7. ♦ Sodamide, or sodium amide, is prepared from sodium metal and gaseous ammonia. Sodamide contains the amide ion (NH_2^-), which reacts with water to form the hydroxide anion by removing an H^+ ion from water. Sodium amide is also used to prepare sodium cyanide.
    1. Write the formula for each of these sodium-containing compounds.
    2. What are the products of the reaction of sodamide with water?

Answers

1. 

2.
3. MgO, magnesium oxide
4.
5. Carbonic acid is H_2CO_3; lithium carbonate is Li_2CO_3.
6.
7. 1. Sodamide is $NaNH_2$, and sodium cyanide is NaCN.
    2. Sodium hydroxide (NaOH) and ammonia (NH_3).

Contributors

- Anonymous

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CHAPTER OVERVIEW

Chapter 11: Stoichiometry

- Chapter 11.1: Again the Mole
- Chapter 11.2: Empirical and Molecular Formulas
- Chapter 11.3: Chemical Equations
- Chapter 11.4: Stoichiometry
- Chapter 11.5: Stoichiometry Involving Gases
- Chapter 11.6: Types of Chemical Reactions
- Chapter 11.7: End of Chapter Material

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Chapter 11.1: Again the Mole

Learning Objective

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

In the rest of Chapter 11 we will use the mole to calculate the outcomes of reactions, how much of one substance reacts with another, how many molecules a mass of a substance contains, what are chemical reactions and how do we account for the number of molecules of one kind that react with another and how many different products molecules the reaction produces. The name that chemists use for such things is stoichiometry. We have been using the mole concept in previous chapters to do problems and you have been also using it in General Chemistry Laboratory. What follows is a bare bones review.

We start on the atomic scale. The **mass number** is the sum of the numbers of protons and neutrons present in the nucleus of an atom. The mass number is an integer that is approximately equal to the numerical value of the atomic mass with the difference being accounted for by binding energy. Although the mass number is unitless, it is assigned units called **atomic mass units (amu)**. Because a molecule or a polyatomic ion is an assembly of atoms whose identities are given in its molecular or ionic formula, we can calculate the average atomic mass of any molecule or polyatomic ion from its composition by adding together the masses of the constituent atoms. The average mass of a monatomic ion is the same as the average mass of an atom of the element because the mass of electrons is so small that it is insignificant in most calculations. We must differentiate between the mass in amu of a single isotope and the atomic weight of an element given in the periodic table chart. The latter is an average over the naturally occurring isotopes accounting for the mass percentage of each as they occur in nature.

Molecular and Formula Masses - Review

The molecular mass (The sum of the average masses of the atoms in one molecule of a substance, each multiplied by its subscript) of a substance is the sum of the average masses of the atoms in one molecule of a substance. It is calculated by adding together the atomic masses of the elements in the substance, each multiplied by its subscript (written or implied) in the molecular formula. Because the units of atomic mass are atomic mass units, the units of molecular mass are also atomic mass units. The procedure for calculating molecular masses is illustrated in Example 11.11.

Example 11.1.1

Calculate the molecular mass of ethanol, whose condensed structural formula is CH_3CH_2OH. Among its many uses, ethanol is a fuel for internal combustion engines.

Given: molecule

Asked for: molecular mass

Strategy:

A Determine the number of atoms of each element in the molecule.

B Obtain the atomic masses of each element from the periodic table and multiply the atomic mass of each element by the number of atoms of that element.

C Add together the masses to give the molecular mass.

Solution:

A The molecular formula of ethanol may be written in three different ways: CH_3CH_2OH (which illustrates the presence of an ethyl group, CH_3CH_2-, and an $-OH$ group), C_2H_5OH, and C_2H_6O; all show that ethanol has two carbon atoms, six hydrogen atoms, and one oxygen atom.

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

$$2 \times \text{ atomic mass of carbon} = 2 \text{ atoms} \frac{12.011 \text{ amu}}{\text{atom}} = 24.022 \text{ amu}$$

$$6 \times \text{ atomic mass of hydrogen} = 6 \text{ atoms} \frac{1.0079 \text{ amu}}{\text{atom}} = 6.0474 \text{ amu} \quad \text{(Chapter 11.1.1)}$$

$$1 \times \text{ atomic mass of oxygen} = 1 \text{ atoms} \frac{15.994 \text{ amu}}{\text{atom}} = 15.994 \text{ amu}$$

C Adding together the masses gives the molecular mass:

24.022 amu + 6.0474 amu + 15.9994 amu = 46.069 amu

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

$$\left[2 \text{ atoms } C \left(\frac{12.011 \text{ amu}}{1 \text{ atom } C}\right)\right] + \left[6 \text{ atoms } H \left(\frac{1.0079 \text{ amu}}{1 \text{ atom } H}\right)\right] + \left[1 \text{ atoms } O \left(\frac{15.994 \text{ amu}}{1 \text{ atom } C}\right)\right] = 46.069$$

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

2C	(2 atoms)(12.011 amu/atom) = 24.022 amu
6H	(6 atoms)(1.0079 amu/atom) = 6.0474 amu
1O	(1 atoms)(15.9994 amu/atom) = 15.9994 amu
C_2H_6O	molecular mass of ethanol = 46.069 amu

Unlike molecules, which have covalent bonds, ionic compounds do not have a readily identifiable molecular unit. So for ionic compounds we use the *formula mass* (also called the empirical formula massAnother name for formula mass.) of the compound rather than the molecular mass. The formula massThe sum of the atomic masses of all the elements in the empirical formula, each multiplied by its subscript. is the sum of the atomic masses of all the elements in the empirical formula, each multiplied by its subscript (written or implied). It is directly analogous to the molecular mass of a covalent compound. Once again, the units are atomic mass units.

Example 11.1.2

Calculate the formula mass of $Ca_3(PO_4)_2$, commonly called calcium phosphate. This compound is the principal source of calcium found in bovine milk.

Given: ionic compound

Asked for: formula mass

Strategy:

A Determine the number of atoms of each element in the empirical formula.

B Obtain the atomic masses of each element from the periodic table and multiply the atomic mass of each element by the number of atoms of that element.

C Add together the masses to give the formula mass.

Solution:

A The empirical formula—$Ca_3(PO_4)_2$—indicates that the simplest electrically neutral unit of calcium phosphate contains three Ca^{2+} ions and two PO_4^{3-} ions. The formula mass of this molecular unit is calculated by adding together the atomic masses of three calcium atoms, two phosphorus atoms, and eight oxygen atoms.

B Taking atomic masses from the periodic table, we obtain

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

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

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

C Adding together the masses gives the formula mass of $Ca_3(PO_4)_2$:

$$120.234 \text{ amu} + 61.947522 \text{ amu} + 127.9952 \text{ amu} = 310.177 \text{ amu} \qquad \text{(Chapter 11.1.2)}$$

We could also find the formula mass of $Ca_3(PO_4)_2$ in one step by using unit conversions or a tabular format:

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

3Ca	(3 atoms)(40.078 amu/atom) = 24.022 amu
2P	(2 atoms)(30.973761 amu/atom) = 6.0474 amu
8O	(8 atoms)(15.9994 amu/atom) = 127.9952 amu
$Ca_3P_2O_8$	formula mass of $Ca_3(PO_4)$ = 310.177 $_2$amu

The Mole

Chemistry is the study of how atoms and molecules interact with each other which occurs on the atomic scale. Chemists need a way of simply determining how many molecules they have in a beaker. The mole concept bridges that gap by relating the mass of a single atom or molecule in amu to the mass of a collection of a large number of such molecules in grams. Grams rather than kilograms are used, because the mole concept was introduced at a time when the base units of the measuring system were centimeters, grams and seconds, rather than today's SI units of meters, kilograms and seconds. Also, because, well a kilogram of a compound is a rather large amount of stuff.

A **mole** is defined as the amount of a substance that contains the number of carbon atoms in exactly 12 g of isotopically pure carbon-12. According to the most recent experimental measurements, this mass of carbon-12 contains 6.022142×10^{23} atoms, but for most purposes 6.022×10^{23} provides an adequate number of significant figures. The number in a mole is called Avogadro's number The number of units (e.g., atoms, molecules, or formula units) in 1 mol): \(6.022 \times 10^{23}\), after the 19th-century Italian scientist who first proposed a relationship between the volumes of gases and the numbers of particles they contain. Since gas in a volume can be weighted on a sensitive balance, we can determine the mass in grams (g) of a number of molecules. This, indeed, up until the beginning of the 20th century, was the most accurate way of determining the molecular weight of a molecule that could be volatized.

The definition of a mole—that is, the decision to base it on 12 g of carbon-12—is also arbitrary. The important point is that *1 mol of carbon—or of anything else, whether atoms, compact discs, or houses—always has the same number of objects: 6.022×10^{23}.*

Note the Pattern

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

The concept of the mole allows us to count a specific number of individual atoms and molecules by weighing measurable quantities of elements and compounds. To obtain 1 mol of carbon-12 atoms, we would weigh out 12 g of isotopically pure carbon-12. Because each element has a different atomic mass, however, a mole of each element has a different mass, even though it contains the same number of atoms (6.022×10^{23}).

Because of the way in which the mole is defined, for every element the number of grams in a mole is the same as the number of atomic mass units in the atomic mass of the element. For example, the mass of 1 mol of magnesium (atomic mass = 24.305 amu) is 24.305 g. Because the atomic mass of magnesium (24.305 amu) is slightly more than twice that of a carbon-12 atom (12 amu), the mass of 1 mol of magnesium atoms (24.305 g) is slightly more than twice that of 1 mol of carbon-12 (12 g). Similarly, the mass of 1 mol of helium (atomic mass = 4.002602 amu) is 4.002602 g, which is about one-third that of 1 mol of carbon-12.

Using the concept of the mole, we can now restate Dalton's theory: *1 mol of a compound is formed by combining elements in amounts whose mole ratios are small whole numbers.* For example, 1 mol of water (H_2O) has 2 mol of hydrogen atoms and 1 mol of oxygen atoms.

Molar Mass

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

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

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

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

The molar mass of ethanol is the mass of ethanol (C_2H_5OH) that contains 6.022×10^{23} ethanol molecules. As you calculated in Example 11.1.1, the molecular mass of ethanol is 46.069 amu. Because 1 mol of ethanol contains 2 mol of carbon atoms (2×12.011 g), 6 mol of hydrogen atoms (6×1.0079 g), and 1 mol of oxygen atoms (1×15.9994 g), its molar mass is 46.069 g/mol. Similarly, the formula mass of calcium phosphate [$Ca_3(PO_4)_2$] is 310.177 amu, so its molar mass is 310.177 g/mol. This is the mass of calcium phosphate that contains 6.022×10^{23} formula units.

The mole is the basis of quantitative chemistry. It provides chemists with a way to convert easily between the mass of a substance and the number of individual atoms, molecules, or formula units of that substance. Conversely, it enables chemists to calculate the mass of a substance needed to obtain a desired number of atoms, molecules, or formula units. For example, to convert moles of a substance to mass, we use the relationship we discussed in Section 1.4

$$(moles)(molar\ mass) \rightarrow mass \tag{1.41}$$

or, more specifically,

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

Conversely, to convert the mass of a substance to moles, we use

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

$$\left(\frac{mass}{molar\ mass}\right) \rightarrow moles$$

$$\left(\frac{grams}{grams/mole}\right) = grams\left(\frac{mole}{grams}\right) = moles$$

Be sure to pay attention to the units when converting between mass and moles.

Figure 1.4.2 below is a copy from Chapter 1 of the flow chart for converting between mass; the number of moles; and the number of atoms, molecules, or formula units. The use of these conversions is illustrated in Example 11.1.3 and Example 11.1.4.

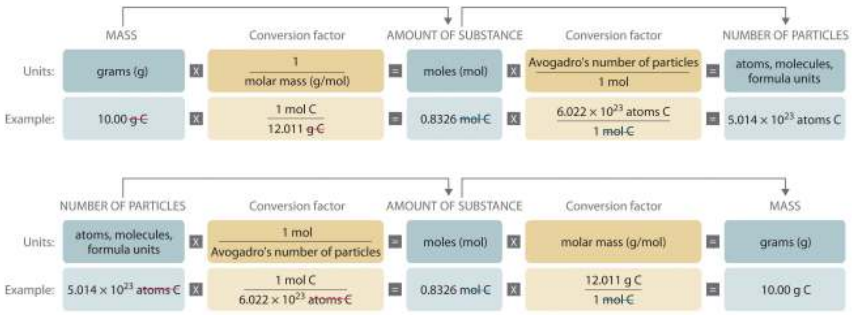


Figure 1.4.2 A Flowchart for Converting between Mass; the Number of Moles; and the Number of Atoms, Molecules, or Formula Units

Example 11.1.3

For 35.00 g of ethylene glycol ($HOCH_2CH_2OH$), which is used in inks for ballpoint pens, calculate the number of

1. moles.
2. molecules.

Given: mass and molecular formula

Asked for: number of moles and number of molecules

Strategy:

A Use the molecular formula of the compound to calculate its molecular mass in grams per mole.

B Convert from mass to moles by dividing the mass given by the compound's molar mass.

C Convert from moles to molecules by multiplying the number of moles by Avogadro's number.

Solution:

A The molecular mass of ethylene glycol can be calculated from its molecular formula using the method illustrated in Example 1:

2C	(2 atoms)(12.011 amu/atom) = 24.022 amu
6H	(6 atoms)(1.0079 amu/atom) = 6.0474 amu
2O	(2 atoms)(15.9994 amu/atom) = 31.9988 amu
C2H6O	molecular mass of ethanol = 62.068 amu

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

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

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

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

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

$$molecules\ of\ ethylene\ glycol = 0.5639\ mol\left(\frac{6.022 \times 10^{23}}{1\ mol}\right)$$

$$= 3.396 \times 10^{23}\ molecules$$

Example 11.1.4

Calculate the mass of 1.75 mol of each compound.

1. S_2Cl_2 (common name: sulfur monochloride; systematic name: disulfur dichloride)
2. $Ca(ClO)_2$ (calcium hypochlorite)

Given: number of moles and molecular or empirical formula

Asked for: mass

Strategy:

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

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

Solution:

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

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

2S	(2 atoms)(32.065 amu/atom) = 64.130 amu
2Cl	(2 atoms)(35.353 amu/atom) = 70.906 amu
S_2Cl_2	molecular mass of S_2Cl_2 = 135.036 amu

The molar mass of S_2Cl_2 is 135.036 g/mol.

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

$$moles\ S_2Cl_2\left[molar\ mass\frac{g}{mol}\right] = mass\ S_2Cl_2$$

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

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

1Ca	(1 atom)(40.078 amu/atom) = 40.078 amu
2Cl	(2 atoms)(35.453 amu/atom) = 70.906 amu
2O	(2 atoms)(15.9994 amu/atom) = 31.9988 amu
$Ca(ClO)_2$	**formula** mass of $Ca(ClO)_2$ = 142.983 amu

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

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

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

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

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

Exercise

Calculate the mass of 0.0122 mol of each compound.

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

Answer:

1. 1.71 g
2. 0.721 g

Summary

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

Key Takeaway

- To analyze chemical transformations, it is essential to use a standardized unit of measure called the mole.

Conceptual Problems

1. Describe the relationship between an atomic mass unit and a gram.
2. Is it correct to say that ethanol has a formula mass of 46? Why or why not?
3. If 2 mol of sodium react completely with 1 mol of chlorine to produce sodium chloride, does this mean that 2 g of sodium reacts completely with 1 g of chlorine to give the same product? Explain your answer.
4. Construct a flowchart to show how you would calculate the number of moles of silicon in a 37.0 g sample of orthoclase ($KAlSi_3O_8$), a mineral used in the manufacture of porcelain.
5. Construct a flowchart to show how you would calculate the number of moles of nitrogen in a 22.4 g sample of nitroglycerin that contains 18.5% nitrogen by mass.

Answer

1.
2.
3.
4.
5. A = %N by mass, expressed as a decimal

$$B = \frac{1}{molar\ mass\ of\ nitrogen\ in\ g}$$

$$g\ nitroglycerine \xrightarrow{\times A} gN \xrightarrow{\times B} molN$$

Numerical Problems

These are the same problems as in Section 1.7

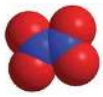
1. Derive an expression that relates the number of molecules in a sample of a substance to its mass and molecular mass.
2. Calculate the molecular mass or formula mass of each compound.
    1. KCl (potassium chloride)
    2. NaCN (sodium cyanide)
    3. H_2S (hydrogen sulfide)
    4. NaN_3 (sodium azide)
    5. H_2CO_3 (carbonic acid)
    6. K_2O (potassium oxide)

7. $Al(NO_3)_3$ (aluminum nitrate)
8. $Cu(ClO_4)_2$ [copper(II) perchlorate]

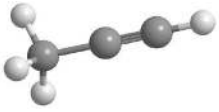
3. Calculate the molecular mass or formula mass of each compound.

1. V_2O_4 (vanadium(IV) oxide)
2. $CaSiO_3$ (calcium silicate)
3. BiOCl (bismuth oxychloride)
4. CH_3COOH (acetic acid)
5. Ag_2SO_4 (silver sulfate)
6. Na_2CO_3 (sodium carbonate)
7. $(CH_3)_2CHOH$ (isopropyl alcohol)

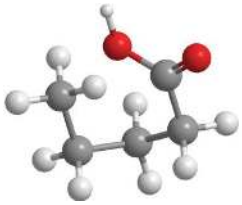
4. Calculate the molar mass of each compound.

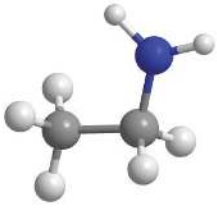
1. 
2. 
3. 
4. 
5. 

5. Calculate the molar mass of each compound.

1. 
2. 
3. 
4. 

6. For each compound, write the condensed formula, name the compound, and give its molar mass.

1. 
2. 

7. For each compound, write the condensed formula, name the compound, and give its molar mass.
   1. 
   2. 
8. Calculate the number of moles in 5.00×10^2 g of each substance. How many molecules or formula units are present in each sample?
   1. CaO (lime)
   2. $CaCO_3$ (chalk)
   3. $C_{12}H_{22}O_{11}$ [sucrose (cane sugar)]
   4. NaOCl (bleach)
   5. CO_2 (dry ice)
9. Calculate the mass in grams of each sample.
   1. 0.520 mol of N_2O_4
   2. 1.63 mol of $C_6H_4Br_2$
   3. 4.62 mol of $(NH_4)_2SO_3$
10. Give the number of molecules or formula units in each sample.
    1. 1.30×10^{-2} mol of SCl_2
    2. 1.03 mol of N_2O_5
    3. 0.265 mol of $Ag_2Cr_2O_7$
11. Give the number of moles in each sample.
    1. 9.58×10^{26} molecules of Cl_2
    2. 3.62×10^{27} formula units of KCl
    3. 6.94×10^{28} formula units of $Fe(OH)_2$
12. Solutions of iodine are used as antiseptics and disinfectants. How many iodine atoms correspond to 11.0 g of molecular iodine (I_2)?
13. What is the total number of atoms in each sample?
    1. 0.431 mol of Li
    2. 2.783 mol of methanol (CH_3OH)
    3. 0.0361 mol of $CoCO_3$

4. 1.002 mol of $SeBr_2O$

14. What is the total number of atoms in each sample?

    1. 0.980 mol of Na
    2. 2.35 mol of O_2
    3. 1.83 mol of Ag_2S
    4. 1.23 mol of propane (C_3H_8)

15. What is the total number of atoms in each sample?

    1. 2.48 g of HBr
    2. 4.77 g of CS_2
    3. 1.89 g of NaOH
    4. 1.46 g of SrC_2O_4

16. Decide whether each statement is true or false and explain your reasoning.

    1. There are more molecules in 0.5 mol of Cl_2 than in 0.5 mol of H_2.
    2. One mole of H_2 has 6.022×10^{23} hydrogen atoms.
    3. The molecular mass of H_2O is 18.0 amu.
    4. The formula mass of benzene is 78 amu.

17. Complete the following table.

Substance	Mass (g)	Number of Moles	Number of Molecules or Formula Units	Number of Atoms or Ions
$MgCl_2$	37.62			
$AgNO_3$		2.84		
BH_4Cl			8.93×10^{25}	
K_2S				7.69×10^{26}
H_2SO_4		1.29		
C_6H_{14}	11.84			
$HClO_3$			2.45×10^{26}	

18. Give the formula mass or the molecular mass of each substance.

    1. PbClF
    2. $Cu_2P_2O_7$
    3. $BiONO_3$
    4. Tl_2SeO_4

19. Give the formula mass or the molecular mass of each substance.

    1. $MoCl_5$
    2. B_2O_3
    3. UO_2CO_3
    4. $NH_4UO_2AsO_4$

Contributors

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Chapter 11.2: Empirical and Molecular Formulas

Learning Objective

- To determine the empirical formula of a compound from its composition by mass.
- To derive the molecular formula of a compound from its empirical formula.

When a new chemical compound, such as a potential new pharmaceutical, is synthesized in the laboratory or isolated from a natural source, chemists determine its elemental composition, its empirical formula, and its structure to understand its properties. In this section, we focus on how to determine the empirical formula of a compound and then use it to determine the molecular formula if the molar mass of the compound is known.

Calculating Mass Percentages

The law of definite proportions states that a chemical compound always contains the same proportion of elements by mass; that is, the percent compositionThe percentage of each element present in a pure substance. With few exceptions, the percent composition of a chemical compound is constant (see law of definite proportions).—the percentage of each element present in a pure substance—is constant (although we now know there are exceptions to this law). For example, sucrose (cane sugar) is 42.11% carbon, 6.48% hydrogen, and 51.41% oxygen by mass. This means that 100.00 g of sucrose always contains 42.11 g of carbon, 6.48 g of hydrogen, and 51.41 g of oxygen. First we will use the molecular formula of sucrose ($C_{12}H_{22}O_{11}$) to calculate the mass percentage of the component elements; then we will show how mass percentages can be used to determine an empirical formula.

According to its molecular formula, each molecule of sucrose contains 12 carbon atoms, 22 hydrogen atoms, and 11 oxygen atoms. A mole of sucrose molecules therefore contains 12 mol of carbon atoms, 22 mol of hydrogen atoms, and 11 mol of oxygen atoms. We can use this information to calculate the mass of each element in 1 mol of sucrose, which will give us the molar mass of sucrose. We can then use these masses to calculate the percent composition of sucrose. To three decimal places, the calculations are the following:

$$mass\ of\ C/mol\ of\ sucrose = 12\ \cancel{mol}\left(\frac{12.011\ g\ C}{1\ \cancel{mol\ C}}\right) = 144.132\ g\ C$$

$$mass\ of\ H/mol\ of\ sucrose = 22\ \cancel{mol}\left(\frac{1.008\ g\ H}{1\ \cancel{mol\ H}}\right) = 22.176\ g\ H\ )$$

$$mass\ of\ O/mol\ of\ sucrose = 11\ \cancel{mol}\left(\frac{15.999\ g\ O}{1\ \cancel{mol\ O}}\right) = 175.989\ g\ O$$

Thus 1 mol of sucrose has a mass of 342.297 g; note that more than half of the mass (175.989 g) is oxygen, and almost half of the mass (144.132 g) is carbon.

The mass percentage of each element in sucrose is the mass of the element present in 1 mol of sucrose divided by the molar mass of sucrose, multiplied by 100 to give a percentage. The result is shown to two decimal places:

$$mass\ \%\ C\ in\ sucrose = \frac{mass\ of\ C/mol\ sucrose}{molar\ mass\ of\ sucrose} \times 100 = \frac{144.132\ g\ C}{342.297\ g/mol} \times 100 = 42.12\%$$

$$mass\ \%\ H\ in\ sucrose = \frac{mass\ of\ H/mol\ sucrose}{molar\ mass\ of\ sucrose} \times 100 = \frac{22.176\ g\ H}{342.297\ g/mol} \times 100 = 6.48\%$$

$$mass\ \%\ O\ in\ sucrose = \frac{mass\ of\ O/mol\ sucrose}{molar\ mass\ of\ sucrose} \times 100 = \frac{175.989\ g\ O}{342.297\ g/mol} \times 100 = 51.41\%$$

You can check your work by verifying that the sum of the percentages of all the elements in the compound is 100%:

42.12% + 6.48% + 51.41% = 100.01%

If the sum is not 100%, you have made an error in your calculations. (Rounding to the correct number of decimal places can, however, cause the total to be slightly different from 100%.) Thus 100.00 g of sucrose contains 42.12 g of carbon, 6.48 g of

hydrogen, and 51.41 g of oxygen; to two decimal places, the percent composition of sucrose is indeed 42.12% carbon, 6.48% hydrogen, and 51.41% oxygen.

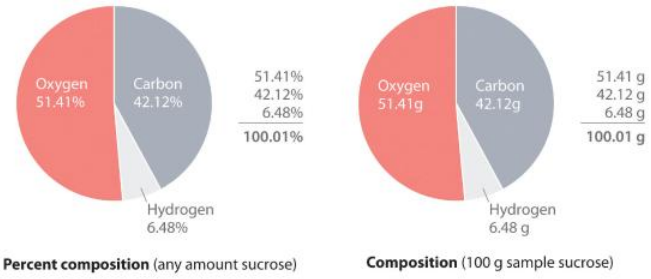


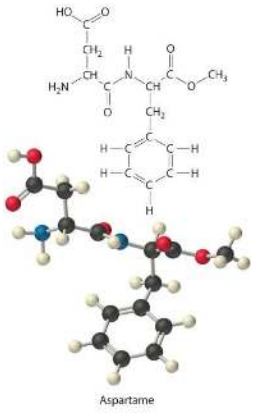
Figure 11.2.1 Percent Composition

We could also calculate the mass percentages using atomic masses and molecular masses, with atomic mass units. Because the answer we are seeking is a ratio, expressed as a percentage, the units of mass cancel whether they are grams (using molar masses) or atomic mass units (using atomic and molecular masses).

Example 11.2.1

Aspartame is the artificial sweetener sold as NutraSweet and Equal. Its molecular formula is $C_{14}H_{18}N_2O_5$.

1. Calculate the mass percentage of each element in aspartame.
2. Calculate the mass of carbon in a 1.00 g packet of Equal, assuming it is pure aspartame.



Given: molecular formula and mass of sample

Asked for: mass percentage of all elements and mass of one element in sample

Strategy:

A Use atomic masses from the periodic table to calculate the molar mass of aspartame.

B Divide the mass of each element by the molar mass of aspartame; then multiply by 100 to obtain percentages.

C To find the mass of an element contained in a given mass of aspartame, multiply the mass of aspartame by the mass percentage of that element, expressed as a decimal.

Solution:

1. **A** We calculate the mass of each element in 1 mol of aspartame and the molar mass of aspartame, here to three decimal places:

14 C	(14 mol C)(12.011 g/mol C) =	168.154 g
18 H	(18 mol H)(1.008 g/mol H) =	18.114 g
2N	(2 mol N)(14.007 g/mol N) =	28.014 g
+5O	(5 mol O)(15.999 g/mol O) =	79.995 g
$C_{14}H_{18}N_2O_5$	molar mass of aspartame	294.277 g/mol

Thus more than half the mass of 1 mol of aspartame (294.277 g) is carbon (168.154 g).

B To calculate the mass percentage of each element, we divide the mass of each element in the compound by the molar mass of aspartame and then multiply by 100 to obtain percentages, here reported to two decimal places:

$$mass\ \%\ C\ = \frac{168.154\ g\ C}{294.277\ g\ aspartame} \times 100\ = 57.14\%\ C$$

$$mass\ \%\ N\ = \frac{18.114\ g\ H}{294.277\ g\ aspartame} \times 100\ = 6.16\%\ C$$

$$mass\ \%\ N\ = \frac{28.014\ g\ N}{294.277\ g\ aspartame} \times 100\ = 9.52\%\ C$$

$$mass\ \%\ O\ = \frac{79.995\ g\ O}{294.277\ g\ aspartame} \times 100\ = 27.18\%\ C$$

As a check, we can add the percentages together:

57.14% + 6.16% + 9.52% + 27.18% = 100.00%

If you obtain a total that differs from 100% by more than about ±1%, there must be an error somewhere in the calculation.

2. **C** The mass of carbon in 1.00 g of aspartame is calculated as follows:

$$mass\ of\ C = 1.00\ \cancel{g\ aspartame} \times \frac{57.14\ g\ C}{100\ \cancel{g\ aspartame}} = 0.57\`\ g\ C$$

Exercise

Calculate the mass percentage of each element in aluminum oxide (Al_2O_3). Then calculate the mass of aluminum in a 3.62 g sample of pure aluminum oxide.

Figure 11.2.2 Penicillium Answer: 52.93% aluminum; 47.08% oxygen; 1.92 g Al

Determining the Empirical Formula of Penicillin

Just as we can use the empirical formula of a substance to determine its percent composition, we can use the percent composition of a sample to determine its empirical formula, which can then be used to determine its molecular formula. Such a procedure was actually used to determine the empirical and molecular formulas of the first antibiotic to be discovered: penicillin.

Antibiotics are chemical compounds that selectively kill microorganisms, many of which cause diseases. Although we may take antibiotics for granted today, penicillin was discovered only about 80 years ago. The subsequent development of a wide array of other antibiotics for treating many common diseases has contributed greatly to the substantial increase in life expectancy over the past 50 years. The discovery of penicillin is a historical detective story in which the use of mass percentages to determine empirical formulas played a key role.

In 1928, Alexander Fleming, a young microbiologist at the University of London, was working with a common bacterium that causes boils and other infections such as blood poisoning. For laboratory study, bacteria are commonly grown on the surface of a nutrient-containing gel in small, flat culture dishes. One day Fleming noticed that one of his cultures was contaminated by a bluish-green mold similar to the mold found on spoiled bread or fruit. Such accidents are rather common, and most laboratory workers would have simply thrown the cultures away. Fleming noticed, however, that the bacteria were growing everywhere on the gel *except* near the contaminating mold (part (a) in Figure 11.2.2, and he hypothesized that the mold must be producing a substance that either killed the bacteria or prevented their growth. To test this hypothesis, he grew the mold in a liquid and then filtered the liquid and added it to various bacteria cultures. The liquid killed not only the bacteria Fleming had originally been studying but also a wide range of other disease-causing bacteria. Because the mold was a member of the *Penicillium* family (named for their pencil-shaped branches under the microscope) (part (b) in Figure 11.2.2), Fleming called the active ingredient in the broth *penicillin*.

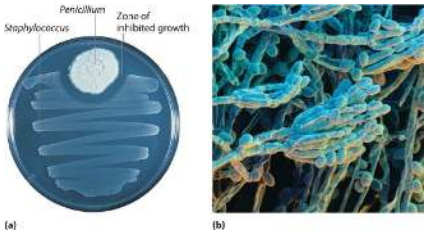


Figure 11.2.2 Penicillium *(a) Penicillium mold is growing in a culture dish; the photo shows its effect on bacterial growth. (b) In this photomicrograph of Penicillium, its rod- and pencil-shaped branches are visible. The name comes from the Latin penicillus, meaning "paintbrush."*

Although Fleming was unable to isolate penicillin in pure form, the medical importance of his discovery stimulated researchers in other laboratories. Finally, in 1940, two chemists at Oxford University, Howard Florey (1898–1968) and Ernst Chain (1906–1979), were able to isolate an active product, which they called penicillin G. Within three years, penicillin G was in widespread use for treating pneumonia, gangrene, gonorrhea, and other diseases, and its use greatly increased the survival rate of wounded soldiers in World War II. As a result of their work, Fleming, Florey, and Chain shared the Nobel Prize in Medicine in 1945.

As soon as they had succeeded in isolating pure penicillin G, Florey and Chain subjected the compound to a procedure called combustion analysis (described later in this section) to determine what elements were present and in what quantities. The results of such analyses are usually reported as mass percentages. They discovered that a typical sample of penicillin G contains 53.9% carbon, 4.8% hydrogen, 7.9% nitrogen, 9.0% sulfur, and 6.5% sodium by mass. The sum of these numbers is only 82.1%, rather than 100.0%, which implies that there must be one or more additional elements. A reasonable candidate is oxygen, which is a common component of compounds that contain carbon and hydrogen;Do not assume that the "missing" mass is always due to oxygen. It could be any other element. for technical reasons, however, it is difficult to analyze for oxygen directly. If we assume that all the missing mass is due to oxygen, then penicillin G contains (100.0% − 82.1%) = 17.9% oxygen. From these mass percentages, the empirical formula and eventually the molecular formula of the compound can be determined.

To determine the empirical formula from the mass percentages of the elements in a compound such as penicillin G, we need to convert the mass percentages to relative numbers of atoms. For convenience, we assume that we are dealing with a 100.0 g sample of the compound, even though the sizes of samples used for analyses are generally much smaller, usually in milligrams. This assumption simplifies the arithmetic because a 53.9% mass percentage of carbon corresponds to 53.9 g of carbon in a 100.0 g sample of penicillin G; likewise, 4.8% hydrogen corresponds to 4.8 g of hydrogen in 100.0 g of penicillin G; and so forth for the other elements. We can then divide each mass by the molar mass of the element to determine how many moles of each element are present in the 100.0 g sample:

$$\frac{mass\,(g)}{molar\ mass\,(g/mol)} = (\cancel{g})\left(\frac{mol}{\cancel{g}}\right) = mol$$

$$53.9\ \cancel{g\,C}\ \frac{1\ mol\ C}{12.011\ \cancel{g\,C}} = 4.49\ mol\ C$$

$$4.8\ \cancel{g\,H}\ \frac{1\ mol\ H}{1.008\ \cancel{g\,H}} = 4.49\ mol\ H$$

$$7.9\ \cancel{g\,N}\ \frac{1\ mol\ N}{14.007\ \cancel{g\,N}} = 0.56\ mol\ N$$

$$9.0\ \cancel{g\,S}\ \frac{1\ mol\ S}{32.065\ \cancel{g\,S}} = 0.28\ mol\ S$$

$$6.5\ \cancel{g\,Na}\ \frac{1\ mol\ Na}{22.990\ \cancel{g\,Na}} = 0.28\ mol\ Na$$

$$17.9\ \cancel{g\,O}\ \frac{1\ mol\ O}{15.999\ \cancel{g\,O}} = 1.12\ mol\ O$$

Thus 100.0 g of penicillin G contains 4.49 mol of carbon, 4.8 mol of hydrogen, 0.56 mol of nitrogen, 0.28 mol of sulfur, 0.28 mol of sodium, and 1.12 mol of oxygen (assuming that all the missing mass was oxygen). The number of significant figures in the numbers of moles of elements varies between two and three because some of the analytical data were reported to only two significant figures.

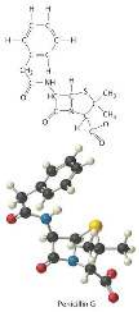
These results tell us the ratios of the moles of the various elements in the sample (4.49 mol of carbon to 4.8 mol of hydrogen to 0.56 mol of nitrogen, and so forth), but they are not the whole-number ratios we need for the empirical formula—the empirical formula expresses the *relative* numbers of atoms in the *smallest whole numbers possible*. To obtain whole numbers, we divide the numbers of moles of all the elements in the sample by the number of moles of the element present in the lowest relative amount, which in this example is sulfur or sodium. The results will be the subscripts of the elements in the empirical formula. To two significant figures, the results are

$$C: \frac{4.49}{0.28} = 16 \quad H: \frac{4.8}{0.28} = 17 \quad N: \frac{0.56}{0.28} = 2.0$$

$$S: \frac{0.28}{0.28} = 1.0 \quad Na: \frac{0.28}{0.28} = 1.0 \quad O: \frac{1.12}{0.28} = 1.0$$

The empirical formula of penicillin G is therefore $C_{16}H_{17}N_2NaO_4S$. Other experiments have shown that penicillin G is actually an ionic compound that contains Na^+ cations and $[C_{16}H_{17}N_2O_4S]^-$ anions in a 1:1 ratio. The complex structure of penicillin G (Figure 11.2.3) was not determined until 1948.

Figure 11.2.3 Structural Formula and Ball-and-Stick Model of the Anion of Penicillin G



In some cases, one or more of the subscripts in a formula calculated using this procedure may not be integers. Does this mean that the compound of interest contains a nonintegral number of atoms? No; rounding errors in the calculations as well as experimental errors in the data can result in nonintegral ratios. When this happens, you must exercise some judgment in interpreting the results, as illustrated in Example 6. In particular, ratios of 1.50, 1.33, or 1.25 suggest that you should multiply *all* subscripts in the formula by 2, 3, or 4, respectively. Only if the ratio is within 5% of an integral value should you consider rounding to the nearest integer.

Example 11.2.2

Calculate the empirical formula of the ionic compound calcium phosphate, a major component of fertilizer and a polishing agent in toothpastes. Elemental analysis indicates that it contains 38.77% calcium, 19.97% phosphorus, and 41.27% oxygen.

Given: percent composition

Asked for: empirical formula

Strategy:

A Assume a 100 g sample and calculate the number of moles of each element in that sample.

B Obtain the relative numbers of atoms of each element in the compound by dividing the number of moles of each element in the 100 g sample by the number of moles of the element present in the smallest amount.

C If the ratios are not integers, multiply all subscripts by the same number to give integral values.

D Because this is an ionic compound, identify the anion and cation and write the formula so that the charges balance.

Solution:

A A 100 g sample of calcium phosphate contains 38.77 g of calcium, 19.97 g of phosphorus, and 41.27 g of oxygen. Dividing the mass of each element in the 100 g sample by its molar mass gives the number of moles of each element in the sample:

$$\text{moles Ca} = 38.77 \ \cancel{\text{g Ca}} \frac{1 \text{ mol Ca}}{40.078 \ \cancel{\text{g Ca}}} = 0.9674 \text{ mol Ca}$$

$$\text{moles P} = 19.97 \ \cancel{\text{g P}} \frac{1 \text{ mol P}}{30.9738 \ \cancel{\text{g Ca}}} = 0.6447 \text{ mol P}$$

$$\text{moles O} = 41.27 \ \cancel{\text{g O}} \frac{1 \text{ mol O}}{15.994 \ \cancel{\text{g O}}} = 2.5800 \text{ mol O}$$

B To obtain the *relative* numbers of atoms of each element in the compound, divide the number of moles of each element in the 100-g sample by the number of moles of the element in the smallest amount, in this case phosphorus:

$$P: \frac{0.6447\ molP}{0.6447\ molP} = 1.00 \quad Ca: \frac{0.9674}{0.6447} = 1.501 \quad O: \frac{2.5800}{0.6447} = 4.002$$

C We could write the empirical formula of calcium phosphate as $Ca_{1.501}P_{1.000}O_{4.002}$, but the empirical formula should show the ratios of the elements as small whole numbers. To convert the result to integral form, multiply all the subscripts by 2 to get $Ca_{3.002}P_{2.000}O_{8.004}$. The deviation from integral atomic ratios is small and can be attributed to minor experimental errors; therefore, the empirical formula is $Ca_3P_2O_8$.

D The calcium ion (Ca^{2+}) is a cation, so to maintain electrical neutrality, phosphorus and oxygen must form a polyatomic anion. We know from Section 10.2 that phosphorus and oxygen form the phosphate ion (PO_4^{3-}; see Table 10.2.1). Because there are two phosphorus atoms in the empirical formula, two phosphate ions must be present. So we write the formula of calcium phosphate as $Ca_3(PO_4)_2$.

Exercise

Calculate the empirical formula of ammonium nitrate, an ionic compound that contains 35.00% nitrogen, 5.04% hydrogen, and 59.96% oxygen by mass; refer to Table 10.2.1 if necessary. Although ammonium nitrate is widely used as a fertilizer, it can be dangerously explosive. For example, it was a major component of the explosive used in the 1995 Oklahoma City bombing.

Answer: $N_2H_4O_3$ is $NH_4^+NO_3^-$, written as NH_4NO_3

Combustion Analysis

One of the most common ways to determine the elemental composition of an unknown hydrocarbon is an analytical procedure called *combustion analysis*. A small, carefully weighed sample of an unknown compound that may contain carbon, hydrogen, nitrogen, and/or sulfur is burned in an oxygen atmosphere,Other elements, such as metals, can be determined by other methods. and the quantities of the resulting gaseous products (CO_2, H_2O, N_2, and SO_2, respectively) are determined by one of several possible methods. One procedure used in combustion analysis is outlined schematically in Figure 11.2.4 , and a typical combustion analysis is illustrated in Example11.2.3.

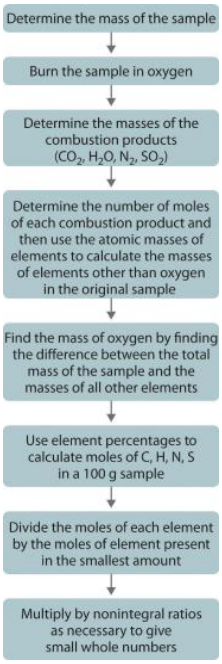


Figure 11.2.4 Steps for Obtaining an Empirical Formula from Combustion Analysis

Example 11.2.3

Naphthalene, the active ingredient in one variety of mothballs, is an organic compound that contains carbon and hydrogen only. Complete combustion of a 20.10 mg sample of naphthalene in oxygen yielded 69.00 mg of CO_2 and 11.30 mg of H_2O. Determine the empirical formula of naphthalene.

Given: mass of sample and mass of combustion products

Asked for: empirical formula

Strategy:

A Use the masses and molar masses of the combustion products, CO_2 and H_2O, to calculate the masses of carbon and hydrogen present in the original sample of naphthalene.

B Use those masses and the molar masses of the elements to calculate the empirical formula of naphthalene.

Solution:

A Upon combustion, 1 mol of CO_2 is produced for each mole of carbon atoms in the original sample. Similarly, 1 mol of H_2O is produced for every 2 mol of hydrogen atoms present in the sample. The masses of carbon and hydrogen in the original sample can be calculated from these ratios, the masses of CO_2 and H_2O, and their molar masses. Because the units of molar mass are grams per mole, we must first convert the masses from milligrams to grams:

$$\begin{aligned} mass\ of\ C &= 69.00\ \cancel{mg\ CO_2} \times \frac{1\ \cancel{g}}{1000\ \cancel{mg}} \times \frac{1\ \cancel{mol\ CO_2}}{44.010\ \cancel{g\ CO_2}} \times \frac{1\ \cancel{mol\ C}}{1\ \cancel{mol\ CO_2}} \times \frac{12.011\ g}{1\ \cancel{mol\ C}} \\ &= 1.883 \times 10^{-2}\ g\ C) \end{aligned}$$

$$\begin{aligned} mass\ of\ H &= 11.30\ \cancel{mg\ H_2O} \times \frac{1\ \cancel{g}}{1000\ \cancel{mg}} \times \frac{1\ \cancel{mol\ H_2O}}{18.015\ \cancel{g\ H_2O}} \times \frac{2\ \cancel{mol\ H}}{1\ \cancel{mol\ H_2O}} \times \frac{1.0079\ g}{1\ \cancel{mol\ C}} \\ &= 1.264 \times 10^{-3}\ g\ H) \end{aligned}$$

B To obtain the *relative* numbers of atoms of both elements present, we need to calculate the number of moles of each and divide by the number of moles of the element present in the smallest amount:

$$moles\ C = 1.883 \times 10^{-2}\ \cancel{g\ C} \times \frac{1\ mol\ C}{12.011\ \cancel{g\ C}} = 1.568 \times 10^{-3}\ mol\ C$$

$$moles\ H = 1.264 \times 10^{-3}\ \cancel{g\ H} \times \frac{1\ mol\ H}{1.0079\ \cancel{g\ H}} = 1.254 \times 10^{-3}\ mol\ H$$

Dividing each number by the number of moles of the element present in the smaller amount gives

$$H: \frac{1.254 \times 10^{-3}}{1.254 \times 10^{-3}} = 1.000 \quad C: \frac{1.568 \times 10^{-3}}{1.254 \times 10^{-3}} = 1.250$$

Thus naphthalene contains a 1.25:1 ratio of moles of carbon to moles of hydrogen: $C_{1.25}H_{1.0}$. Because the ratios of the elements in the empirical formula must be expressed as small whole numbers, multiply both subscripts by 4, which gives C_5H_4 as the empirical formula of naphthalene. In fact, the molecular formula of naphthalene is $C_{10}H_8$, which is consistent with our results.

Exercise

1. Xylene, an organic compound that is a major component of many gasoline blends, contains carbon and hydrogen only. Complete combustion of a 17.12 mg sample of xylene in oxygen yielded 56.77 mg of CO_2 and 14.53 mg of H_2O. Determine the empirical formula of xylene.
2. The empirical formula of benzene is CH (its molecular formula is C_6H_6). If 10.00 mg of benzene is subjected to combustion analysis, what mass of CO_2 and H_2O will be produced?

Answer:

1. The empirical formula is C_4H_5. (The molecular formula of xylene is actually C_8H_{10}.)
2. 33.81 mg of CO_2; 6.92 mg of H_2O

From Empirical Formula to Molecular Formula

The empirical formula gives only the *relative* numbers of atoms in a substance in the smallest possible ratio. For a covalent substance, we are usually more interested in the molecular formula, which gives the actual number of atoms of each kind present per molecule. Without additional information, however, it is impossible to know whether the formula of penicillin G, for example, is $C_{16}H_{17}N_2NaO_4S$ or an integral multiple, such as $C_{32}H_{34}N_4Na_2O_8S_2$, $C_{48}H_{51}N_6Na_3O_{12}S_3$, or $(C_{16}H_{17}N_2NaO_4S)_n$, where n is an integer. (The actual structure of penicillin G is shown in Figure 11.2.3 .)

Consider glucose, the sugar that circulates in our blood to provide fuel for our bodies and especially for our brains. Results from combustion analysis of glucose report that glucose contains 39.68% carbon and 6.58% hydrogen. Because combustion occurs in the presence of oxygen, it is impossible to directly determine the percentage of oxygen in a compound by using combustion analysis; other more complex methods are necessary. If we assume that the remaining percentage is due to oxygen, then glucose would contain 53.79% oxygen. A 100.0 g sample of glucose would therefore contain 39.68 g of carbon, 6.58 g of hydrogen, and 53.79 g of oxygen. To calculate the number of moles of each element in the 100.0 g sample, we divide the mass of each element by its molar mass:

$$\text{moles C} = 39.68 \cancel{\text{g C}} \frac{1 \text{ mol C}}{12.011 \cancel{\text{g C}}} = 3.304 \text{ mol C}$$

$$\text{moles H} = 6.58 \cancel{\text{g H}} \frac{1 \text{ mol H}}{1.0079 \cancel{\text{g H}}} = 6.53 \text{ mol H}$$

$$\text{moles O} = 53.79 \cancel{\text{g O}} \frac{1 \text{ mol C}}{15.9994 \cancel{\text{g O}}} = 3.362 \text{ mol O}$$

Once again, we find the subscripts of the elements in the empirical formula by dividing the number of moles of each element by the number of moles of the element present in the smallest amount:

$$C: \frac{3.304}{3.304} = 1.000 \quad H: \frac{6.53}{3.304} = 1.98 \quad O: \frac{3.362}{3.304} = 1.018$$

The oxygen:carbon ratio is 1.018, or approximately 1, and the hydrogen:carbon ratio is approximately 2. The empirical formula of glucose is therefore CH_2O, but what is its molecular formula?

Many known compounds have the empirical formula CH_2O, including formaldehyde, which is used to preserve biological specimens and has properties that are very different from the sugar circulating in our blood. At this point, we cannot know whether glucose is CH_2O, $C_2H_4O_2$, or any other $(CH_2O)_n$. We can, however, use the experimentally determined molar mass of glucose (180 g/mol) to resolve this dilemma.

First, we calculate the **formula mass**, the molar mass of the formula unit, which is the sum of the atomic masses of the elements in the empirical formula multiplied by their respective subscripts. For glucose,

$$\text{formula mass of } CH_2O = \left[1 \cancel{\text{ mol C}} \left(\frac{12.011 \text{ g}}{1 \cancel{\text{ mol C}}}\right)\right] + \left[2 \cancel{\text{ mol H}} \left(\frac{1.0079 \text{ g}}{1 \cancel{\text{ mol H}}}\right)\right] + \left[1 \cancel{\text{ mol O}} \left(\frac{15.9994 \text{ g}}{1 \cancel{\text{ mol O}}}\right)\right]$$

This is much smaller than the observed molar mass of 180 g/mol.

Second, we determine the number of formula units per mole. For glucose, we can calculate the number of (CH_2O) units—that is, the n in $(CH_2O)_n$—by dividing the molar mass of glucose by the formula mass of CH_2O:

$$n = \frac{180 \text{ g}}{30.026 \text{ g } CH_2O} = 5.99 \approx 6 \text{ } CH_2O \text{ formula units}$$

Each glucose contains six CH_2O formula units, which gives a molecular formula for glucose of $(CH_2O)_6$, which is more commonly written as $C_6H_{12}O_6$. The molecular structures of formaldehyde and glucose, both of which have the empirical formula CH_2O, are shown in Figure 11.2.5.

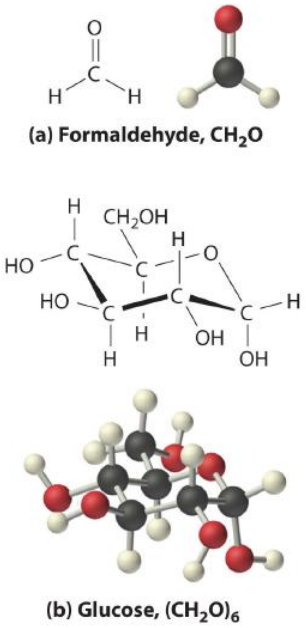


Figure 11.2.5 Structural Formulas and Ball-and-Stick Models of (a) Formaldehyde and (b) Glucose

Example 11.2.4

Calculate the molecular formula of caffeine, a compound found in coffee, tea, and cola drinks that has a marked stimulatory effect on mammals. The chemical analysis of caffeine shows that it contains 49.18% carbon, 5.39% hydrogen, 28.65% nitrogen, and 16.68% oxygen by mass, and its experimentally determined molar mass is 196 g/mol.

Given: percent composition and molar mass

Asked for: molecular formula

Strategy:

A Assume 100 g of caffeine. From the percentages given, use the procedure given in Example 6 to calculate the empirical formula of caffeine.

B Calculate the formula mass and then divide the experimentally determined molar mass by the formula mass. This gives the number of formula units present.

C Multiply each subscript in the empirical formula by the number of formula units to give the molecular formula.

Solution:

A We begin by dividing the mass of each element in 100.0 g of caffeine (49.18 g of carbon, 5.39 g of hydrogen, 28.65 g of nitrogen, 16.68 g of oxygen) by its molar mass. This gives the number of moles of each element in 100 g of caffeine.

$$moles\ C = 49.18\ \cancel{g\,C}\ \frac{1\ mol\ C}{12.011\ \cancel{g\,C}} = 4.095\ mol\ C$$

$$moles\ H = 5.93\ \cancel{g\,H}\ \frac{1\ mol\ H}{1.0079\ \cancel{g\,H}} = 5.35\ mol\ H$$

$$moles\ N = 28.65\ \cancel{g\,N}\ \frac{1\ mol\ H}{14.0067\ \cancel{g\,H}} = 2.045\ mol\ N$$

$$moles\ O = 16.68\ \cancel{g\,O}\ \frac{1\ mol\ C}{15.9994\ \cancel{g\,O}} = 1.043\ mol\ O$$

To obtain the relative numbers of atoms of each element present, divide the number of moles of each element by the number of moles of the element present in the least amount:

$$O: \frac{1.043}{1.043} = 1.000 \quad C: \frac{4.095}{1.043} = 3.926 \quad H: \frac{5.35}{1.043} = 5.13 \quad N: \frac{2.045}{1.043} = 1.960$$

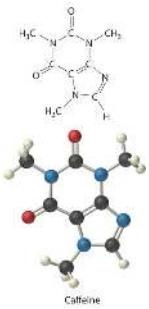
These results are fairly typical of actual experimental data. None of the atomic ratios is exactly integral but all are within 5% of integral values. Just as in Example 6, it is reasonable to assume that such small deviations from integral values are due to minor experimental errors, so round to the nearest integer. The empirical formula of caffeine is thus $C_4H_5N_2O$.

B The *molecular* formula of caffeine could be $C_4H_5N_2O$, but it could also be any integral multiple of this. To determine the actual molecular formula, we must divide the experimentally determined molar mass by the formula mass. The formula mass is calculated as follows:

Dividing the measured molar mass of caffeine (196 g/mol) by the calculated formula mass gives

$$\frac{196\ g/mol}{97.096\ g/C_4H_5N_2O} = 2.02 \approx 2C_4H_5N_2O$$

C There are two $C_4H_5N_2O$ formula units in caffeine, so the molecular formula must be $(C_4H_5N_2O)_2 = C_8H_{10}N_4O_2$. The structure of caffeine is as follows:



Exercise

Calculate the molecular formula of Freon-114, which has 13.85% carbon, 41.89% chlorine, and 44.06% fluorine. The experimentally measured molar mass of this compound is 171 g/mol. Like Freon-11, Freon-114 is a commonly used refrigerant that has been implicated in the destruction of the ozone layer.

Answer: $C_2Cl_2F_4$

Summary

The empirical formula of a substance can be calculated from the experimentally determined **percent composition**, the percentage of each element present in a pure substance by mass. In many cases, these percentages can be determined by *combustion analysis*. If the molar mass of the compound is known, the molecular formula can be determined from the empirical formula.

Key Takeaway

- The empirical formula of a substance can be calculated from its percent composition, and the molecular formula can be determined from the empirical formula and the compound's molar mass.

Conceptual Problems

1. What is the relationship between an empirical formula and a molecular formula?
2. Construct a flowchart showing how you would determine the empirical formula of a compound from its percent composition.

Numerical Problems

1. What is the mass percentage of water in each hydrate?
    1. $H_3AsO_4 \cdot 0.5H_2O$
    2. $NH_4NiCl_3 \cdot 6H_2O$
    3. $Al(NO_3)_3 \cdot 9H_2O$

2. What is the mass percentage of water in each hydrate?
    1. $CaSO_4 \cdot 2H_2O$
    2. $Fe(NO_3)_3 \cdot 9H_2O$
    3. $(NH_4)_3ZrOH(CO_3)_3 \cdot 2H_2O$
3. Which of the following has the greatest mass percentage of oxygen—$KMnO_4$, $K_2Cr_2O_7$, or Fe_2O_3?
4. Which of the following has the greatest mass percentage of oxygen—$ThOCl_2$, $MgCO_3$, or NO_2Cl?
5. Calculate the percent composition of the element shown in bold in each compound.
    1. $Sb\mathbf{Br}_3$
    2. $\mathbf{As}_2I_4$
    3. $Al\mathbf{P}O_4$
    4. $\mathbf{C}_6H_{10}O$
6. Calculate the percent composition of the element shown in bold in each compound.
    1. $H\mathbf{Br}O_3$
    2. $\mathbf{Cs}ReO_4$
    3. $\mathbf{C}_3H_8O$
    4. $Fe\mathbf{S}O_4$
7. A sample of a chromium compound has a molar mass of 151.99 g/mol. Elemental analysis of the compound shows that it contains 68.43% chromium and 31.57% oxygen. What is the identity of the compound?
8. The percentages of iron and oxygen in the three most common binary compounds of iron and oxygen are given in the following table. Write the empirical formulas of these three compounds.

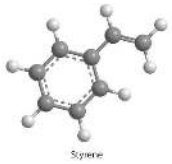
Compound	% Iron	% Oxygen	Empirical Formula
1	69.9	30.1	
2	77.7	22.3	
3	72.4	27.6	

9. What is the mass percentage of water in each hydrate?
    1. $LiCl \cdot H_2O$
    2. $MgSO_4 \cdot 7H_2O$
    3. $Sr(NO_3)_2 \cdot 4H_2O$
10. What is the mass percentage of water in each hydrate?
    1. $CaHPO_4 \cdot 2H_2O$
    2. $FeCl_2 \cdot 4H_2O$
    3. $Mg(NO_3)_2 \cdot 4H_2O$
11. Two hydrates were weighed, heated to drive off the waters of hydration, and then cooled. The residues were then reweighed. Based on the following results, what are the formulas of the hydrates?

Compound	Initial Mass (g)	Mass after Cooling (g)
$NiSO_4 \cdot xH_2O$	2.08	1.22
$CoCl_2 \cdot xH_2O$	1.62	0.88

12. Which contains the greatest mass percentage of sulfur—FeS_2, $Na_2S_2O_4$, or Na_2S?

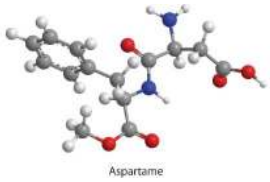
13. Given equal masses of each, which contains the greatest mass percentage of sulfur—$NaHSO_4$ or K_2SO_4?
14. Calculate the mass percentage of oxygen in each polyatomic ion.
    1. bicarbonate
    2. chromate
    3. acetate
    4. sulfite
15. Calculate the mass percentage of oxygen in each polyatomic ion.
    1. oxalate
    2. nitrite
    3. dihydrogen phosphate
    4. thiocyanate
16. The empirical formula of garnet, a gemstone, is $Fe_3Al_2Si_3O_{12}$. An analysis of a sample of garnet gave a value of 13.8% for the mass percentage of silicon. Is this consistent with the empirical formula?
17. A compound has the empirical formula C_2H_4O, and its formula mass is 88 g. What is its molecular formula?
18. Mirex is an insecticide that contains 22.01% carbon and 77.99% chlorine. It has a molecular mass of 545.59 g. What is its empirical formula? What is its molecular formula?
19. How many moles of CO_2 and H_2O will be produced by combustion analysis of 0.010 mol of styrene?



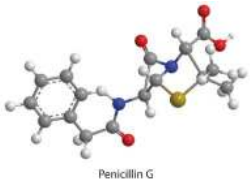
20. How many moles of CO_2, H_2O, and N_2 will be produced by combustion analysis of 0.0080 mol of aniline?



21. How many moles of CO_2, H_2O, and N_2 will be produced by combustion analysis of 0.0074 mol of aspartame?



22. How many moles of CO_2, H_2O, N_2, and SO_2 will be produced by combustion analysis of 0.0060 mol of penicillin G?



23. Combustion of a 34.8 mg sample of benzaldehyde, which contains only carbon, hydrogen, and oxygen, produced 101 mg of CO_2 and 17.7 mg of H_2O.

1. What was the mass of carbon and hydrogen in the sample?
2. Assuming that the original sample contained only carbon, hydrogen, and oxygen, what was the mass of oxygen in the sample?
3. What was the mass percentage of oxygen in the sample?
4. What is the empirical formula of benzaldehyde?
5. The molar mass of benzaldehyde is 106.12 g/mol. What is its molecular formula?

24. Salicylic acid is used to make aspirin. It contains only carbon, oxygen, and hydrogen. Combustion of a 43.5 mg sample of this compound produced 97.1 mg of CO_2 and 17.0 mg of H_2O.

    1. What is the mass of oxygen in the sample?
    2. What is the mass percentage of oxygen in the sample?
    3. What is the empirical formula of salicylic acid?
    4. The molar mass of salicylic acid is 138.12 g/mol. What is its molecular formula?

25. Given equal masses of the following acids, which contains the greatest amount of hydrogen that can dissociate to form H^+—nitric acid, hydroiodic acid, hydrocyanic acid, or chloric acid?

26. Calculate the formula mass or the molecular mass of each compound.

    1. heptanoic acid (a seven-carbon carboxylic acid)
    2. 2-propanol (a three-carbon alcohol)
    3. $KMnO_4$
    4. tetraethyllead
    5. sulfurous acid
    6. ethylbenzene (an eight-carbon aromatic hydrocarbon)

27. Calculate the formula mass or the molecular mass of each compound.

    1. $MoCl_5$
    2. B_2O_3
    3. bromobenzene
    4. cyclohexene
    5. phosphoric acid
    6. ethylamine

28. Given equal masses of butane, cyclobutane, and propene, which contains the greatest mass of carbon?

29. Given equal masses of urea $[(NH_2)_2CO]$ and ammonium sulfate, which contains the most nitrogen for use as a fertilizer?

Answers

1. To two decimal places, the percentages are:

    1. 5.97%
    2. 37.12%
    3. 43.22%

2.

3. % oxygen: $KMnO_4$, 40.50%; $K_2Cr_2O_7$, 38.07%; Fe_2O_3, 30.06%

4.

5. To two decimal places, the percentages are:

    1. 66.32% Br
    2. 22.79% As
    3. 25.40% P
    4. 73.43% C

6.

7. Cr_2O_3.

8.

9. To two decimal places, the percentages are:

    1. 29.82%
    2. 51.16%
    3. 25.40%

10.

11. $NiSO_4 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$

12.

13. $NaHSO_4$

14.

15.
    1. 72.71%
    2. 69.55%
    3. 65.99%
    4. 0%

16.

17. $C_4H_8O_2$

18.

19.

20.

21.

22.

23.
    1. 27.6 mg C and 1.98 mg H
    2. 5.2 mg O
    3. 15%
    4. C_7H_6O
    5. C_7H_6O

24.

25. hydrocyanic acid, HCN

26.

27. To two decimal places, the values are:

    1. 273.23 amu
    2. 69.62 amu
    3. 157.01 amu
    4. 82.14 amu
    5. 98.00 amu
    6. 45.08 amu

28.

29. Urea

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Chapter 11.3: Chemical Equations

Learning Objective

- To describe a chemical reaction.
- To calculate the quantities of compounds produced or consumed in a chemical reaction.

As shown in Figure 11.3.1, applying a small amount of heat to a pile of orange ammonium dichromate powder results in a vigorous reaction known as the ammonium dichromate volcano. Heat, light, and gas are produced as a large pile of fluffy green chromium(III) oxide forms. We can describe this reaction with a chemical equationAn expression that gives the identities and quantities of the substances in a chemical reaction. Chemical formulas are used to indicate the reactants on the left and the products on the right. An arrow points from reactants to products., an expression that gives the identities and quantities of the substances in a chemical reaction. Chemical formulas and other symbols are used to indicate the starting material(s), or reactant(s)The starting material(s) in a chemical reaction., which by convention are written on the left side of the equation, and the final compound(s), or product(s)The final compound(s) produced in a chemical reaction., which are written on the right. An arrow points from the reactant to the products:





Figure 11.3.1 An Ammonium Dichromate Volcano: Change during a Chemical Reaction

The starting material (left) is solid ammonium dichromate. A chemical reaction (right) transforms it to solid chromium(III) oxide, depicted showing a portion of its chained structure, nitrogen gas, and water vapor. (In addition, energy in the form of heat and light is released.) During the reaction, the distribution of atoms changes, but the *number* of atoms of each element does not change. Because the numbers of each type of atom are the same in the reactants and the products, the chemical equation is balanced.

$$\underset{reactant}{(NH_4)_2Cr_2O_7} \rightarrow \underset{products}{Cr_2O_3 + N^2 + 4H_2)}$$

The arrow is read as “yields” or “reacts to form.” So Equation 11.3.1 tells us that ammonium dichromate (the reactant) yields chromium(III) oxide, nitrogen, and water (the products).

The equation for this reaction is even more informative when written as

$$(NH_4)_2Cr_2O_7\,(s) \rightarrow Cr_2O_3\,(s) + N_2\,(g) + 4H_2O\,(g) \qquad (11.3.2)$$

Equation 11.3.2 is identical to Equation 11.3.1 except for the addition of abbreviations in parentheses to indicate the physical state of each species. The abbreviations are (s) for solid, (l) for liquid, (g) for gas, and (aq) for an *aqueous solution*, a solution of the substance in water.

Consistent with the law of conservation of mass, the numbers of each type of atom are the same on both sides of Equation 11.3.1 and Equation 11.3.2. Each side has two chromium atoms, seven oxygen atoms, two nitrogen atoms, and eight hydrogen atoms. In a *balanced chemical equation*, both the numbers of each type of atom and the total charge are the same on both sides. Equation 11.3.1 and Equation 11.3.2 are balanced chemical equations. What is different on each side of the equation is how the atoms are arranged to make molecules or ions. *A chemical reaction represents a change in the distribution of atoms in molecules but not in the number of atoms*. In this reaction, and in most chemical reactions, bonds are broken in the reactants (here, Cr–O and N–H bonds), and new bonds are formed to create the products (here, O–H and N≡N bonds). If the numbers of each type of atom are different on the two sides of a chemical equation, then the equation is unbalanced, and it cannot correctly describe what happens during the reaction. To proceed, *the equation must first be balanced*.

Note the Pattern

A chemical reaction changes only the distribution of atoms, *not* the number of atoms.

Interpreting Chemical Equations

In addition to providing qualitative information about the identities and physical states of the reactants and products, a balanced chemical equation provides *quantitative* information. Specifically, it tells the relative amounts of reactants and products consumed or produced in a reaction. The number of atoms, molecules, or formula units of a reactant or a product in a balanced chemical equation is the coefficientA number greater than 1 preceding a formula in a balanced chemical equation and indicating the number of atoms, molecules, or formula units of a reactant or a product. of that species (e.g., the 4 preceding H_2O in Equation 11.3.1). When no coefficient is written in front of a species, the coefficient is assumed to be 1. As illustrated in Figure 11.3.2, the coefficients allow us to interpret Equation 11.3.1 in any of the following ways:

- Two NH_4^+ ions and one $Cr_2O_7^{2-}$ ion yield 1 formula unit of Cr_2O_3, 1 N_2 molecule, and 4 H_2O molecules.
- One mole of $(NH_4)_2Cr_2O_7$ yields 1 mol of Cr_2O_3, 1 mol of N_2, and 4 mol of H_2O.
- A mass of 252 g of $(NH_4)_2Cr_2O_7$ yields 152 g of Cr_2O_3, 28 g of N_2, and 72 g of H_2O.
- A total of 6.022×10^{23} formula units of $(NH_4)_2Cr_2O_7$ yields 6.022×10^{23} formula units of Cr_2O_3, 6.022×10^{23} molecules of N_2, and 24.09×10^{23} molecules of H_2O.

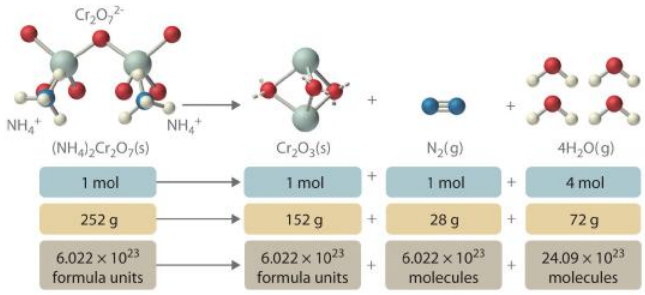


Figure 11.3.2 The Relationships among Moles, Masses, and Formula Units of Compounds in the Balanced Chemical Reaction for the Ammonium Dichromate Volcano

These are all *chemically equivalent* ways of stating the information given in the balanced chemical equation, using the concepts of the mole, molar or formula mass, and Avogadro's number. The ratio of the number of moles of one substance to the number of moles of another is called the mole ratioThe ratio of the number of moles of one substance to the number of moles of another, as depicted by a balanced chemical equation.. For example, the mole ratio of H_2O to N_2 in Equation 11.3.1 is 4:1. The total mass of reactants equals the total mass of products, as predicted by Dalton's law of conservation of mass: 252 g of $(NH_4)_2Cr_2O_7$ yields 152 + 28 + 72 = 252 g of products. The chemical equation does *not*, however, show the rate of the reaction (rapidly, slowly, or not at all) or whether energy in the form of heat or light is given off. We will consider these issues in more detail in the second semester.

An important chemical reaction was analyzed by Antoine Lavoisier, an 18th-century French chemist, who was interested in the chemistry of living organisms as well as simple chemical systems. In a classic series of experiments, he measured the carbon dioxide and heat produced by a guinea pig during respiration, in which organic compounds are used as fuel to produce energy, carbon dioxide, and water. Lavoisier found that the ratio of heat produced to carbon dioxide exhaled was similar to the ratio observed for the reaction of charcoal with oxygen in the air to produce carbon dioxide—a process chemists call *combustion*. Based on these experiments, he proposed that "Respiration is a combustion, slow it is true, but otherwise perfectly similar to that of charcoal." Lavoisier was correct, although the organic compounds consumed in respiration are substantially different from those found in charcoal. One of the most important fuels in the human body is glucose ($C_6H_{12}O_6$), which is virtually the only fuel used in the brain. Thus combustion and respiration are examples of chemical reactions.

Example 11.3.1

The balanced chemical equation for the combustion of glucose in the laboratory (or in the brain) is as follows:

$$C_6H_{12}O_6\,(s) + 6O_2\,(g) \rightarrow 6CO_2\,(g) + 6H_2O\,(l) \qquad \text{(Chapter 11.3.1)}$$

Construct a table showing how to interpret the information in this equation in terms of

1. a single molecule of glucose.
2. moles of reactants and products.
3. grams of reactants and products represented by 1 mol of glucose.
4. numbers of molecules of reactants and products represented by 1 mol of glucose.

Given: balanced chemical equation

Asked for: molecule, mole, and mass relationships

Strategy:

A Use the coefficients from the balanced chemical equation to determine both the molecular and mole ratios.

B Use the molar masses of the reactants and products to convert from moles to grams.

C Use Avogadro's number to convert from moles to the number of molecules.

Solution:

This equation is balanced as written: each side has 6 carbon atoms, 18 oxygen atoms, and 12 hydrogen atoms. We can therefore use the coefficients directly to obtain the desired information.

A One molecule of glucose reacts with 6 molecules of O_2 to yield 6 molecules of CO_2 and 6 molecules of H_2O.

B One mole of glucose reacts with 6 mol of O_2 to yield 6 mol of CO_2 and 6 mol of H_2O.

C To interpret the equation in terms of masses of reactants and products, we need their molar masses and the mole ratios from part b. The molar masses in grams per mole are as follows: glucose, 180.16; O_2, 31.9988; CO_2, 44.010; and H_2O, 18.015.

$$\textit{mass of reactants} = \textit{mass of products}$$

$$\textit{g glucose} = \textit{g } CO_2 + \textit{g } H_2O$$

$$1\ \cancel{mol\ glucose}\left(\frac{180.16\ g}{1\ \cancel{mol\ glucose}}\right) + 6\ \cancel{mol\ O_2}\left(\frac{31.9988\ g}{1\ \cancel{mol\ O_2}}\right)\left(\frac{6\ \cancel{mol\ CO_2}}{1\ \cancel{mol\ O_2}}\right)\left(\frac{44.010\ g}{1\ \cancel{mol\ CO_2}}\right) + 6\ \cancel{mol\ H_2O}\left(\frac{18.0158\ g}{1\ \cancel{mol\ H_2O}}\right)$$

$$372.15\ g = 372.15\ g$$

1. **C** One mole of glucose contains Avogadro's number (6.022×10^{23}) of glucose molecules. Thus 6.022×10^{23} glucose molecules react with ($6 \times 6.022 \times 10^{23}$) = 3.613×10^{24} oxygen molecules to yield ($6 \times 6.022 \times 10^{23}$) = 3.613×10^{24} molecules each of CO_2 and H_2O.

   In tabular form:

	$C_6H_{12}O_6(s)$	+	$6O_2(g)$	→	$6CO_2(g)$	+	$6H_2O(l)$
a.	1 molecule		6 molecules		6 molecules		6 molecules
b.	1 mol		6 mol		6 mol		6 mol
c.	180.16 g		191.9928 g		264.06 g		108.09 g
d.	6.022×10^{23} molecules		3.613×10^{24} molecules		3.613×10^{24} molecules		3.613×10^{24} molecules

Exercise

Ammonium nitrate is a common fertilizer, but under the wrong conditions it can be hazardous. In 1947, a ship loaded with ammonium nitrate caught fire during unloading and exploded, destroying the town of Texas City, Texas. The explosion resulted from the following reaction:

$$2NH_4NO_3\,(s) \rightarrow 2N_2\,(g) + 4H_2O\,(g) + O_2\,(g) \qquad \textbf{(Chapter 11.3.2)}$$

Construct a table showing how to interpret the information in the equation in terms of

1. individual molecules and ions.
2. moles of reactants and products.
3. grams of reactants and products given 2 mol of ammonium nitrate.
4. numbers of molecules or formula units of reactants and products given 2 mol of ammonium nitrate.

Answer:

	$2NH_4NO_3(s)$	→	$2N_2(g)$	+	$4H_2O(g)$	+	$O_2(g)$
a.	$2NH_4^+$ ions and $2NO_3^-$ ions		2 molecules		4 molecules		1 molecule
b.	2 mol		2 mol		4 mol		1 mol
c.	160.0864 g		56.0268 g		72.0608 g		31.9988 g
d.	1.204×10^{24} formula units		1.204×10^{24} molecules		2.409×10^{24} molecules		6.022×10^{23} molecules



Ammonium nitrate can be hazardous. *This aerial photograph of Texas City, Texas, shows the devastation caused by the explosion of a shipload of ammonium nitrate on April 16, 1947.*

Balancing Simple Chemical Equations

When a chemist encounters a new reaction, it does not usually come with a label that shows the balanced chemical equation. Instead, the chemist must identify the reactants and products and then write them in the form of a chemical equation that may or may not be balanced as first written. Consider, for example, the combustion of *n*-heptane (C_7H_{16}), an important component of gasoline:

$$C_7H_{16}\,(l) + O_2\,(g) \rightarrow CO_2\,(g) + H_2O\,(g) \tag{11.3.3}$$

The complete combustion of any hydrocarbon with sufficient oxygen *always* yields carbon dioxide and water (Figure 11.3.3).



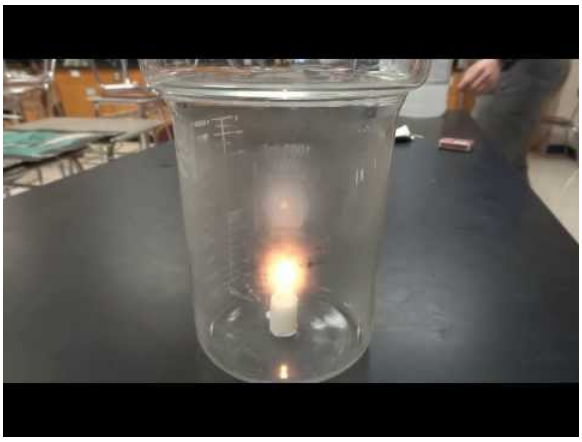


Figure 11.3.3 An Example of a Combustion Reaction *The wax in a candle is a high-molecular-mass hydrocarbon, which produces gaseous carbon dioxide and water vapor in a combustion reaction. When the candle is allowed to burn inside a flask, drops of water, one of the products of combustion, form which we can verify using cobalt chloride test paper. We can demonstrate that carbon dioxide is a product by precipitating calcium carbonate from limewater.*.

Equation 11.3.3 is not balanced: the numbers of each type of atom on the reactant side of the equation (7 carbon atoms, 16 hydrogen atoms, and 2 oxygen atoms) is not the same as the numbers of each type of atom on the product side (1 carbon atom, 2 hydrogen atoms, and 3 oxygen atoms). Consequently, we must adjust the coefficients of the reactants and products to give the same numbers of atoms of each type on both sides of the equation. Because the identities of the reactants and products are fixed, we *cannot* balance the equation by changing the subscripts of the reactants or the products. To do so would change the chemical identity of the species being described, as illustrated in Figure 11.3.4.

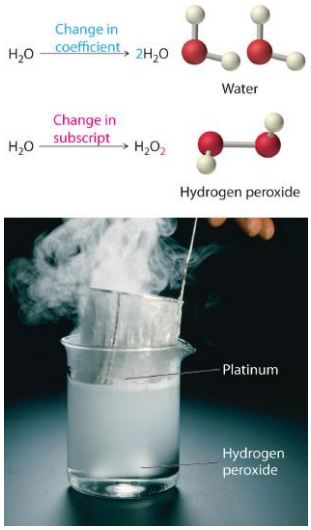


Figure 11.3.4 Balancing Equations

You cannot change subscripts in a chemical formula to balance a chemical equation; you can change only the coefficients. Changing subscripts changes the ratios of atoms in the molecule and the resulting chemical properties. For example, water (H_2O) and hydrogen peroxide (H_2O_2) are chemically distinct substances. H_2O_2 decomposes to H_2O and O_2 gas when it comes in contact with the metal platinum, whereas no such reaction occurs between water and platinum.

The simplest and most generally useful method for balancing chemical equations is “inspection,” better known as trial and error. We present an efficient approach to balancing a chemical equation using this method.

Steps in Balancing a Chemical Equation

1. Identify the most complex substance.
2. Beginning with that substance, choose an element that appears in only one reactant and one product, if possible. Adjust the coefficients to obtain the same number of atoms of this element on both sides.
3. Balance polyatomic ions (if present) as a unit.
4. Balance the remaining atoms, usually ending with the least complex substance and using fractional coefficients if necessary. If a fractional coefficient has been used, multiply both sides of the equation by the denominator to obtain whole numbers for the coefficients.
5. Count the numbers of atoms of each kind on both sides of the equation to be sure that the chemical equation is balanced.

To demonstrate this approach, let's use the combustion of *n*-heptane (Equation 11.3.3) as an example.

1. **Identify the most complex substance.** The most complex substance is the one with the largest number of different atoms, which is C_7H_{16}. We will assume initially that the final balanced chemical equation contains 1 molecule or formula unit of this substance.
2. **Adjust the coefficients.** Try to adjust the coefficients of the molecules on the other side of the equation to obtain the same numbers of atoms on both sides. Because one molecule of *n*-heptane contains 7 carbon atoms, we need 7 CO_2 molecules, each of which contains 1 carbon atom, on the right side:

$$C_7H_{16} + O_2 \rightarrow 7CO_2 + H_2O \tag{11.3.3}$$

3. **Balance polyatomic ions as a unit.** There are no polyatomic ions to be considered in this reaction.
4. **Balance the remaining atoms.** Because one molecule of *n*-heptane contains 16 hydrogen atoms, we need 8 H_2O molecules, each of which contains 2 hydrogen atoms, on the right side:

$$C_7H_{16} + O_2 \rightarrow 7CO_2 + 8H_2O \tag{11.3.4}$$

5. The carbon and hydrogen atoms are now balanced, but we have 22 oxygen atoms on the right side and only 2 oxygen atoms on the left. We can balance the oxygen atoms by adjusting the coefficient in front of the least complex substance, O_2, on the reactant side:

$$C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O \tag{11.3.5}$$

6. **Check your work.** The equation is now balanced, and there are no fractional coefficients: there are 7 carbon atoms, 16 hydrogen atoms, and 22 oxygen atoms on each side. *Always check to be sure that a chemical equation is balanced.*

The assumption that the final balanced chemical equation contains only one molecule or formula unit of the most complex substance is not always valid, but it is a good place to start. Consider, for example, a similar reaction, the combustion of isooctane (C_8H_{18}). Because the combustion of any hydrocarbon with oxygen produces carbon dioxide and water, the unbalanced chemical equation is as follows:

$$C_8H_{18}\,(l) + O_2\,(g) \rightarrow CO_2\,(g) + H_2O\,(g) \tag{11.3.6}$$

1. **Identify the most complex substance.** Begin the balancing process by assuming that the final balanced chemical equation contains a single molecule of isooctane.
2. **Adjust the coefficients.** The first element that appears only once in the reactants is carbon: 8 carbon atoms in isooctane means that there must be 8 CO_2 molecules in the products:

$$C_8H_{18}\,(l) + O_2\,(g) \rightarrow 8CO_2\,(g) + H_2O\,(g) \tag{11.3.7}$$

3. **Balance polyatomic ions as a unit.** This step does not apply to this equation.
4. **Balance the remaining atoms.** Eighteen hydrogen atoms in isooctane means that there must be 9 H_2O molecules in the products:

$$C_8H_{18}\,(l) + O_2\,(g) \;\rightarrow\; 8CO_2\,(g) + 9H_2O\,(g) \tag{11.3.8}$$

The carbon and hydrogen atoms are now balanced, but we have 25 oxygen atoms on the right side and only 2 oxygen atoms on the left. We can balance the least complex substance, O_2, but because there are 2 oxygen atoms per O_2 molecule, we must use a fractional coefficient (25/2) to balance the oxygen atoms:

$$C_8H_{18}\,(l) + 25/2\;O_2\,(g) \;\rightarrow\; 8CO_2\,(g) + 9H_2O\,(g) \tag{11.3.9}$$

Equation 11.3.9 is now balanced, but we usually write equations with whole-number coefficients. We can eliminate the fractional coefficient by multiplying all coefficients on both sides of the chemical equation by 2:

$$2C_8H_{18}\,(l) + 25O_2\,(g) \;\rightarrow\; 16CO_2\,(g) + 18H_2O\,(g) \tag{11.3.10}$$

5. **Check your work.** The balanced chemical equation has 16 carbon atoms, 36 hydrogen atoms, and 50 oxygen atoms on each side.

Balancing equations requires some practice on your part as well as some common sense. If you find yourself using very large coefficients or if you have spent several minutes without success, go back and make sure that you have written the formulas of the reactants and products correctly.

Example 11.3.2

The reaction of the mineral hydroxyapatite [$Ca_5(PO_4)_3(OH)$] with phosphoric acid and water gives $Ca(H_2PO_4)_2{\cdot}H_2O$ (calcium dihydrogen phosphate monohydrate). Write and balance the equation for this reaction.

Given: reactants and product

Asked for: balanced chemical equation

Strategy:

A Identify the product and the reactants and then write the unbalanced chemical equation.

B Follow the steps for balancing a chemical equation.

Solution:

We must first identify the product and reactants and write an equation for the reaction. The formulas for hydroxyapatite and calcium dihydrogen phosphate monohydrate are given in the problem. Recall from Chapter 10.5 that phosphoric acid is H_3PO_4. The initial (unbalanced) equation is as follows:

$$Ca_5(PO_4)_3\,(OH)\,(s) + H_3PO_4\,(aq) + H_2O\,(l) \;\rightarrow\; Ca(H_2PO_4)_2 \cdot H_2O\,(s) \tag{Chapter 11.3.3}$$

1. **Identify the most complex substance.** We start by assuming that only one molecule or formula unit of the most complex substance, $Ca_5(PO_4)_3(OH)$, appears in the balanced chemical equation.

2. **Adjust the coefficients.** Because calcium is present in only one reactant and one product, we begin with it. One formula unit of $Ca_5(PO_4)_3(OH)$ contains 5 calcium atoms, so we need 5 $Ca(H_2PO_4)_2{\cdot}H_2O$ on the right side:

$$Ca_5(PO_4)_3\,(OH) + H_3PO_4 + H_2O \;\rightarrow\; 5Ca(H_2PO_4)_2 \cdot H_2O \tag{Chapter 11.3.4}$$

3. **Balance polyatomic ions as a unit.** It is usually easier to balance an equation if we recognize that certain combinations of atoms occur on both sides. In this equation, the polyatomic phosphate ion (PO_4^{3-}), shows up in three places.In H_3PO_4, the phosphate ion is combined with three H^+ ions to make phosphoric acid (H_3PO_4), whereas in $Ca(H_2PO_4)_2{\cdot}H_2O$ it is combined with two H^+ ions to give the dihydrogen phosphate ion. Thus it is easier to balance PO_4 as a unit rather than counting individual phosphorus and oxygen atoms. There are 10 PO_4 units on the right side but only 4 on the left. The simplest way to balance the PO_4 units is to place a coefficient of 7 in front of H_3PO_4:

$$Ca_5(PO_4)_3\,(OH) + 7H_3PO_4 + H_2O \;\rightarrow\; 5Ca(H_2PO_4)_2 \cdot H_2O \tag{Chapter 11.3.5}$$

Although OH^- is also a polyatomic ion, it does not appear on both sides of the equation. So oxygen and hydrogen must be balanced separately.

4. **Balance the remaining atoms.** We now have 30 hydrogen atoms on the right side but only 24 on the left. We can balance the hydrogen atoms using the least complex substance, H_2O, by placing a coefficient of 4 in front of H_2O on the left side, giving a total of 4 H_2O molecules:

$$Ca_5(PO_4)_3(OH)(s) + 7H_3PO_4(aq) + 4H_2O(l) \rightarrow 5Ca(H_2PO_4)_2 \cdot H_2O(s) \quad \text{(Chapter 11.3.6)}$$

The equation is now balanced. Even though we have not explicitly balanced the oxygen atoms, there are 45 oxygen atoms on each side.

5. **Check your work.** Both sides of the equation contain 5 calcium atoms, 7 phosphorus atoms, 30 hydrogen atoms, and 45 oxygen atoms.

Exercise

Fermentation is a biochemical process that enables yeast cells to live in the absence of oxygen. Humans have exploited it for centuries to produce wine and beer and make bread rise. In fermentation, sugars such as glucose are converted to ethanol and carbon dioxide. Write a balanced chemical reaction for the fermentation of glucose.



Commercial use of fermentation. *(a) Microbrewery vats are used to prepare beer. (b) The fermentation of glucose by yeast cells is the reaction that makes beer production possible.*

Answer: $C_6H_{12}O_6(s) \rightarrow 2C_2H_5OH(l) + 2CO_2(g)$

Summary

In a chemical reaction, one or more substances are transformed to new substances. A chemical reaction is described by a **chemical equation**, an expression that gives the identities and quantities of the substances involved in a reaction. A chemical equation shows the starting compound(s)—the **reactants**—on the left and the final compound(s)—the **products**—on the right, separated by an arrow. In a *balanced chemical equation*, the numbers of atoms of each element and the total charge are the same on both sides of the equation. The number of atoms, molecules, or formula units of a reactant or product in a balanced chemical equation is the **coefficient** of that species. The **mole ratio** of two substances in a chemical reaction is the ratio of their coefficients in the balanced chemical equation.

Key Takeaway

- A chemical reaction is described by a chemical equation that gives the identities and quantities of the reactants and the products.

Conceptual Problems

1. How does a balanced chemical equation agree with the law of definite proportions?
2. What is the difference between S_8 and 8S? Use this example to explain why subscripts in a formula must not be changed.

3. What factors determine whether a chemical equation is balanced?
4. What information can be obtained from a balanced chemical equation? Does a balanced chemical equation give information about the rate of a reaction?

Numerical Problems

1. Balance each chemical equation.
    1. $KI(aq) + Br_2(l) \rightarrow KBr(aq) + I_2(s)$
    2. $MnO_2(s) + HCl(aq) \rightarrow MnCl_2(aq) + Cl_2(g) + H_2O(l)$
    3. $Na_2O(s) + H_2O(l) \rightarrow NaOH(aq)$
    4. $Cu(s) + AgNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + Ag(s)$
    5. $SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$
    6. $S_2Cl_2(l) + NH_3(l) \rightarrow S_4N_4(s) + S_8(s) + NH_4Cl(s)$
2. Balance each chemical equation.
    1. $Be(s) + O_2(g) \rightarrow BeO(s)$
    2. $N_2O_3(g) + H_2O(l) \rightarrow HNO_2(aq)$
    3. $Na(s) + H_2O(l) \rightarrow NaOH(aq) + H_2(g)$
    4. $CaO(s) + HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l)$
    5. $CH_3NH_2(g) + O_2(g) \rightarrow H_2O(g) + CO_2(g) + N_2(g)$
    6. $Fe(s) + H_2SO_4(aq) \rightarrow FeSO_4(aq) + H_2(g)$
3. Balance each chemical equation.
    1. $N_2O_5(g) \rightarrow NO_2(g) + O_2(g)$
    2. $NaNO_3(s) \rightarrow NaNO_2(s) + O_2(g)$
    3. $Al(s) + NH_4NO_3(s) \rightarrow N_2(g) + H_2O(l) + Al_2O_3(s)$
    4. $C_3H_5N_3O_9(l) \rightarrow CO_2(g) + N_2(g) + H_2O(g) + O_2(g)$
    5. reaction of butane with excess oxygen
    6. $IO_2F(s) + BrF_3(l) \rightarrow IF_5(l) + Br_2(l) + O_2(g)$
4. Balance each chemical equation.
    1. $H_2S(g) + O_2(g) \rightarrow H_2O(l) + S_8(s)$
    2. $KCl(aq) + HNO_3(aq) + O_2(g) \rightarrow KNO_3(aq) + Cl_2(g) + H_2O(l)$
    3. $NH_3(g) + O_2(g) \rightarrow NO(g) + H_2O(g)$
    4. $CH_4(g) + O_2(g) \rightarrow CO(g) + H_2(g)$
    5. $NaF(aq) + Th(NO_3)_4(aq) \rightarrow NaNO_3(aq) + ThF_4(s)$
    6. $Ca_5(PO_4)_3F(s) + H_2SO_4(aq) + H_2O(l) \rightarrow H_3PO_4(aq) + CaSO_4{\cdot}2H_2O(s) + HF(aq)$
5. Balance each chemical equation.
    1. $NaCl(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + HCl(g)$
    2. $K(s) + H_2O(l) \rightarrow KOH(aq) + H_2(g)$
    3. reaction of octane with excess oxygen
    4. $S_8(s) + Cl_2(g) \rightarrow S_2Cl_2(l)$
    5. $CH_3OH(l) + I_2(s) + P_4(s) \rightarrow CH_3I(l) + H_3PO_4(aq) + H_2O(l)$
    6. $(CH_3)_3Al(s) + H_2O(l) \rightarrow CH_4(g) + Al(OH)_3(s)$
6. Write a balanced chemical equation for each reaction.
    1. Aluminum reacts with bromine.
    2. Sodium reacts with chlorine.
    3. Aluminum hydroxide and acetic acid react to produce aluminum acetate and water.
    4. Ammonia and oxygen react to produce nitrogen monoxide and water.
    5. Nitrogen and hydrogen react at elevated temperature and pressure to produce ammonia.

6. An aqueous solution of barium chloride reacts with a solution of sodium sulfate.

7. Write a balanced chemical equation for each reaction.

    1. Magnesium burns in oxygen.
    2. Carbon dioxide and sodium oxide react to produce sodium carbonate.
    3. Aluminum reacts with hydrochloric acid.
    4. An aqueous solution of silver nitrate reacts with a solution of potassium chloride.
    5. Methane burns in oxygen.
    6. Sodium nitrate and sulfuric acid react to produce sodium sulfate and nitric acid.

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Chapter 11.4: Stoichiometry

Learning Objective

- To calculate the quantities of compounds produced or consumed in a chemical reaction.

A balanced chemical equation gives the identity of the reactants and the products as well as the accurate number of molecules or moles of each that are consumed or produced. StoichiometryA collective term for the quantitative relationships between the masses, the numbers of moles, and the numbers of particles (atoms, molecules, and ions) of the reactants and the products in a balanced chemical equation. is a collective term for the quantitative relationships between the masses, the numbers of moles, and the numbers of particles (atoms, molecules, and ions) of the reactants and the products in a balanced chemical equation. A stoichiometric quantityThe amount of product or reactant specified by the coefficients in a balanced chemical equation. is the amount of product or reactant specified by the coefficients in a balanced chemical equation. In Section 11.3 , for example, you learned how to express the stoichiometry of the reaction for the ammonium dichromate volcano in terms of the atoms, ions, or molecules involved and the numbers of moles, grams, and formula units of each (recognizing, for instance, that 1 mol of ammonium dichromate produces 4 mol of water). This section describes how to use the stoichiometry of a reaction to answer questions like the following: How much oxygen is needed to ensure complete combustion of a given amount of isooctane? (This information is crucial to the design of nonpolluting and efficient automobile engines.) How many grams of pure gold can be obtained from a ton of low-grade gold ore? (The answer determines whether the ore deposit is worth mining.) If an industrial plant must produce a certain number of tons of sulfuric acid per week, how much elemental sulfur must arrive by rail each week?

All these questions can be answered using the concepts of the mole and molar and formula masses, along with the coefficients in the appropriate balanced chemical equation.

Stoichiometry Problems

When we carry out a reaction in either an industrial setting or a laboratory, it is easier to work with *masses* of substances than with the numbers of molecules or moles. We will first present the method used in most other books for converting from the mass of any reactant or product to the mass of any other reactant or product using a balanced chemical equation outlined in Figure 11.4.1 and described below. We will then show how this can be simplified by into a tabular algorithm. The key to everything is to start with a balanced chemical reaction

Steps in Converting between Masses of Reactant and Product

1. Convert the mass of one substance (substance A) to the corresponding number of moles using its molar mass.
2. From the balanced chemical equation, obtain the number of moles of another substance (B) from the number of moles of substance A using the appropriate mole ratio (the ratio of their coefficients).
3. Convert the number of moles of substance B to mass using its molar mass. It is important to remember that some species are in excess by virtue of the reaction conditions. For example, if a substance reacts with the oxygen in air, then oxygen is in obvious (but unstated) excess.

Converting amounts of substances to moles—and vice versa—is the key to all stoichiometry problems, whether the amounts are given in units of mass (grams or kilograms), weight (pounds or tons), or volume (liters or gallons).

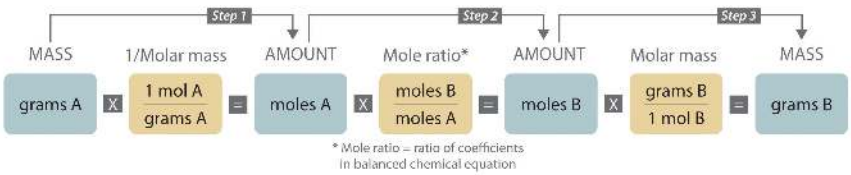


Figure 11.4.1 A Flowchart for Stoichiometric Calculations Involving Pure Substances *The molar masses of the reactants and the products are used as conversion factors so that you can calculate the mass of product from the mass of reactant and vice versa.*

To illustrate this procedure, let's return to the combustion of glucose. We saw earlier that glucose reacts with oxygen to produce carbon dioxide and water:

$$C_6H_{12}O_6\,(s) + 6O_2\,(g) \rightarrow 6CO_2\,(g) + 6H_2O\,(l) \tag{11.4.1}$$

Just before a chemistry exam, suppose a friend reminds you that glucose is the major fuel used by the human brain. You therefore decide to eat a candy bar to make sure that your brain doesn't run out of energy during the exam (even though there is no direct evidence that consumption of candy bars improves performance on chemistry exams). If a typical 2 oz candy bar contains the equivalent of 45.3 g of glucose and the glucose is completely converted to carbon dioxide during the exam, how many grams of carbon dioxide will you produce and exhale into the exam room?

The initial step in solving a problem of this type must be to write the balanced chemical equation for the reaction. Inspection of Equation 11.4.1 shows that it is balanced as written, so we can proceed to the strategy outlined in Figure 11.4.1, adapting it as follows:

1. Use the molar mass of glucose (to one decimal place, 180.2 g/mol) to determine the number of moles of glucose in the candy bar:

$$moles\ glucose = 45.3\ \cancel{g\ glucose} \times \frac{1\ mol\ glucose}{180.2\ \cancel{g\ glucose}} = 0.251 mol glucose$$

2. According to the balanced chemical equation, 6 mol of CO_2 is produced per mole of glucose; the mole ratio of CO_2 to glucose is therefore 6:1. If we divide the number of moles of CO2 by its stoichiometric coefficient 6 and the number of moles of glucose by its stoichiometric coefficient of one the ratios, which can be called the reaction equivalents, are equal. We will use this below in demonstrating another method of solving stoichiometric problems of all types

$$\frac{moles\ CO_2}{6\ mol\ CO_2} = \frac{moles\ glucose}{1\ mol\ glucose}$$

The number of moles of CO_2 produced is thus

$$\begin{aligned} moles CO_2 &= mol\ glucose \times \frac{6\ mol\ CO_2}{1\ mol\ glucose} \\ &= 0.251\ \cancel{mol\ glucose} \times \frac{6\ mol\ CO_2}{1\ \cancel{mol\ glucose}} \\ &= 1.51\ mol\ CO_2 \end{aligned}$$

3. Use the molar mass of CO_2 (44.010 g/mol) to calculate the mass of CO_2 corresponding to 1.51 mol of CO_2:

$$mass\ of CO_2 = 1.51\ \cancel{mol\ CO_2} \times \frac{44.010\ g\ CO_2}{1;\ \cancel{mol\ CO_2}} = 66.5\ g\ CO_2$$

4 We can summarize these operations as follows:

$$45.3\ g\ glucose \underset{step\ 1}{\times \frac{1\ mol\ glucose}{180.2\ g\ glucose}} \underset{step\ 2}{\times \frac{6\ mol\ CO_2}{1\ mol\ glucose}} \underset{step\ 3}{\times \frac{44.010\ g\ CO_2}{1\ mol\ CO_2}} = 66.4\ g\ CO_2$$

Discrepancies between the two values are attributed to rounding errors resulting from using stepwise calculations in steps 1–3. In Chapter 6, you discovered that this amount of gaseous carbon dioxide occupies an enormous volume—more than 33 L. We could use similar methods to calculate the amount of oxygen consumed or the amount of water produced.

We just used the balanced chemical equation to calculate the mass of product that is formed from a certain amount of reactant. We can also use the balanced chemical equation to determine the masses of reactants that are necessary to form a certain amount of product or, as shown in Example 11.4.1, the mass of one reactant that is required to consume a given mass of another reactant.

There is another way of dealing with such problems which is easier to carry out. It starts by writing the balanced chemical equation and then drawing a table with five rows and as many columns as there are reactants and products and writing in the given mass.

	$C_6H_{12}O_6(s)$	$+ 6O_2(g)$	$\rightarrow 6CO_2(g)$	$+ 6H_2O(l)$
Mass (g)	45.3			
Molecular Weight (g/mol)				
Moles				
Stoichiometric Coefficients				
Stoichiometric Equivalents				

We then simply fill in the stoichiometric coefficients and the molecular weights of the reactants and the products that we are concerned with

	$C_6H_{12}O_6(s)$	$+ 6O_2(g)$	$\rightarrow 6CO_2(g)$	$+ 6H_2O(l)$
Mass (g)	45.3			
Molecular Weight (g/mol)	180.2			
Moles				
Stoichiometric Coefficients	1		6	
Stoichiometric Equivalents				

Divide the mass of the glucose by the molecular weight to find the number of moles of glucose. In the next step divide the number of moles by the stoichiometric coefficient to find the stoichiometric equivalents (this is the same as step 2a above. The rule is to divide going down the table. You divide the Mass by the Molecular Weight to find the number of Moles, you divide the number of Moles by the Stoichiometric Coefficients to find the number of Stoichiometric Equivalents

	$C_6H_{12}O_6(s)$	$+ 6O_2(g)$	$\rightarrow 6CO_2(g)$	$+ 6H_2O(l)$
Mass (g)	45.3			
Molecular Weight (g/mol)	180.2			
Moles	0.251			
Stoichiometric Coefficients	1		6	
Stoichiometric Equivalents	0.251			

For each of the products and reactants, the Stoichiometric Equivalents will be the same (they are equivalent, simply copy across).

	$C_6H_{12}O_6(s)$	$+ 6O_2(g)$	$\rightarrow 6CO_2(g)$	$+ 6H_2O(l)$
Mass (g)	45.3		66.4	
Molecular Weight (g/mol)	180.2		44.01	
Moles	0.251		1.51	
Stoichiometric Coefficients	1		6	
Stoichiometric Equivalents	0.251		0.251	

Now multiply going up. Multiply the Stoichiometric Equivalents by the Stoichiometric Coefficient to find the number of Moles of CO_2 produced, then multiply the number of Moles of COsub>2 by the Molecular Weight of CO_2 to find the Mass of CO_2 produced in the reaction.

Close inspection of both methods will show that they are equivalent. The table has the advantage that it is a "fill in the spaces" exercise and practically automatic. In fact you could easily write and Excel spreadsheet to do it. Further, if we want to answer additional questions such as how much water will be produced or how much oxygen will be consumed little extra work is required. As you will see the table method is also simpler for more complicated questions such as limiting reactant problems.

As an example, we can now figure out how much oxygen is used up and how much water will be produced by the reaction. Simply repeat the process we used for calculating the amount of CO_2 that was produced

	$C_6H_{12}O_6(s)$	$+ 6O_2(g)$	$\rightarrow 6CO_2(g)$	$+ 6H_2O(l)$
Mass (g)	45.3	48.32	66.4	27.2
Molecular Weight (g/mol)	180.2 ↓	32.00 ↑	44.01 ↑	18.02 ↑
Moles	0.251 ↓	1.51 ↑	1.51 ↑	1.51 ↑
Stoichiometric Coefficients	1 ↓	6 ↑	6 ↑	6 ↑
Stoichiometric Equivalents	0.251 → →	0.251 → →	0.251 → →	0.251

The Stoichiometric Equivalents for all of the reactants and products are the same. Once the Stoichiometric Equivalents (SE) have been determined from the given information, to find the number of Moles produced or consumed one simply multiplies the SE by the Stoichiometric Coefficients to find the number of moles and then to find the mass you multiply the number of Moles by the Molecular Weight.

The rule is divide going down to find the SE and then multiply going up to find the mass.

Example 11.4.1

The combustion of hydrogen with oxygen to produce gaseous water is extremely vigorous, producing one of the hottest flames known. Because so much energy is released for a given mass of hydrogen or oxygen, this reaction was used to fuel the NASA (National Aeronautics and Space Administration) space shuttles, which have recently been retired from service. NASA engineers calculated the exact amount of each reactant needed for the flight to make sure that the shuttles did not carry excess fuel into orbit. Calculate how many tons of hydrogen a space shuttle needed to carry for each 1.00 tn of oxygen (1 tn = 2000 lb).



The US space shuttle *Discovery* during liftoff. The large cylinder in the middle contains the oxygen and hydrogen that fueled the shuttle's main engine.

Given: reactants, products, and mass of one reactant

Asked for: mass of other reactant

Strategy:

A Write the balanced chemical equation for the reaction.

B Convert mass of oxygen to moles. From the mole ratio in the balanced chemical equation, determine the number of moles of hydrogen required. Then convert the moles of hydrogen to the equivalent mass in tons.

Solution:

We use the same general strategy for solving stoichiometric calculations as in the preceding example. Because the amount of oxygen is given in tons rather than grams, however, we also need to convert tons to units of mass in grams. Another conversion is needed at the end to report the final answer in tons.

A We first use the information given to write a balanced chemical equation. Because we know the identity of both the reactants and the product, we can write the reaction as follows:

$$H_2\,(g) + O_2\,(g) \;\rightarrow H_2O\,(g) \qquad \text{(Chapter 11.4.1)}$$

This equation is not balanced because there are two oxygen atoms on the left side and only one on the right. Assigning a coefficient of 2 to both H_2O and H_2 gives the balanced chemical equation:

$$2H_2\,(g) + O_2\,(g) \;\rightarrow 2H_2O\,(g) \qquad \text{(Chapter 11.4.2)}$$

Thus 2 mol of H_2 react with 1 mol of O_2 to produce 2 mol of H_2O.

B To convert tons of oxygen to units of mass in grams, we multiply by the appropriate conversion factors:

$$mass\ of\ O_2 = 1.0\ \cancel{tn} \times \frac{2000\ \cancel{lb}}{\cancel{tn}} \times \frac{4453.6\ g}{\cancel{lb}} = 9.07 \times 10^5\ g\ O_2$$

Using the molar mass of O_2 (32.00 g/mol to four significant figures) we can calculate the number of moles of O_2 contained in this mass of O_2

$$mol\ O_2 = 9.07 \times 10^5\ \cancel{g\,O_2} \times \frac{1\ mol\ O_2}{32.00\ \cancel{g\,O_2}} = 2.83 \times 10^4\ mol\ O_2$$

1. Now use the coefficients in the balanced chemical equation to obtain the number of moles of H_2 needed to react with this number of moles of O_2:
2. The molar mass of H_2 (2.016 g/mol) allows us to calculate the corresponding mass of H_2:

   Finally, convert the mass of H_2 to the desired units (tons) by using the appropriate conversion factors:

The space shuttle had to be designed to carry 0.126 tn of H_2 for each 1.00 tn of O_2. Even though 2 mol of H_2 are needed to react with each mole of O_2, the molar mass of H_2 is so much smaller than that of O_2 that only a relatively small mass of H_2 is needed compared to the mass of O_2.

	$2H_2(s)$	$+ O_2(g)$	$\rightarrow 2H_2O(g)$
Mass (g)	1.14×10^5	9.07×10^5	
Molecular Weight (g/mol)	2.02 ↑	32.00 ↓	
Moles	5.66×10^4 ↑	2.83×10^4 ↓	
Stoichiometric Coefficients	2 ↑	1 ↓	
Stoichiometric Equivalents	2.83×10^4	← ← 2.83×10^4	

Exercise

Alchemists produced elemental mercury by roasting the mercury-containing ore cinnabar (HgS) in air:

$$HgS\,(s) + O_2\,(g) \rightarrow Hg\,(l) + SO_2\,(g) \qquad \text{(Chapter 11.4.3)}$$

The volatility and toxicity of mercury make this a hazardous procedure, which likely shortened the life span of many alchemists. Given 100 g of cinnabar, how much elemental mercury can be produced from this reaction?

Answer: 86.2 g

Limiting Reactants

In all the examples discussed thus far, the reactants were assumed to be present in stoichiometric quantities. Consequently, none of the reactants was left over at the end of the reaction. This is often desirable, as in the case of a space shuttle, where excess oxygen or hydrogen was not only extra freight to be hauled into orbit but also an explosion hazard. More often, however, reactants are present in mole ratios that are not the same as the ratio of the coefficients in the balanced chemical equation. As a result, one or more of them will not be used up completely but will be left over when the reaction is completed. In this situation, the amount of product that can be obtained is limited by the amount of only one of the reactants. The reactant that restricts the amount of product obtained is called the limiting reactantThe reactant that restricts the amount of product obtained in a chemical reaction.. The reactant that remains after a reaction has gone to completion is *in excess*.

To be certain you understand these concepts, let's first consider a nonchemical example. Assume you have invited some friends for dinner and want to bake brownies for dessert. You find two boxes of brownie mix in your pantry and see that each package requires two eggs. The balanced equation for brownie preparation is thus

$$1\ box\ mix + 2\ eggs \rightarrow 1\ batch\ brownies \qquad (11.4.2)$$

If you have a dozen eggs, which ingredient will determine the number of batches of brownies that you can prepare? Because each box of brownie mix requires two eggs and you have two boxes, you need four eggs. Twelve eggs is eight more eggs than you need. Although the ratio of eggs to boxes in Equation 11.4.2 is 2:1, the ratio in your possession is 6:1. Hence the eggs are the ingredient (reactant) present in excess, and the brownie mix is the limiting reactant (Figure 11.4.2). Even if you had a refrigerator full of eggs, you could make only two batches of brownies.

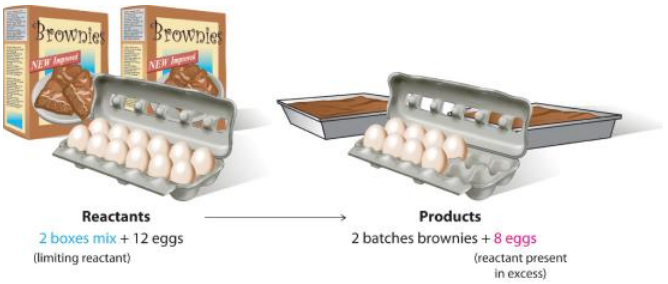
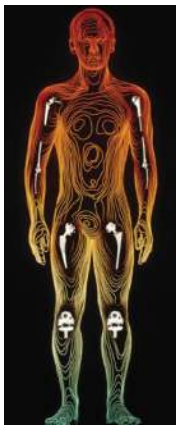


Figure 11.4.2 The Concept of a Limiting Reactant in the Preparation of Brownies

Let's now turn to a chemical example of a limiting reactant: the production of pure titanium. This metal is fairly light (45% lighter than steel and only 60% heavier than aluminum) and has great mechanical strength (as strong as steel and twice as strong as aluminum). Because it is also highly resistant to corrosion and can withstand extreme temperatures, titanium has many applications in the aerospace industry. Titanium is also used in medical implants and portable computer housings because it is light and resistant to corrosion. Although titanium is the ninth most common element in Earth's crust, it is relatively difficult to extract from its ores. In the first step of the extraction process, titanium-containing oxide minerals react with solid carbon and chlorine gas to form titanium tetrachloride ($TiCl_4$) and carbon dioxide. Titanium tetrachloride is then converted to metallic titanium by reaction with magnesium metal at high temperature:

$$TiCl_4\,(g) + 2Mg\,(l) \rightarrow Ti\,(s) + 2MgCl_2\,(l) \tag{11.4.3}$$

Because titanium ores, carbon, and chlorine are all rather inexpensive, the high price of titanium (about $100 per kilogram) is largely due to the high cost of magnesium metal. Under these circumstances economically one would want to maximize the use of magnesium making sure that none was left during the production of titanium metal. If a little bit of the titanium (IV) chloride were left over that would not be so concerning.



Medical use of titanium. *Here is an example of its successful use in joint replacement implants.*

Suppose you have 1.00 kg of titanium tetrachloride and 200 g of magnesium metal. How much titanium metal can you produce according to Equation 11.4.3? Solving this type of problem requires that you carry out the following steps:

1. Determine the number of moles of each reactant.
2. Compare the mole ratio of the reactants with the ratio in the balanced chemical equation to determine which reactant is limiting.
3. Calculate the number of moles of product that can be obtained from the limiting reactant.
4. Convert the number of moles of product to mass of product.

1. To determine the number of moles of reactants present, you must calculate or look up their molar masses: 189.679 g/mol for titanium tetrachloride and 24.305 g/mol for magnesium. The number of moles of each is calculated as follows:

$$moles TiCl_4 = \frac{mass\ TiCl_4}{molar\ mass\ TiCl_4}$$

$$= 1000\ \cancel{g\ TiCl_4} \times \frac{1\ mol\ TiCl_4}{189.679\ \cancel{g\ TiCl_4}} = 5.272\ mol\ TiCl_4$$

$$moles Mg = \frac{mass\ Mg}{molar\ mass\ Mg}$$

$$= 200\ \cancel{g\ Mg} \times \frac{1\ mol\ Mg}{24.305\ \cancel{g\ Mg}} = 8.23\ mol\ Mg$$

2. You have more moles of magnesium than of titanium tetrachloride, but the ratio is only

$$\frac{mol\ Mg}{mol\ TiCl_4} = \frac{8.23\ mol}{5.272\ mol} = 1.56 \qquad \text{(Chapter 11.4.4)}$$

Because the ratio of the coefficients in the balanced chemical equation is

$$\frac{2\ mol\ Mg}{1 mol\ TiCl_4} = 2 \qquad \text{(Chapter 11.4.5)}$$

you do not have enough magnesium to react with all the titanium tetrachloride. If this point is not clear from the mole ratio, you should calculate the number of moles of one reactant that is required for complete reaction of the other reactant. For example, you have 8.23 mol of Mg, so you need (8.23 ÷ 2) = 4.12 mol of $TiCl_4$ for complete reaction. Because you have 5.272 mol of $TiCl_4$, titanium tetrachloride *is present in excess*. Conversely, 5.272 mol of $TiCl_4$ requires 2 × 5.272 = 10.54 mol of Mg, but you have only 8.23 mol. So *magnesium is the limiting reactant*.

3. Because magnesium is the limiting reactant, the number of moles of magnesium determines the number of moles of titanium that can be formed:

$$moles\ Ti = 8.23\ \cancel{mol\ Mg} \times \frac{1\ molTi}{2\ \cancel{mol\ Mg}} = 4.12\ mol\ Ti$$

Thus only 4.12 mol of Ti can be formed.

4. To calculate the mass of titanium metal that you can obtain, multiply the number of moles of titanium by the molar mass of titanium (47.867 g/mol):

$$moles\ Ti = mass\ Ti \times molar\ mass\ Ti \qquad \text{(Chapter 11.4.6)}$$
$$= 4.12\ \cancel{mol\ Ti} \times \frac{47.867\ g\ Ti}{1\ mol\ Ti} = 197\ g\ Ti$$

Here is a simple and reliable way to identify the limiting reactant in any problem of this sort:

1. Calculate the number of moles of each reactant present: 5.272 mol of $TiCl_4$ and 8.23 mol of Mg.
2. Divide the actual number of moles of each reactant by its stoichiometric coefficient in the balanced chemical equation:

$$TiCl_4 : \frac{5.272\ mol\ (actual)}{1\ mol\ \ (stoich)} = 5.272 \quad Mg : \frac{8.23\ mol\ (actual)}{2\ mol\ \ (stoich)} = 4.12 \qquad \text{(Chapter 11.4.7)}$$

3. The reactant with the smallest mole ratio is limiting. Magnesium, with a calculated stoichiometric mole ratio of 4.12, is the limiting reactant.

Here is is a narrated PowerPoint presentation for the problem done using the Table method.



oblem is written out starting with the balanced reaction, the Mass of the reactants and the Molecular Mass of he Mass of both reactants by the Molecular Weight to find the number of Moles of each reactant. After that divide the number of Moles by the Stoichiometric Coefficients to find the Stoichiometric Equivalents of each.

	$TiCl_4(s)$	+ 2Mg(s)	→ $2MgCl_2(s)$	+ Ti(s)
Mass (g)	1000	200		
Molecular Weight (g/mol)	189.67	24.31		
Moles	5.27	8.23		
Stoichiometric Coefficients	1	2		
Stoichiometric Equivalents	5.27	4.11		

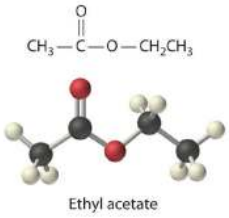
Because the number of Stoichiometric Equivalents for the Mg is smaller, it is the limiting reagant. We now simply carry out the Table calculation for Ti(s) to find the mass of Ti produced. Similarly we could calculate the mass of $MgCl_2(s)$ produced or even the amount of $TiCl_4(s)$ that was consumed in the reaction. Remember we divide going down the table and multiply going up.

	$TiCl_4(s)$	+ 2Mg(s)	→ 2 $MgCl_2(s)$	+ Ti(s)
Mass (g)	1000	200		196.9
Molecular Weight (g/mol)	189.67	24.31		47.87
Moles	5.27	8.23		4.11
Stoichiometric Coefficients	1	2		1
Stoichiometric Equivalents	5.27	4.11		4.11

Density is the mass per unit volume of a substance. If we are given the density of a substance, we can use it in stoichiometric calculations involving liquid reactants and/or products, as Example 11.4.2 demonstrates.

Example 11.4.2

Ethyl acetate ($CH_3CO_2C_2H_5$) is the solvent in many fingernail polish removers and is used to decaffeinate coffee beans and tea leaves. It is prepared by reacting ethanol (C_2H_5OH) with acetic acid (CH_3CO_2H); the other product is water. A small amount of sulfuric acid is used to accelerate the reaction, but the sulfuric acid is not consumed and does not appear in the balanced chemical equation. Given 10.0 mL each of acetic acid and ethanol, how many grams of ethyl acetate can be prepared from this reaction? The densities of acetic acid and ethanol are 1.0492 g/mL and 0.7893 g/mL, respectively.



Ethyl acetate

Given: reactants, products, and volumes and densities of reactants

Asked for: mass of product

Strategy:

A Balance the chemical equation for the reaction.

B Use the given densities to convert from volume to mass. Then use each molar mass to convert from mass to moles.

C Using mole ratios, determine which substance is the limiting reactant. After identifying the limiting reactant, use mole ratios based on the number of moles of limiting reactant to determine the number of moles of product.

D Convert from moles of product to mass of product.

Solution:

A We always begin by writing the balanced chemical equation for the reaction:

$$C_2H_5OH\,(l) + CH_3CO_2H(aq) \rightarrow CH_3CO_2C_2H_5(aq) + H_2O\,(l) \qquad \text{(Chapter 11.4.8)}$$

B We need to calculate the number of moles of ethanol and acetic acid that are present in 10.0 mL of each. Recall from Chapter 1 " that the density of a substance is the mass divided by the volume:

$$density = \frac{mass}{volume} \qquad \text{(Chapter 11.4.9)}$$

Rearranging this expression gives mass = (density)(volume). We can replace mass by the product of the density and the volume to calculate the number of moles of each substance in 10.0 mL (remember, 1 mL = 1 cm^3):

$$\begin{aligned} moles\ C2H_5OH &= \frac{mass\ C2H_5OH}{molar\ mass\ C2H_5OH} \\ &= \frac{volume\ C2H_5OH \times density\ C2H_5OH}{molar\ mass\ C2H_5OH} \\ &= 100.0\ \cancel{mL\ C2H_5OH} \times \frac{0.789\ \cancel{g\ C2H_5OH}}{1\ \cancel{mL\ C2H_5OH}} \frac{1\ mol\ mL\ C2H_5OH}{46.07\ \cancel{g\ C2H_5OH}} \\ &= 0.171\ mol\ C2H_5OH \end{aligned} \quad \text{(Chapter 11.4.10)}$$

and

$$\begin{aligned} moles\ CH_3CO_2H &= \frac{mass\ CH_3CO_2H}{molar\ mass\ CH_3CO_2H} \\ &= \frac{volume\ CH_3CO_2H \times density\ CH_3CO_2H}{molar\ mass\ CH_3CO_2H} \\ &= 10.0\ \cancel{mL\ CH_3CO_2H} \times \frac{1.0492\ \cancel{g\ CH_3CO_2H}}{1\ \cancel{mL\ CH_3CO_2H}} \frac{1\ mol\ mL\ CH_3CO_2H}{60.05\ \cancel{g\ CH_3CO_2H}} \\ &= 0.175\ mol\ CH_3CO_2H \end{aligned} \quad \text{(Chapter 11.4.11)}$$

C The number of moles of acetic acid exceeds the number of moles of ethanol. Because the reactants both have coefficients of 1 in the balanced chemical equation, the mole ratio is 1:1. We have 0.171 mol of ethanol and 0.175 mol of acetic acid, so ethanol is the limiting reactant and acetic acid is in excess. The coefficient in the balanced chemical equation for the product (ethyl acetate) is also 1, so the mole ratio of ethanol and ethyl acetate is also 1:1. This means that given 0.171 mol of ethanol, the amount of ethyl acetate produced must also be 0.171 mol:

$$\begin{aligned} moles\ ethyl\ acetate &= mol\ ethanol \times \frac{1\ mol\ ethyl\ acetate}{1\ mol\ ethanol} \\ &= 0.171\ \cancel{mol\ ethanol} \times \frac{1\ mol\ ethyl\ acetate}{1\ \cancel{mol\ ethanol}} \\ &= 0.171\ mol\ CH_3CO_2C_2H_5 \end{aligned} \quad \text{(Chapter 11.4.12)}$$

D The final step is to determine the mass of ethyl acetate that can be formed, which we do by multiplying the number of moles by the molar mass:

$$\begin{aligned} mass\ of\ ethyl\ acetate &= mol\ ethyl\ acetate \times molar\ mass\ ethyl\ acetate \\ &= 0.171\ \cancel{mol\ CH_3CO_2C_2H_5} \times \frac{88.1\ g\ CH_3CO_2C_2H_5}{1\ \cancel{mol\ CH_3CO_2C_2H_5}} \\ &= 15.1\ g\ CH_3CO_2C_2H_5 \end{aligned} \quad \text{(Chapter 11.4.13)}$$

Thus 15.1 g of ethyl acetate can be prepared in this reaction. If necessary, you could use the density of ethyl acetate (0.9003 g/cm^3) to determine the volume of ethyl acetate that could be produced:

$$\begin{aligned} volume\ of\ ethyl\ acetate &= 15.1\ g\ CH_3CO_2C_2H_5 \times \frac{1\ mLCH_3CO_2C_2H_5}{0.9003\ \cancel{g\ CH_3CO_2C_2H_5}} \\ &= 16.8\ mL\ CH_3CO_2C_2H_5 \end{aligned} \quad \text{(Chapter 11.4.14)}$$

And again using the table

	$C_2H_5OH(l)$	$+ CH_3CO_2(aq)$	$\rightarrow CH_3CO_2C_2H_5(aq)$	$+ H_2O(l)$
Mass (g)	10.0 mL x 0.789 g/mL	10.0 mL x 1.0492 g/mL	15.1 g	
Molecular Weight (g/mol)	46.07 ↓	60.05 ↓	88.1 ↑	
Moles	0.171 ↓	0.175 ↓	0.171 ↑	
Stoichiometric Coefficients	1 ↓	1 ↓	1 ↑	
Stoichiometric Equivalents	0.171	~~0.175~~	0.171	

We then divide the mass of the ethyl acetate by its density to find (as in the first method) that 16.8 mL of ethyl acetate will be produced

Exercise

Under appropriate conditions, the reaction of elemental phosphorus and elemental sulfur produces the compound P_4S_{10}. How much P_4S_{10} can be prepared starting with 10.0 g of P_4 and 30.0 g of S_8?

Answer: 35.9 g

Percent Yield

You have learned that when reactants are not present in stoichiometric quantities, the limiting reactant determines the maximum amount of product that can be formed from the reactants. The amount of product calculated in this way is the theoretical yieldThe maximum amount of product that can be formed from the reactants in a chemical reaction, which theoretically is the amount of product that would be obtained if the reaction occurred perfectly and the method of purifying the product were 100% efficient., the amount you would obtain if the reaction occurred perfectly and your method of purifying the product were 100% efficient.

In reality, you almost always obtain less product than is theoretically possible because of mechanical losses (such as spilling), separation procedures that are not 100% efficient, competing reactions that form undesired products, and reactions that simply do not go all the way to completion, thus resulting in a mixture of products and reactants. This last possibility is a common occurrence, which we call a chemical equilibrium. This is not a static equilibrium where two people are standing holding three balls, but a situation where the rate of forward reaction is balanced by the rate of reverse reaction. You could think of this as jugglers tossing the balls back and forth. So the actual yieldThe measured mass of products actually obtained from a reaction. The actual yield is nearly always less than the theoretical yield., the measured mass of products obtained from a reaction, is almost always less than the theoretical yield (often much less). The percent yieldThe ratio of the actual yield of a reaction to the theoretical yield multiplied by 100 to give a percentage. of a reaction is the ratio of the actual yield to the theoretical yield, multiplied by 100 to give a percentage:

$$percent\ yield = \frac{actual\ yield\ (g)}{theoretical\ yield\ (g)} \times 100 \quad \text{(Chapter 11.4.15)}$$

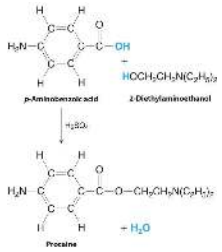
The method used to calculate the percent yield of a reaction is illustrated in Example 13.

Example 11.4.3

Procaine is a key component of Novocain, an injectable local anesthetic used in dental work and minor surgery. Procaine can be prepared in the presence of H_2SO_4 (indicated above the arrow) by the reaction

$$\underset{p-aminobenzonic\ acid}{C_7H_7NO_2} + \underset{2-diethylaminoethanol}{C_6H_{15}NO} \xrightarrow{H_2SO_4} \underset{procaine}{C_{13}H_{20}N_2O_2} + H_2O \qquad \text{(Chapter 11.4.16)}$$

If we carried out this reaction using 10.0 g of *p*-aminobenzoic acid and 10.0 g of 2-diethylaminoethanol, and we isolated 15.7 g of procaine, what was the percent yield?



The preparation of procaine. A reaction of *p*-aminobenzoic acid with 2-diethylaminoethanol yields procaine and water.

Given: masses of reactants and product

Asked for: percent yield

Strategy:

A Write the balanced chemical equation.

B Convert from mass of reactants and product to moles using molar masses and then use mole ratios to determine which is the limiting reactant. Based on the number of moles of the limiting reactant, use mole ratios to determine the theoretical yield.

C Calculate the percent yield by dividing the actual yield by the theoretical yield and multiplying by 100.

Solution:

A From the formulas given for the reactants and the products, we see that the chemical equation is balanced as written. According to the equation, 1 mol of each reactant combines to give 1 mol of product plus 1 mol of water.

B To determine which reactant is limiting, we need to know their molar masses, which are calculated from their structural formulas: *p*-aminobenzoic acid ($C_7H_7NO_2$), 137.14 g/mol; 2-diethylaminoethanol ($C_6H_{15}NO$), 117.19 g/mol. Thus the reaction used the following numbers of moles of reactants:

$$\begin{aligned} moles\ p-aminobenzoic\ acid &= 10.0\ \cancel{g}\ \frac{1\ mol}{137.14\ \cancel{g}} = 0.0729\ mol\ p-ABA \\ moles\ 2-diethylaminoethanol &= 10.0\ \cancel{g}\ \frac{1\ mol}{117.19\ \cancel{g}} = 0.0853\ mol\ 2-dAE \end{aligned} \qquad \text{(Chapter 11.4.17)}$$

The reaction requires a 1:1 mole ratio of the two reactants, so *p*-aminobenzoic acid is the limiting reactant. Based on the coefficients in the balanced chemical equation, 1 mol of *p*-aminobenzoic acid yields 1 mol of procaine. We can therefore obtain only a maximum of 0.0729 mol of procaine. To calculate the corresponding mass of procaine, we use its structural formula ($C_{13}H_{20}N_2O_2$) to calculate its molar mass, which is 236.31 g/mol.

$$\begin{aligned} &theoretical\ yield\ of\ procaine \\ &= 0.0729\ \cancel{mol} \times \frac{236.31\ g}{1\ \cancel{mol}} = 17.2\ g \end{aligned} \qquad \text{(Chapter 11.4.18)}$$

C The actual yield was only 15.7 g of procaine, so the percent yield was

$$\textit{percent yield} = \frac{15.7\ g}{17.2\ g} \times 100 = 91.3\% \qquad \text{(Chapter 11.4.19)}$$

(If the product were pure and dry, this yield would indicate that we have very good lab technique!)

Exercise

Lead was one of the earliest metals to be isolated in pure form. It occurs as concentrated deposits of a distinctive ore called galena (PbS), which is easily converted to lead oxide (PbO) in 100% yield by roasting in air via the following reaction:

$$2PbS\,(s) + 3O_2\,(g) \rightarrow 2PbO\,(s) + 2SO_2\,(g) \qquad \text{(Chapter 11.4.20)}$$

The resulting PbO is then converted to the pure metal by reaction with charcoal. Because lead has such a low melting point (327°C), it runs out of the ore-charcoal mixture as a liquid that is easily collected. The reaction for the conversion of lead oxide to pure lead is as follows:

$$PbO\,(s) + C\,(s) \rightarrow Pb\,(l) + CO\,(g) \qquad \text{(Chapter 11.4.21)}$$

If 93.3 kg of PbO is heated with excess charcoal and 77.3 kg of pure lead is obtained, what is the percent yield?

Answer: 89.2%

Percent yield can range from 0% to 100%.In the laboratory, a student will occasionally obtain a yield that appears to be greater than 100%. This usually happens when the product is impure or is wet with a solvent such as water. If this is not the case, then the student *must* have made an error in weighing either the reactants or the products. The law of conservation of mass applies even to undergraduate chemistry laboratory experiments! A 100% yield means that everything worked perfectly, and you obtained all the product that could have been produced. Anyone who has tried to do something as simple as fill a salt shaker or add oil to a car's engine without spilling knows how unlikely a 100% yield is. At the other extreme, a yield of 0% means that *no* product was obtained. A percent yield of 80%–90% is usually considered good to excellent; a yield of 50% is only fair. In part because of the problems and costs of waste disposal, industrial production facilities face considerable pressures to optimize the yields of products and make them as close to 100% as possible.

Summary

The **stoichiometry** of a reaction describes the relative amounts of reactants and products in a balanced chemical equation. A **stoichiometric quantity** of a reactant is the amount necessary to react completely with the other reactant(s). If a quantity of a reactant remains unconsumed after complete reaction has occurred, it is *in excess*. The reactant that is consumed first and limits the amount of product(s) that can be obtained is the **limiting reactant**. To identify the limiting reactant, calculate the number of moles of each reactant present and compare this ratio to the mole ratio of the reactants in the balanced chemical equation. The maximum amount of product(s) that can be obtained in a reaction from a given amount of reactant(s) is the **theoretical yield** of the reaction. The **actual yield** is the amount of product(s) actually obtained in the reaction; it cannot exceed the theoretical yield. The **percent yield** of a reaction is the ratio of the actual yield to the theoretical yield, expressed as a percentage.

Key Takeaway

- The stoichiometry of a balanced chemical equation identifies the maximum amount of product that can be obtained.

Conceptual Problems

1. Engineers use conservation of mass, called a "mass balance," to determine the amount of product that can be obtained from a chemical reaction. Mass balance assumes that the total mass of reactants is equal to the total mass of products. Is this a chemically valid practice? Explain your answer.

2. Given the equation $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$, is it correct to say that 10 g of hydrogen will react with 10 g of oxygen to produce 20 g of water vapor?
3. What does it mean to say that a reaction is *stoichiometric*?
4. When sulfur is burned in air to produce sulfur dioxide, what is the limiting reactant? Explain your answer.
5. Is it possible for the percent yield to be greater than the theoretical yield? Justify your answer.

Numerical Problems

1. What is the formula mass of each species?
    1. ammonium chloride
    2. sodium cyanide
    3. magnesium hydroxide
    4. calcium phosphate
    5. lithium carbonate
    6. hydrogen sulfite ion
2. What is the molecular or formula mass of each compound?
    1. potassium permanganate
    2. sodium sulfate
    3. hydrogen cyanide
    4. potassium thiocyanate
    5. ammonium oxalate
    6. lithium acetate
3. How many moles are in each of the following?
    1. 10.76 g of Si
    2. 8.6 g of Pb
    3. 2.49 g of Mg
    4. 0.94 g of La
    5. 2.68 g of chlorine gas
    6. 0.089 g of As
4. How many moles are in each of the following?
    1. 8.6 g of CO_2
    2. 2.7 g of CaO
    3. 0.89 g of KCl
    4. 4.3 g of $SrBr_2$
    5. 2.5 g of NaOH
    6. 1.87 g of $Ca(OH)_2$
5. Convert the following to moles and millimoles.
    1. 1.68 g of $Ba(OH)_2$
    2. 0.792 g of H_3PO_4
    3. 3.21 g of K_2S
    4. 0.8692 g of $Cu(NO_3)_2$
    5. 10.648 g of $Ba_3(PO_4)_2$
    6. 5.79 g of $(NH_4)_2SO_4$
    7. 1.32 g of $Pb(C_2H_3O_2)_2$
    8. 4.29 g of $CaCl_2 \cdot 6H_2O$
6. Convert the following to moles and millimoles.

1. 0.089 g of silver nitrate
2. 1.62 g of aluminum chloride
3. 2.37 g of calcium carbonate
4. 1.004 g of iron(II) sulfide
5. 2.12 g of dinitrogen pentoxide
6. 2.68 g of lead(II) nitrate
7. 3.02 g of ammonium phosphate
8. 5.852 g of sulfuric acid
9. 4.735 g of potassium dichromate

7. What is the mass of each substance in grams and milligrams?

    1. 5.68 mol of Ag
    2. 2.49 mol of Sn
    3. 0.0873 mol of Os
    4. 1.74 mol of Si
    5. 0.379 mol of H_2
    6. 1.009 mol of Zr

8. What is the mass of each substance in grams and milligrams?

    1. 2.080 mol of CH_3OH
    2. 0.288 mol of P_4
    3. 3.89 mol of $ZnCl_2$
    4. 1.800 mol of $Fe(CO)_5$
    5. 0.798 mol of S_8
    6. 4.01 mol of NaOH

9. What is the mass of each compound in kilograms?

    1. 6.38 mol of P_4O_{10}
    2. 2.26 mol of $Ba(OH)_2$
    3. 4.35 mol of K_3PO_4
    4. 2.03 mol of $Ni(ClO_3)_2$
    5. 1.47 mol of NH_4NO_3
    6. 0.445 mol of $Co(NO_3)_3$

10. How many atoms are contained in each?

    1. 2.32 mol of Bi
    2. 0.066 mol of V
    3. 0.267 mol of Ru
    4. 4.87 mol of C
    5. 2.74 g of I_2
    6. 1.96 g of Cs
    7. 7.78 g of O_2

11. Convert each number of atoms to milligrams.

    1. 5.89×10^{22} Pt atoms
    2. 2.899×10^{21} Hg atoms
    3. 4.826×10^{22} atoms of chlorine

12. Write a balanced chemical equation for each reaction and then determine which reactant is in excess.

    1. 2.46 g barium(s) plus 3.89 g bromine(l) in water to give barium bromide
    2. 1.44 g bromine(l) plus 2.42 g potassium iodide(s) in water to give potassium bromide and iodine

3. 1.852 g of Zn metal plus 3.62 g of sulfuric acid in water to give zinc sulfate and hydrogen gas
4. 0.147 g of iron metal reacts with 0.924 g of silver acetate in water to give iron(II) acetate and silver metal
5. 3.142 g of ammonium phosphate reacts with 1.648 g of barium hydroxide in water to give ammonium hydroxide and barium phosphate

13. Under the proper conditions, ammonia and oxygen will react to form dinitrogen monoxide (nitrous oxide, also called laughing gas) and water. Write a balanced chemical equation for this reaction. Determine which reactant is in excess for each combination of reactants.
    1. 24.6 g of ammonia and 21.4 g of oxygen
    2. 3.8 mol of ammonia and 84.2 g of oxygen
    3. 3.6×10^{24} molecules of ammonia and 318 g of oxygen
    4. 2.1 mol of ammonia and 36.4 g of oxygen
14. When a piece of zinc metal is placed in aqueous hydrochloric acid, zinc chloride is produced, and hydrogen gas is evolved. Write a balanced chemical equation for this reaction. Determine which reactant is in excess for each combination of reactants.
    1. 12.5 g of HCl and 7.3 g of Zn
    2. 6.2 mol of HCl and 100 g of Zn
    3. 2.1×10^{23} molecules of Zn and 26.0 g of HCl
    4. 3.1 mol of Zn and 97.4 g of HCl
15. Determine the mass of each reactant needed to give the indicated amount of product. Be sure that the chemical equations are balanced.
    1. $NaI(aq) + Cl_2(g) \rightarrow NaCl(aq) + I_2(s)$; 1.0 mol of NaCl
    2. $NaCl(aq) + H_2SO_4(aq) \rightarrow HCl(g) + Na_2SO_4(aq)$; 0.50 mol of HCl
    3. $NO_2(g) + H_2O(l) \rightarrow HNO_2(aq) + HNO_3(aq)$; 1.5 mol of HNO_3
16. Determine the mass of each reactant needed to give the indicated amount of product. Be sure that the chemical equations are balanced.
    1. $AgNO_3(aq) + CaCl_2(s) \rightarrow AgCl(s) + Ca(NO_3)_2(aq)$; 1.25 mol of AgCl
    2. $Pb(s) + PbO_2(s) + H_2SO_4(aq) \rightarrow PbSO_4(s) + H_2O(l)$; 3.8 g of $PbSO_4$
    3. $H_3PO_4(aq) + MgCO_3(s) \rightarrow Mg_3(PO_4)_2(s) + CO_2(g) + H_2O(l)$; 6.41 g of $Mg_3(PO_4)_2$
17. Determine the percent yield of each reaction. Be sure that the chemical equations are balanced. Assume that any reactants for which amounts are not given are in excess. (The symbol Δ indicates that the reactants are heated.)
    1. For $KClO_3(s) \rightarrow KCl(s) + O_2(g)$, 2.14 g of $KClO_3$ produces 0.67 g of O_2
    2. $Cu(s) + H_2SO_4(aq) \rightarrow CuSO_4(aq) + SO_2(g) + H_2O(l)$; 4.00 g of copper gives 1.2 g of sulfur dioxide
    3. $AgC_2H_3O_2(aq) + Na_3PO_4(aq) \rightarrow Ag_3PO_4(s) + NaC_2H_3O_2(aq)$; 5.298 g of silver acetate produces 1.583 g of silver phosphate
18. Each step of a four-step reaction has a yield of 95%. What is the percent yield for the overall reaction?
19. A three-step reaction yields of 87% for the first step, 94% for the second, and 55% for the third. What is the percent yield of the overall reaction?
20. Give a general expression relating the theoretical yield (in grams) of product that can be obtained from *x* grams of B, assuming neither A nor B is limiting.

$$A + 3B \rightarrow 2C \qquad \text{(Chapter 11.4.22)}$$

21. Under certain conditions, the reaction of hydrogen with carbon monoxide can produce methanol.
    1. Write a balanced chemical equation for this reaction.
    2. Calculate the percent yield if exactly 200 g of methanol is produced from exactly 300 g of carbon monoxide.
22. Chlorine dioxide is a bleaching agent used in the paper industry. It can be prepared by the following reaction:

$$NaClO_2\,(s) + Cl_2\,(g) \rightarrow ClO_2(aq) + NaCl(aq) \qquad \text{(Chapter 11.4.23)}$$

1. What mass of chlorine is needed for the complete reaction of 30.5 g of $NaClO_2$?
2. Give a general equation for the conversion of *x* grams of sodium chlorite to chlorine dioxide.

23. The reaction of propane gas ($CH_3CH_2CH_3$) with chlorine gas (Cl_2) produces two monochloride products: $CH_3CH_2CH_2Cl$ and $CH_3CHClCH_3$. The first is obtained in a 43% yield and the second in a 57% yield.
    1. If you use 2.78 g of propane gas, how much chlorine gas would you need for the reaction to go to completion?
    2. How many grams of each product could theoretically be obtained from the reaction starting with 2.78 g of propane?
    3. Use the actual percent yield to calculate how many grams of each product would actually be obtained.
24. Protactinium (Pa), a highly toxic metal, is one of the rarest and most expensive elements. The following reaction is one method for preparing protactinium metal under relatively extreme conditions:

$$2PaI_5\,(s) \xrightarrow{\Delta} 2Pa\,(s) + 5I_2\,(s) \qquad \text{(Chapter 11.4.24)}$$

    1. Given 15.8 mg of reactant, how many milligrams of protactinium could be synthesized?
    2. If 3.4 mg of Pa was obtained, what was the percent yield of this reaction?
    3. If you obtained 3.4 mg of Pa and the percent yield was 78.6%, how many grams of PaI_5 were used in the preparation?
25. Aniline ($C_6H_5NH_2$) can be produced from chlorobenzene (C_6H_5Cl) via the following reaction:

$$C_6H_5Cl\,(l) + 2NH_3\,(g) \rightarrow C_6H_5NH_2\,(l) + NH_4Cl\,(s) \qquad \text{(Chapter 11.4.25)}$$

    Assume that 20.0 g of chlorobenzene at 92% purity is mixed with 8.30 g of ammonia.
    1. Which is the limiting reactant?
    2. Which reactant is present in excess?
    3. What is the theoretical yield of ammonium chloride in grams?
    4. If 4.78 g of NH_4Cl was recovered, what was the percent yield?
    5. Derive a general expression for the theoretical yield of ammonium chloride in terms of grams of chlorobenzene reactant, if ammonia is present in excess.
26. A stoichiometric quantity of chlorine gas is added to an aqueous solution of NaBr to produce an aqueous solution of sodium chloride and liquid bromine. Write the chemical equation for this reaction. Then assume an 89% yield and calculate the mass of chlorine given the following:
    1. 9.36×10^{24} formula units of NaCl
    2. 8.5×10^{4} mol of Br_2
    3. 3.7×10^{8} g of NaCl

Answers

1. 1. 53.941 amu
   2. 49.0072 amu
   3. 58.3197 amu
   4. 310.177 amu
   5. 73.891 amu
   6. 81.071 amu
2.
3. 1. 0.3831 mol Si
   2. 4.2×10^{-2} mol Pb

3. 0.102 mol Mg
4. 6.8×10^{-3} mol La
5. 3.78×10^{-2} mol Cl_2
6. 1.2×10^{-3} mol As

4.

5. 1. 9.80×10^{-3} mol or 9.80 mmole $Ba(OH)_2$
   2. 8.08×10^{-3} mol or 8.08 mmole H_3PO_4
   3. 2.91×10^{-2} mol or 29.1 mmole K_2S
   4. 4.634×10^{-3} mol or 4.634 mmole $Cu(NO_3)_2$
   5. 1.769×10^{-2} mol 17.69 mmole $Ba_3(PO_4)_2$
   6. 4.38×10^{-2} mol or 43.8 mmole $(NH_4)_2SO_4$
   7. 4.06×10^{-3} mol or 4.06 mmole $Pb(C_2H_3O_2)_2$
   8. 1.96×10^{-2} mol or 19.6 mmole $CaCl_2 \cdot 6H_2O$

6.

7. 1. 613 g or 6.13×10^5 mg Ag
   2. 296 g or 2.96×10^5 mg Sn
   3. 16.6 g or 1.66×10^4 mg Os
   4. 48.9 g or 4.89×10^4 mg Si
   5. 0.764 g or 764 mg H_2
   6. 92.05 g or 9.205×10^4 mg Zr

8.

9. 1. 1.81 kg P_4O_{10}
   2. 0.387 kg $Ba(OH)_2$
   3. 0.923 kg K_3PO_4
   4. 0.458 kg $Ni(ClO_3)_2$
   5. 0.118 kg $(NH_4)NO_3$
   6. 0.109 kg $Co(NO_3)_3$

10.

11. 1. 1.91×10^4 mg Pt
    2. 965.6 mg Hg
    3. 2841 mg Cl

12.

13. The balanced chemical equation for this reaction is

    $2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O$

    1. NH_3
    2. NH_3
    3. O_2
    4. NH_3

14.

15. 1. 150 g NaI and 35 g Cl_2
    2. 29 g NaCl and 25 g H_2SO_4
    3. 140 g NO_2 and 27 g H_2O

16.

17. 1. 80%
    2. 30%
    3. 35.7%

18.

19. 45%.

20.

21. 1. $CO + 2H_2 \rightarrow CH_3OH$
    2. 58.28%

22.

23. 1. 2.24 g Cl_2
    2. 4.95 g
    3. 2.13 g $CH_3CH_2CH_2Cl$ plus 2.82 g $CH_3CHClCH_3$

24.

25. 1. chlorobenzene
    2. ammonia
    3. 8.74 g ammonium chloride.
    4. 55%
    5.

26.

Contributors

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Chapter 11.5: Stoichiometry Involving Gases

Learning Objective

- To relate the amount of gas consumed or released in a chemical reaction to the stoichiometry of the reaction.

With the ideal gas law, we can use the relationship between the amounts of gases (in moles) and their volumes (in liters) to calculate the stoichiometry of reactions involving gases, if the pressure and temperature are known. This is important for several reasons. Many reactions that are carried out in the laboratory involve the formation or reaction of a gas, so chemists must be able to quantitatively treat gaseous products and reactants as readily as they quantitatively treat solids or solutions. Furthermore, many, if not most, industrially important reactions are carried out in the gas phase for practical reasons. Gases mix readily, are easily heated or cooled, and can be transferred from one place to another in a manufacturing facility via simple pumps and plumbing. As a chemical engineer said to one of the authors, “Gases always go where you want them to, liquids sometimes do, but solids almost never do.”

Example 11.5.1

Sulfuric acid, the industrial chemical produced in greatest quantity (almost 45 million tons per year in the United States alone), is prepared by the combustion of sulfur in air to give SO_2, followed by the reaction of SO_2 with O_2 in the presence of a catalyst to give SO_3, which reacts with water to give H_2SO_4. The overall chemical equation is as follows:

$$2S(s) + 3O_2(g) + 2H_2O(l) \rightarrow 2H_2SO_4(aq) \qquad \text{(Chapter 11.5.1)}$$

What volume of O_2 (in liters) at 22°C and 745 mmHg pressure is required to produce 1.00 ton of H_2SO_4?

Given: reaction, temperature, pressure, and mass of one product

Asked for: volume of gaseous reactant

Strategy:

A Calculate the number of moles of H_2SO_4 in 1.00 ton. From the stoichiometric coefficients in the balanced chemical equation, calculate the number of moles of O_2 required.

B Use the ideal gas law to determine the volume of O_2 required under the given conditions. Be sure that all quantities are expressed in the appropriate units.

Solution:

We can see from the stoichiometry of the reaction that 3/2 mol of O_2 is required to produce 1 mol of H_2SO_4. This is a standard stoichiometry problem of the type presented in Section 11.4, except this problem asks for the volume of one of the reactants (O_2) rather than its mass. We proceed exactly as in Section 11.4, using the strategy

mass of H_2SO_4 → moles H_2SO_4 → moles O_2 → liters O_2

A We begin by calculating the number of moles of H_2SO_4 in 1.00 tn:

$$\frac{907.18 \times 10^3 \text{ g } H_2SO_4}{(2 \times 1.008 + 32.06 + 4 \times 16.00) \text{ g/mol}} = 9250 \text{ mol } H_2SO_4 \qquad \text{(Chapter 11.5.2)}$$

We next calculate the number of moles of O_2 required:

$$9250 \text{ mol } H_2SO_4 \times \frac{3 \text{mol } O_2}{2 \text{mol } H_2SO_4} = 1.389 \times 10^4 \text{ mol } O_2$$

Or

	3S(s)	+ $3O_2$(g)	+ $2H_2O$(l)	→ $2H_2SO_4$(aq)
Mass (g)				907.18×10^3
Molecular Weight (g/mol)				98.07
Moles		1.39×10^4		9.25×10^3
Stoichiometric Coefficients		3		2
Stoichiometric Equivalents		4.62×10^3		4.62×10^3

B If we know the number of moles of O_2 produces we can use the ideal gas law to convert the number of moles to the volume at STP (or any other conditions of temperature and pressure if we know them

$$V = \frac{nRT}{P} = \frac{1.389 \times 10^4 \text{ mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times (273 + 22) \text{ K}}{745 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} = 3.43 \times 10^5 \text{ L} \qquad \text{(Chapter 11.5.3)}$$

The answer means that more than 300,000 L of oxygen gas are needed to produce 1 tn of sulfuric acid. These numbers may give you some appreciation for the magnitude of the engineering and plumbing problems faced in industrial chemistry.

Exercise

In Example 5, we saw that Charles used a balloon containing approximately 31,150 L of H_2 for his initial flight in 1783. The hydrogen gas was produced by the reaction of metallic iron with dilute hydrochloric acid according to the following balanced chemical equation:

Fe(s) + 2 HCl(aq) → H_2(g) + $FeCl_2$(aq)

How much iron (in kilograms) was needed to produce this volume of H_2 if the temperature was 30°C and the atmospheric pressure was 745 mmHg?

Answer: 68.6 kg of Fe (approximately 150 lb)

Many of the advances made in chemistry during the 18th and 19th centuries were the result of careful experiments done to determine the identity and quantity of gases produced in chemical reactions. For example, in 1774, Joseph Priestley was able to isolate oxygen gas by the thermal decomposition of mercuric oxide (HgO). In the 1780s, Antoine Lavoisier conducted experiments that showed that combustion reactions, which require oxygen, produce what we now know to be carbon dioxide. Both sets of experiments required the scientists to collect and manipulate gases produced in chemical reactions, and both used a simple technique that is still used in chemical laboratories today: collecting a gas by the displacement of water. As shown in Figure 11.5.1 , the gas produced in a reaction can be channeled through a tube into inverted bottles filled with water. Because the gas is less dense than liquid water, it bubbles to the top of the bottle, displacing the water. Eventually, all the water is forced out and the bottle contains only gas. If a calibrated bottle is used (i.e., one with markings to indicate the volume of the gas) and the bottle is raised or lowered until the level of the water is the same both inside and outside, then the pressure within the bottle will exactly equal the atmospheric pressure measured separately with a barometer.

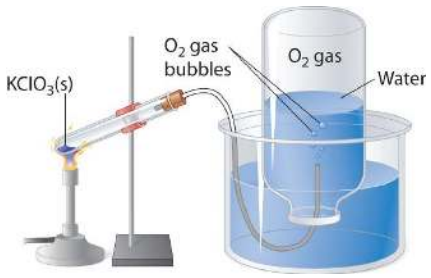


Figure 11.5.1 An Apparatus for Collecting Gases by the Displacement of Water *When $KClO_3(s)$ is heated, O_2 is produced according to the equation*

$$KClO_3\,(s) \rightarrow KCl\,(s) + \frac{3}{2}O_2\,(g) \qquad \text{(Chapter 11.5.4)}$$

. The oxygen gas travels through the tube, bubbles up through the water, and is collected in a bottle as shown.

The only gases that cannot be collected using this technique are those that readily dissolve in water (e.g., NH_3, H_2S, and CO_2) and those that react rapidly with water (such as F_2 and NO_2). Remember, however, when calculating the amount of gas formed in the reaction, the gas collected inside the bottle is *not* pure. Instead, it is a mixture of the product gas and water vapor. As we discussed in Chapter 7 , all liquids (including water) have a measurable amount of vapor in equilibrium with the liquid because molecules of the liquid are continuously escaping from the liquid's surface, while other molecules from the vapor phase collide with the surface and return to the liquid. The vapor thus exerts a pressure above the liquid, which is called the liquid's *vapor pressure*. In the case shown in Figure 11.5.1 the bottle is therefore actually filled with a mixture of O_2 and water vapor, and the total pressure is, by Dalton's law of partial pressures, the sum of the pressures of the two components:

$$P_{tot} = P_{gas} + P_{H_2O} = P_{bar.} \qquad \text{(Chapter 11.5.5)}$$

If we want to know the pressure of the gas generated in the reaction to calculate the amount of gas formed, we must first subtract the pressure due to water vapor from the total pressure. This is done by referring to tabulated values of the vapor pressure of water as a function of temperature (Table 11.5.1). As shown in Figure 11.5.2, the vapor pressure of water increases rapidly with increasing temperature, and at the normal boiling point (100°C), the vapor pressure is exactly 1 atm. The methodology is illustrated in Example 11.5.2.

Table 11.5.1 Vapor Pressure of Water at Various Temperatures

T (°C)	*P* (in mmHg)	*T*	*P*	*T*	*P*	*T*	*P*
0	4.58	21	18.66	35	42.2	92	567.2
5	6.54	22	19.84	40	55.4	94	611.0
10	9.21	23	21.08	45	71.9	96	657.7
12	10.52	24	22.39	50	92.6	98	707.3
14	11.99	25	23.77	55	118.1	100	760.0
16	13.64	26	25.22	60	149.5	102	815.8
17	14.54	27	26.75	65	187.7	104	875.1
18	15.48	28	28.37	70	233.8	106	937.8
19	16.48	29	30.06	80	355.3	108	1004.2
20	17.54	30	31.84	90	525.9	110	1074.4

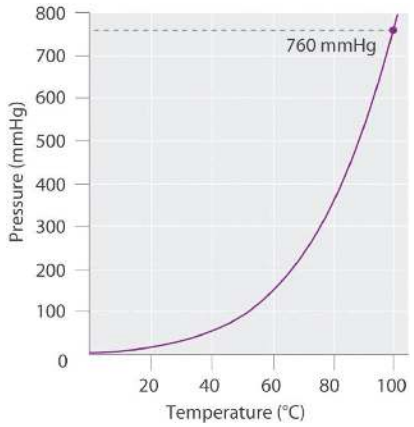


Figure 11.5.2 A Plot of the Vapor Pressure of Water versus Temperature. *The vapor pressure is very low (but not zero) at 0°C and reaches 1 atm = 760 mmHg at the normal boiling point, 100°C.*

Example 11.5.2

Sodium azide (NaN_3) decomposes to form sodium metal and nitrogen gas according to the following balanced chemical equation:

$$2NaN_3 \rightarrow 2Na_{(s)} + 3N_{2\ (g)} \qquad \text{(Chapter 11.5.6)}$$

This reaction is used to inflate the air bags that cushion passengers during automobile collisions. The reaction is initiated in air bags by an electrical impulse and results in the rapid evolution of gas. If the N_2 gas that results from the decomposition of a 5.00 g sample of NaN_3 could be collected by displacing water from an inverted flask, as in Figure 11.5.1, what volume of gas would be produced at 22°C and 762 mmHg?

Given: reaction, mass of compound, temperature, and pressure

Asked for: volume of nitrogen gas produced

Strategy:

A Calculate the number of moles of N_2 gas produced. From the data in Table 11.5.1, determine the partial pressure of N_2 gas in the flask.

B Use the ideal gas law to find the volume of N_2 gas produced.

Solution:

A Because we know the mass of the reactant and the stoichiometry of the reaction, our first step is to calculate the number of moles of N_2 gas produced:

$$\frac{5.00\ g\ NaN_3}{(22.99 + 3 \times 14.01)\ g/mol} \times \frac{3\ mol\ N_2}{2\ mol\ NaN_3} = 0.115\ mol\ N_2$$

or

	$2NaN_3$	) → 2Na(s)	+ $3N_2$(g)
Mass (g)	5.00		
Molecular Weight (g/mol)	65.02		
Moles	0.0769	1.39 x 10^4	0.115
Stoichiometric Coefficients	2	3	3
Stoichiometric Equivalents	0.0385	0.0385	0.0385

The pressure given (762 mmHg) is the *total* pressure in the flask, which is the sum of the pressures due to the N_2 gas and the water vapor present. Table 11.5.1 tells us that the vapor pressure of water is 19.84 mmHg at 22°C (295 K), so the partial pressure of the N_2 gas in the flask is only 762 − 19.84 = 742 mmHg = 0.976 atm.

B Solving the ideal gas law for V and substituting the other quantities (in the appropriate units), we get

$$V = \frac{nRT}{P} = \frac{0.115\ \text{mol} \times 0.08206 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 294\ \text{K}}{0.978\ \text{atm}} = 2.84\ \text{L} \qquad \text{(Chapter 11.5.7)}$$

Exercise

A 1.00 g sample of zinc metal is added to a solution of dilute hydrochloric acid. It dissolves to produce H_2 gas according to the equation Zn(s) + 2 HCl(aq) → H_2(g) + $ZnCl_2$(aq). The resulting H_2 gas is collected in a water-filled bottle at 30°C and an atmospheric pressure of 760 mmHg. What volume does it occupy?

Answer: 0.397 L

Summary

The relationship between the amounts of products and reactants in a chemical reaction can be expressed in units of moles or masses of pure substances, of volumes of solutions, or of volumes of gaseous substances. The ideal gas law can be used to calculate the volume of gaseous products or reactants as needed. In the laboratory, gases produced in a reaction are often collected by the displacement of water from filled vessels; the amount of gas can then be calculated from the volume of water displaced and the atmospheric pressure. A gas collected in such a way is not pure, however, but contains a significant amount of water vapor. The measured pressure must therefore be corrected for the vapor pressure of water, which depends strongly on the temperature.

Key Takeaway

- The ideal gas equation and the stoichiometry of a reaction can be used to calculate the volume of gas produced or consumed in a reaction.

Conceptual Problems

1. Why are so many industrially important reactions carried out in the gas phase?
2. The volume of gas produced during a chemical reaction can be measured by collecting the gas in an inverted container filled with water. The gas forces water out of the container, and the volume of liquid displaced is a measure of the volume of gas. What additional information must be considered to determine the number of moles of gas produced? The volume of some gases cannot be measured using this method. What property of a gas precludes the use of this method?
3. Equal masses of two solid compounds (A and B) are placed in separate sealed flasks filled with air at 1 atm and heated to 50°C for 10 hours. After cooling to room temperature, the pressure in the flask containing A was 1.5 atm. In contrast, the pressure in the flask containing B was 0.87 atm. Suggest an explanation for these observations. Would the masses of samples A and B still be equal after the experiment? Why or why not?

Numerical Problems

1. Balance each chemical equation and then determine the volume of the indicated reactant at STP that is required for complete reaction. Assuming complete reaction, what is the volume of the products?
    1. $SO_2(g) + O_2(g) \rightarrow SO_3(g)$ given 2.4 mol of O_2
    2. $H_2(g) + Cl_2(g) \rightarrow HCl(g)$ given 0.78 g of H_2
    3. $C_2H_6(g) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$ given 1.91 mol of O_2
2. During the smelting of iron, carbon reacts with oxygen to produce carbon monoxide, which then reacts with iron(III) oxide to produce iron metal and carbon dioxide. If 1.82 L of CO_2 at STP is produced,
    1. what mass of CO is consumed?
    2. what volume of CO at STP is consumed?
    3. how much O_2 (in liters) at STP is used?
    4. what mass of carbon is consumed?
    5. how much iron metal (in grams) is produced?
3. Complete decomposition of a sample of potassium chlorate produced 1.34 g of potassium chloride and oxygen gas.

1. What is the mass of $KClO_3$ in the original sample?
2. What mass of oxygen is produced?
3. What is the volume of oxygen produced at STP?

4. The combustion of a 100.0 mg sample of an herbicide in excess oxygen produced 83.16 mL of CO_2 and 72.9 mL of H_2O vapor at STP. A separate analysis showed that the sample contained 16.44 mg of chlorine. If the sample is known to contain only C, H, Cl, and N, determine the percent composition and the empirical formula of the herbicide.
5. The combustion of a 300.0 mg sample of an antidepressant in excess oxygen produced 326 mL of CO_2 and 164 mL of H_2O vapor at STP. A separate analysis showed that the sample contained 23.28% oxygen. If the sample is known to contain only C, H, O, and N, determine the percent composition and the empirical formula of the antidepressant.

Answers

1.
2.
3. 1. 2.20 g $KClO_3$
   2. 0.863 g O_2
   3. 604 mL O_2
4.
5. Percent composition: 58.3% C, 4.93% H, 23.28% O, and 13.5% N; empirical formula: $C_{10}H_{10}O_3N_2$

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Chapter 11.6: Types of Chemical Reactions

Learning Objective

- To identify fundamental types of chemical reactions.<
- To predict the types of reactions substances will undergo.
- To assign oxidation numbers

The chemical reactions we have described are only a tiny sampling of the infinite number of chemical reactions possible. How do chemists cope with this overwhelming diversity? How do they predict which compounds will react with one another and what products will be formed? The key to success is to find useful ways to categorize reactions. Familiarity with a few basic types of reactions will help you to predict the products that form when certain kinds of compounds or elements come in contact.

Most chemical reactions can be classified into one or more of five basic types:

1. **acid–base reactions**: A chemical reaction that has the general form AB + C → AC + B or AB + CD → AD + CB.,
2. **condensation reactions**: A chemical reaction that has the general form A + B → AB. Condensation reactions are the reverse of cleavage reactions. Some, but not all, condensation reactions are also oxidation–reduction reactions.
3. **cleavage reactions**: A chemical reaction that has the general form AB → A + B. Cleavage reactions are the reverse of condensation reactions.), and
4. **oxidation–reduction reactions** A chemical reaction that exhibits a change in the oxidation states of one or more elements in the reactants that has the general form oxidant + reductant → reduced oxidant + oxidized reductant.

The general forms of these five kinds of reactions are summarized in Table 11.6.1, along with examples of each. It is important to note, however, that many reactions can be assigned to more than one classification, as you will see in our discussion. The classification scheme is only for convenience; the same reaction can be classified in different ways, depending on which of its characteristics is most important. Oxidation–reduction reactions, in which there is a net transfer of electrons from one atom to another, and condensation reactions are discussed in this section. Acid–base reactions and one kind of exchange reaction—the formation of an insoluble salt such as barium sulfate when solutions of two soluble salts are mixed together—will be discussed in Section 12.5 .

Table 11.6.1 Basic Types of Chemical Reactions

Name of Reaction	General Form	Example(s)
oxidation–reduction (redox)	oxidant + reductant → reduced oxidant + oxidized reductant	$C_7H_{16}(l) + 11O_2(g) \rightarrow 7CO_2(g) + 8H_2O(g)$
acid–base	acid + base → salt	$NH_3(aq) + HNO_3(aq) \rightarrow NH_4^+(aq) + NO_3^-(aq)$
exchange	AB + C → AC + B	$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$
	AB + CD → AD + CB	$BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$
condensation	A + B → AB	$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$
		$HBr + H_2C{=}CH_2 \rightarrow CH_3CH_2Br$*
cleavage	AB → A + B	$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
		$CH_3CH_2Cl \rightarrow H_2C{=}CH_2 + HCl$**

* In more advanced chemisty courses you will learn that this reaction is also called an *addition* reaction.

** In more advanced chemistry courses you will learn that this reaction is also called an *elimination* reaction.

Oxidation–Reduction Reactions

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

Note the Pattern

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

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

$$Cu_2O\,(s) + H_2\,(g) \rightarrow 2Cu\,(s) + H_2O\,(g)$$

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

$$4Al\,(s) + 3O_2\,(g) \rightarrow 2Al_2O_3\,(s)$$

Each neutral oxygen atom gains two electrons and becomes negatively charged, forming an oxide ion; thus, oxygen has an oxidation state of −2 in the product and has been reduced. Each neutral aluminum atom loses three electrons to produce an aluminum ion with an oxidation state of +3 in the product, so aluminum has been oxidized. In this, and in most cases not involving complex polyatomic ions the oxidation state is equivalent to the usual valence. For atoms which have multiple valence states, the oxidation number will be equal to the valence In the formation of Al_2O_3, electrons are transferred as follows (the superscript 0 emphasizes the oxidation state of the elements):

$$4Al^0 + 3O_2^0 \rightarrow 4Al^{3+}6O^{2-}$$

Equation 11.6.1 and Equation 11.6.2 are examples of oxidation–reduction (redox) reactions. In redox reactions, there is a net transfer of electrons from one reactant to another. In any redox reaction, the total number of electrons lost must equal the total of electrons gained to preserve electrical neutrality. In Equation 11.6.3, for example, the total number of electrons lost by aluminum is equal to the total number gained by oxygen:

$$\begin{aligned} \textit{electrons lost} &= 4\ \cancel{\textit{Al atoms}} \times \frac{3\ e^-\ \textit{lost}}{\cancel{\textit{Al atoms}}} = 12\ e^-\ \textit{lost} \\ \textit{electrons gained} &= 6\ \cancel{\textit{O atoms}} \times \frac{2\ e^-\ \textit{gained}}{\cancel{\textit{O atoms}}} = 12\ e^-\ \textit{gained} \end{aligned} \tag{11.6.4}$$

The same pattern is seen in all oxidation–reduction reactions: the number of electrons lost must equal the number of electrons gained.

Note the Pattern

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

Assigning Oxidation States

Assigning oxidation states to the elements in binary ionic compounds is straightforward: the oxidation states of the elements are identical to the charges on the monatomic ions. In Chapter 6, you learned how to predict the formulas of simple ionic compounds based on the sign and magnitude of the charge on monatomic ions formed by the neutral elements. Examples of such compounds are sodium chloride (NaCl; Figure 11.6.1, magnesium oxide (MgO), and calcium chloride ($CaCl_2$). In covalent compounds, in contrast, atoms share electrons. Oxidation states in covalent compounds can be understood in terms of polar covalent bonds and electronegativity. Oxidation states assume that electrons are completely transferred. While this is not true, it is almost true, and the oxidation state model can help you understand and predict many reactions. For example, in water, the oxidation state of the oxygen atom is -2 and that of each hydrogen is +1. That is the oxidation state model assumes that the hydrogen atoms transfer an electron completely to the oxygen atom. We know this is not the case, but that the electrons from the hydrogen atoms are found closer to the oxygen atom. A more extreme case is carbon dioxide, where the oxidation states of the more electronegative oxygen atoms are -2 and that of the carbon atom is +4. Again, the idea is that the oxidation state model assumes complete transfer, and the atomic bond model tell us that the transfer is only partial. Still, the oxidation state model is useful as we shall see

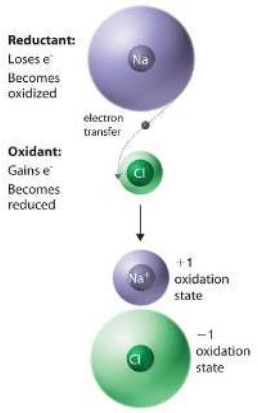


Figure 11.6.1 The Reaction of a Neutral Sodium Atom with a Neutral Chlorine Atom *The result is the transfer of one electron from sodium to chlorine, forming the ionic compound NaCl.*

A set of rules for assigning oxidation states to atoms in chemical compounds follows. The principles underlying these rules have been laid out in the atomic and molecular structure in Chapter 2 , Chapter 3 Chapter 4 and Chapter 5.

Rules for Assigning Oxidation States:

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

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

Rule 3 is required because fluorine attracts electrons more strongly than any other element, for reasons you discovered in Chapter 3 . Hence fluorine provides a reference for calculating the oxidation states of other atoms in chemical compounds. Rule 4 reflects the difference in chemistry observed for compounds of hydrogen with nonmetals (such as chlorine) as opposed to compounds of hydrogen with metals (such as sodium). For example, NaH contains the H^- ion, whereas HCl forms H^+ and Cl^- ions when

dissolved in water. Rule 5 is necessary because fluorine has a greater attraction for electrons than oxygen does; this rule also prevents violations of rule 2. So the oxidation state of oxygen is +2 in OF_2 but −½ in KO_2. Note that an oxidation state of −½ for O in KO_2 is perfectly acceptable. Non-integral oxidation states are encountered occasionally. They are usually due to the presence of two or more atoms of the same element with different oxidation states, so that the "average" oxidation state is a fraction. As with resonance structures, this is a failure of the model.

The reduction of copper(I) oxide shown in Equation 11.6.5 demonstrates how to apply these rules. Rule 1 states that atoms in their elemental form have an oxidation state of zero, which applies to H_2 and Cu. From rule 4, hydrogen in H_2O has an oxidation state of +1, and from rule 5, oxygen in both Cu_2O and H_2O has an oxidation state of −2. Rule 6 states that the sum of the oxidation states in a molecule or formula unit must equal the net charge on that compound. This means that each Cu atom in Cu_2O must have a charge of +1: 2(+1) + (−2) = 0. So the oxidation states are as follows:

$$\overset{+1}{\underset{-2}{Cu_2O}}\,(s) + \overset{0}{H_2} \rightarrow 2\overset{0}{Cu}\,(s) + \overset{+1}{\underset{-2}{H_2O}}\,(g) \tag{11.6.5}$$

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

$$\begin{aligned} \textit{electrons lost} &= 2\,\cancel{H\ atoms} \times \frac{1\ e^-\ lost}{\cancel{H\ atoms}} = 2\ e^-\ lost \\ \textit{electrons gained} &= 2\,\cancel{Cu\ atoms} \times \frac{1\ e^-\ gained}{\cancel{Cu\ atoms}} = 2\ e^-\ gained \end{aligned} \tag{11.6.6}$$

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

Example 11.6.1

Assign oxidation states to all atoms in each compound.

1. sulfur hexafluoride (SF_6)
2. methanol (CH_3OH)
3. ammonium sulfate [$(NH_4)_2SO_4$]
4. magnetite (Fe_3O_4)
5. ethanoic (acetic) acid (CH_3CO_2H)

Given: molecular or empirical formula

Asked for: oxidation states

Strategy:

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

Solution:

1. We know from rule 3 that fluorine always has an oxidation state of −1 in its compounds. The six fluorine atoms in sulfur hexafluoride give a total negative charge of −6. Because rule 1 requires that the sum of the oxidation states of all atoms be zero in a neutral molecule (here SF_6), the oxidation state of sulfur must be +6:

   [(6 F atoms)(−1)] + [(1 S atom) (+6)] = 0

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

   [(4 H atoms)(+1)] + [(1 O atom)(−2)] + [(1 C atom)(−2)] = 0

3. Note that $(NH_4)_2SO_4$ is an ionic compound that consists of both a polyatomic cation (NH_4^+) and a polyatomic anion (SO_4^{2-}) (see Table 6.2.1). We assign oxidation states to the atoms in each polyatomic ion separately. For NH_4^+, hydrogen has an oxidation state of +1 (rule 4), so nitrogen must have an oxidation state of −3:

   [(4 H atoms)(+1)] + [(1 N atom)(−3)] = +1, the charge on the NH_4^+ ion

   For SO_4^{2-}, oxygen has an oxidation state of −2 (rule 5), so sulfur must have an oxidation state of +6:

   [(4 O atoms) (−2)] + [(1 S atom)(+6)] = −2, the charge on the sulfate ion

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

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

5. Initially, we assign oxidation states to the components of CH_3CO_2H in the same way as any other compound. Hydrogen and oxygen have oxidation states of +1 and −2 (rules 4 and 5, respectively), resulting in a total charge for hydrogen and oxygen of

   [

   $$(4Hatoms)(+1)] + [(2Oatoms)(-2)] = 0 \qquad \text{(Chapter 11.6.1)}$$

   So the oxidation state of carbon must also be zero (rule 6). This is, however, an *average* oxidation state for the two carbon atoms present. Because each carbon atom has a different set of atoms bonded to it, they are likely to have different oxidation states. To determine the oxidation states of the individual carbon atoms, we use the same rules as before but with the additional assumption that bonds between atoms of the same element do not affect the oxidation states of those atoms. The carbon atom of the methyl group ($-CH_3$) is bonded to three hydrogen atoms and one carbon atom. We know from rule 4 that hydrogen has an oxidation state of +1, and we have just said that the carbon–carbon bond can be ignored in calculating the oxidation state of the carbon atom. For the methyl group to be electrically neutral, its carbon atom must have an oxidation state of −3. Similarly, the carbon atom of the carboxylic acid group ($-CO_2H$) is bonded to one carbon atom and two oxygen atoms. Again ignoring the bonded carbon atom, we assign oxidation states of −2 and +1 to the oxygen and hydrogen atoms, respectively, leading to a net charge of

   [(2 O atoms)(−2)] + [(1 H atom)(+1)] = −3

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

   $$\overset{-3}{C}\overset{+1}{H_3}\overset{+3}{C}\overset{-2}{O_2}\overset{+1}{H} \qquad \text{(Chapter 11.6.2)}$$

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

Exercise

Assign oxidation states to all atoms in each compound.

1. barium fluoride (BaF_2)
2. formaldehyde (CH_2O)
3. potassium dichromate ($K_2Cr_2O_7$)
4. cesium oxide (CsO_2)
5. ethanol (CH_3CH_2OH)

Answer:

1. Ba, +2; F, −1

2. C, 0; H, +1; O, −2
3. K, +1; Cr, +6; O, −2
4. Cs, +1; O, −½
5. C, −3; H, +1; C, −1; H, +1; O, −2; H, +1

Oxidants and Reductants

Compounds that are capable of accepting electrons, such as O_2 or F_2, are called oxidants (or oxidizing agents)A compound that is capable of accepting electrons; thus it is reduced. because they can oxidize other compounds. *In the process of accepting electrons, an oxidant is reduced.* Compounds that are capable of donating electrons, such as sodium metal or cyclohexane (C_6H_{12}), are called reductants (or reducing agents)A compound that is capable of donating electrons; thus it is oxidized. because they can cause the reduction of another compound. *In the process of donating electrons, a reductant is oxidized.* These relationships are summarized in Equation 11.6.7:

$$oxidant + reductant \rightarrow oxidation - reduction \tag{Chapter 11.6.3}$$

$$\underset{gains\ e^-}{\overset{(is\ reduced)}{O_2}}\ (g) + \underset{loses\ e^-}{\overset{(is\ oxidized)}{4Na}}\ (s) \rightarrow \underset{redox\ reaction}{2Na_2O} \tag{11.6.7}$$

Some oxidants have a greater ability than others to remove electrons from other compounds. Oxidants can range from very powerful, capable of oxidizing most compounds with which they come in contact, to rather weak. Both F_2 and Cl_2 are powerful oxidants: for example, F_2 will oxidize H_2O in a vigorous, potentially explosive reaction. In contrast, S_8 is a rather weak oxidant, and O_2 falls somewhere in between. Conversely, reductants vary in their tendency to donate electrons to other compounds. Reductants can also range from very powerful, capable of giving up electrons to almost anything, to weak. The alkali metals are powerful reductants, so they must be kept away from atmospheric oxygen to avoid a potentially hazardous redox reaction.

A combustion reaction, first introduced in Section 11.2 is an oxidation–reduction reaction in which the oxidant is O_2. One example of a combustion reaction is the burning of a candle. Consider, for example, the combustion of cyclohexane, a typical hydrocarbon, in excess oxygen. The balanced chemical equation for the reaction, with the oxidation state shown for each atom, is as follows:

$$\overset{+1}{\underset{-2}{C_6H_{12}}} + \overset{0}{O_2} \rightarrow \overset{+4}{\underset{-2}{CO_2}} + 6\overset{+1}{\underset{-2}{H_2O}} \tag{11.6.8}$$

If we compare the oxidation state of each element in the products and the reactants, we see that hydrogen is the only element whose oxidation state does not change; it remains +1. Carbon, however, has an oxidation state of −2 in cyclohexane and +4 in CO_2; that is, each carbon atom changes its oxidation state by six electrons during the reaction. Oxygen has an oxidation state of 0 in the reactants, but it gains electrons to have an oxidation state of −2 in CO_2 and H_2O. Because carbon has been oxidized, cyclohexane is the reductant; because oxygen has been reduced, it is the oxidant. All combustion reactions are therefore oxidation–reduction reactions.

Condensation Reactions

The reaction of bromine with ethylene to give 1,2-dibromoethane, which is used in agriculture to kill nematodes in soil, is as follows:

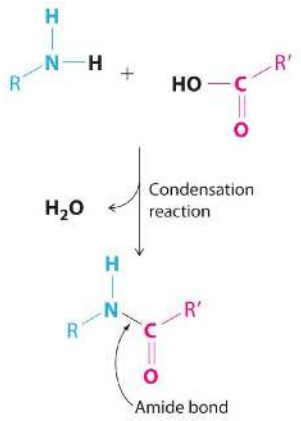
$$C_2H_4\,(g) + Br_2\,(g) \rightarrow BrCH_2CH_2Br\,(g) \tag{11.6.9}$$

According to Table 11.6.1, this is a condensation reaction because it has the general form A + B → AB. This reaction, however, can also be viewed as an oxidation–reduction reaction, in which electrons are transferred from carbon (−2 → −1) to bromine (0 → −1). Another example of a condensation reaction is the one used for the industrial synthesis of ammonia:

$$3H_2\,(g) + N_2\,(g) \rightarrow 2NH_3\,(g) \tag{11.6.10}$$

Although this reaction also has the general form of a condensation reaction, hydrogen has been oxidized (0 → +1) and nitrogen has been reduced (0 → −3), so it can also be classified as an oxidation–reduction reaction.

Not all condensation reactions are redox reactions. The reaction of an amine with a carboxylic acid, for example, is a variant of a condensation reaction (A + B → A′B′ + C): two large fragments condense to form a single molecule, and a much smaller molecule, such as H_2O, is eliminated. In this reaction, the −OH from the carboxylic acid group and −H from the amine group are eliminated as H_2O, and the reaction forms an *amide bond* (also called a *peptide bond*) that links the two fragments. Amide bonds are the essential structural unit linking the building blocks of proteins and many polymers together. Nylon, for example, is produced from a condensation reaction (Figure 11.6.2).



Amide bonds. The reaction of an amine with a carboxylic acid proceeds by eliminating water and forms a new C–N (amide) bond.

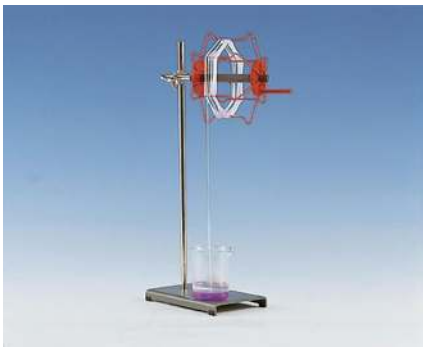


Figure 11.6.2 The Production of Nylon

Example 11.6.2

The following reactions have important industrial applications. Using Table 11.6.1, classify each reaction as an oxidation–reduction reaction, an acid–base reaction, an exchange reaction, a condensation reaction, or a cleavage reaction. For each redox reaction, identify the oxidant and reductant and specify which atoms are oxidized or reduced. (Don't forget that some reactions can be placed into more than one category.)

1. $C_2H_4(g) + Cl_2(g) \rightarrow ClCH_2CH_2Cl(g)$
2. $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$
3. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
4. $Ca_5(PO_4)_3(OH)(s) + 7H_3PO_4(aq) + 4H_2O(l) \rightarrow 5Ca(H_2PO_4)_2{\cdot}H_2O(s)$
5. $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

Given: balanced chemical equation

Asked for: classification of chemical reaction

Strategy:

A Determine the general form of the equation by referring to Table 11.6.1 and then classify the reaction.

B For redox reactions, assign oxidation states to each atom present in the reactants and the products. If the oxidation state of one or more atoms changes, then the reaction is a redox reaction. If not, the reaction must be one of the other types of reaction listed in Table 11.6.1 .

Solution:

1. **A** This reaction is used to prepare 1,2-dichloroethane, one of the top 25 industrial chemicals in Figure 11.6.1. It has the general form A + B → AB, which is typical of a condensation reaction. **B** Because reactions may fit into more than one category, we need to look at the oxidation states of the atoms:

$$\overset{-2}{\underset{+1}{C_2H_4}} + \overset{0}{Cl_2} \rightarrow \overset{-1}{\underset{-1}{Cl}}\overset{-1}{\underset{+1}{CH_2Cl}} \qquad \text{(Chapter 11.6.4)}$$

   The oxidation states show that chlorine is reduced from 0 to −1 and carbon is oxidized from −2 to −1, so this is a redox reaction as well as a condensation reaction. Ethylene is the reductant, and chlorine is the oxidant.

2. **A** This reaction is used to prepare silver chloride for making photographic film. The chemical equation has the general form AB + CD → AD + CB, so it is classified as an exchange reaction. **B** The oxidation states of the atoms are as follows

$$\overset{+1}{\underset{-2}{AgNO_3}}\overset{+5}{} + \overset{+1}{\underset{-1}{NaCl}} \rightarrow \overset{+1}{\underset{-1}{AgCl}} + \overset{+1}{\underset{-2}{NaNO_3}}\overset{+5}{} \qquad \text{(Chapter 11.6.5)}$$

   There is no change in the oxidation states, so this is not a redox reaction.

   AgCl(s) precipitates when solutions of $AgNO_3$(aq) and NaCl(aq) are mixed. *$NaNO_3$ (aq) is in solution as Na^+ and NO_3^- ions.*

3. **A** This reaction is used to prepare lime (CaO) from limestone ($CaCO_3$) and has the general form AB → A + B. The chemical equation's general form indicates that it can be classified as a cleavage reaction, the reverse of a condensation reaction. **B** The oxidation states of the atoms are as follows:

$$\overset{+2}{\underset{-2}{CaCO_3}}\overset{+4}{} \rightarrow \overset{+2}{\underset{-2}{CaO_2}} + \overset{+4}{\underset{-2}{CO_2}} \qquad \text{(Chapter 11.6.6)}$$

   Because the oxidation states of all the atoms are the same in the products and the reactant, this is *not* a redox reaction.

4. **A** This reaction is used to prepare "super triple phosphate" in fertilizer. One of the reactants is phosphoric acid, which transfers a proton (H^+) to the phosphate and hydroxide ions of hydroxyapatite [$Ca_5(PO_4)_3(OH)$] to form $H_2PO_4^-$ and H_2O, respectively. This is an acid–base reaction, in which H_3PO_4 is the acid (H^+ donor) and $Ca_5(PO_4)_3(OH)$ is the base (H^+ acceptor).

   B To determine whether it is also a redox reaction, we assign oxidation states to the atoms:

$$\overset{+2}{Ca_5}\left(\overset{+5}{\underset{-2}{PO_4}}\right)_3\left(\overset{+1}{\underset{-2}{OH}}\right) + 7\overset{+1}{H_3}\overset{+5}{\underset{-2}{PO_4}} \rightarrow 5\overset{+2}{Ca}\left(\overset{+1}{H_2}\overset{+5}{\underset{-2}{PO_4}}\right)_2 \cdot \overset{+1}{\underset{-2}{H_2O}} \qquad \text{(Chapter 11.6.7)}$$

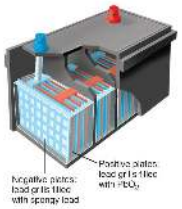
   Because there is no change in oxidation state, this is not a redox reaction.

5. **A** This reaction occurs in a conventional car battery every time the engine is started. An acid (H_2SO_4) is present and transfers protons to oxygen in PbO_2 to form water during the reaction. The reaction can therefore be described as an acid–base reaction.

   B The oxidation states are as follows:

$$\overset{0}{Pb} + \overset{+4}{\underset{-2}{PbO_2}} + 2\overset{+1}{H_2}\overset{+6}{\underset{-2}{SO_4}} \rightarrow 2\overset{+4}{Pb}\overset{+6}{\underset{-2}{SO_4}} + 2\overset{+1}{\underset{-2}{H_2O}} \qquad \text{(Chapter 11.6.8)}$$

   The oxidation state of lead changes from 0 in Pb and +4 in PbO_2 (both reactants) to +2 in $PbSO_4$. This is also a redox reaction, in which elemental lead is the reductant, and PbO_2 is the oxidant. Which description is correct? Both.



Schematic drawing of a 12-volt car battery. The locations of the reactants (lead metal in a spongy form with large surface area) and PbO_2 are shown. The product ($PbSO_4$) forms as a white solid between the plates.

Exercise

Using Table 11.6.1 , classify each reaction as an oxidation–reduction reaction, an acid–base reaction, an exchange reaction, a condensation reaction, or a cleavage reaction. For each redox reaction, identify the oxidant and the reductant and specify which atoms are oxidized or reduced.

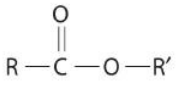
1. $Al(s) + OH^-(aq) + 3H_2O(l) \rightarrow 3/2H_2(g) + [Al(OH)_4]^-(aq)$
2. $TiCl_4(l) + 2Mg(l) \rightarrow Ti(s) + 2MgCl_2(l)$
3. $MgCl_2(aq) + Na_2CO_3(aq) \rightarrow MgCO_3(s) + 2NaCl(aq)$
4. $CO(g) + Cl_2(g) \rightarrow Cl_2CO(l)$
5. $H_2SO_4(l) + 2NH_3(g) \rightarrow (NH_4)_2SO_4(s)$

Answer:

1. Redox reaction; reductant is Al, oxidant is H_2O; Al is oxidized, H is reduced. This is the reaction that occurs when Drano is used to clear a clogged drain.
2. Redox reaction; reductant is Mg, oxidant is $TiCl_4$; Mg is oxidized, Ti is reduced.
3. Exchange reaction. This reaction is responsible for the scale that develops in coffee makers in areas that have hard water.
4. Both a condensation reaction and a redox reaction; reductant is CO, oxidant is Cl_2; C is oxidized, Cl is reduced. The product of this reaction is phosgene, a highly toxic gas used as a chemical weapon in World War I. Phosgene is now used to prepare polyurethanes, which are used in foams for bedding and furniture and in a variety of coatings.
5. Acid–base reaction.

Catalysts

Many chemical reactions, including some of those discussed previously, occur more rapidly in the presence of a catalystA substance that increases the rate of a chemical reaction without undergoing a net chemical change itself., which is a substance that participates in a reaction and causes it to occur more rapidly but can be recovered unchanged at the end of a reaction and reused.



An ester

Because catalysts are not involved in the stoichiometry of a reaction, they are usually shown above the arrow in a net chemical equation. Chemical processes in industry rely heavily on the use of catalysts, which are usually added to a reaction mixture in trace amounts, and most biological reactions do not take place without a biological catalyst or enzymeCatalysts that occur naturally in living organisms and catalyze biological reactions.. Examples of catalyzed reactions in industry are the use of platinum in petroleum cracking and reforming, the reaction of SO_2 and O_2 in the presence of V_2O_5 to produce SO_3 in the industrial synthesis of sulfuric acid, and the use of sulfuric acid in the synthesis of compounds such as ethyl acetate and procaine. Not only do catalysts greatly increase the rates of reactions, but in some cases such as in petroleum refining, they also control which products are formed. The acceleration of a reaction by a catalyst is called catalysisThe acceleration of a chemical reaction by a catalyst..



A heterogeneous catalyst. This large circular gauze, woven from rhodium-platinum wire, is a heterogeneous catalyst in the commercial production of nitric acid by the oxidation of ammonia.

Catalysts may be classified as either homogeneous or heterogeneous. A homogeneous catalystA catalyst that is uniformly dispersed throughout the reactant mixture to form a solution. is uniformly dispersed throughout the reactant mixture to form a solution. Sulfuric acid, for example, is a homogeneous catalyst used in the synthesis of esters such as procaine (Example 13). An ester has a structure similar to that of a carboxylic acid, in which the hydrogen atom attached to oxygen has been replaced by an R group. They are responsible for the fragrances of many fruits, flowers, and perfumes. Other examples of homogeneous catalysts are the enzymes that allow our bodies to function. In contrast, a heterogeneous catalystA catalyst that is in a different physical state than the reactants. is in a different physical state than the reactants. For economic reasons, most industrial processes use heterogeneous catalysts in the form of solids that are added to solutions of the reactants. Because such catalysts often contain expensive precious metals such as platinum or palladium, it makes sense to formulate them as solids that can be easily separated from the liquid or gaseous reactant-product mixture and recovered. Examples of heterogeneous catalysts are the iron oxides used in the industrial

synthesis of ammonia and the catalytic converters found in virtually all modern automobiles, which contain precious metals like palladium and rhodium. Catalysis will be discussed in more detail when we discuss reaction rates, in the second semester but you will encounter the term frequently throughout the text.

Summary

Chemical reactions may be classified as an a**cid–base reaction**, an **exchange reaction**, a **condensation reaction** and its reverse, a **cleavage reaction**, and an **oxidation–reduction (or redox)** reaction. To keep track of electrons in chemical reactions, oxidation states are assigned to atoms in compounds. The **oxidation state** is the charge an atom would have if all its bonding electrons were transferred completely to the atom that has the greater attraction for electrons. In an **oxidation–reduction reaction**, one atom must lose electrons and another must gain electrons. **Oxidation** is the loss of electrons, and an element whose oxidation state increases is said to be *oxidized*. **Reduction** is the gain of electrons, and an element whose oxidation state decreases is said to be *reduced*. **Oxidants** are compounds that are capable of accepting electrons from other compounds, so they are reduced during an oxidation–reduction reaction. In contrast, **reductants** are compounds that are capable of donating electrons to other compounds, so they are oxidized during an oxidation–reduction reaction. A **combustion reaction** is a redox reaction in which the oxidant is $O_2(g)$. An *amide bond* is formed from the condensation reaction between a carboxylic acid and an amine; it is the essential structural unit of proteins and many polymers. A **catalyst** is a substance that increases the rate of a chemical reaction without undergoing a net chemical change itself. A biological catalyst is called an **enzyme**. **Catalysis** is an acceleration in the rate of a reaction caused by the presence of a substance that does not appear in the chemical equation. A **homogeneous catalyst** is uniformly dispersed in a solution of the reactants, whereas a **heterogeneous catalyst** is present as a different phase, usually a solid.

Key Takeaway

- Chemical reactions may be classified as acid–base, exchange, condensation, cleavage, and oxidation–reduction (redox).

Conceptual Problems

1. What is a combustion reaction? How can it be distinguished from an exchange reaction?
2. What two products are formed in the combustion of an organic compound containing only carbon, hydrogen, and oxygen? Is it possible to form only these two products from a reaction that is not a combustion reaction? Explain your answer.
3. What factors determine whether a reaction can be classified as a redox reaction?
4. Name three characteristics of a balanced redox reaction.
5. Does an oxidant accept electrons or donate them?
6. Does the oxidation state of a reductant become more positive or more negative during a redox reaction?
7. Nitrogen, hydrogen, and ammonia are known to have existed on primordial earth, yet mixtures of nitrogen and hydrogen do not usually react to give ammonia. What natural phenomenon would have enough energy to initiate a reaction between these two primordial gases?
8. Catalysts are not added to reactions in stoichiometric quantities. Why?
9. State whether each of the following uses a homogeneous catalyst or a heterogeneous catalyst.
    1. Platinum metal is used in the catalytic converter of an automobile.
    2. Nitrogen is biologically converted to ammonia by an enzyme.
    3. Carbon monoxide and hydrogen combine to form methane and water with a nickel catalyst.
    4. A dissolved rhodium compound is used as a catalyst for the conversion of an alkene to an alkane.
10. State whether each of the following uses a homogeneous catalyst or a heterogeneous catalyst.
    1. Pellets of ZSM-5, an aluminum- and silicon-containing mineral, are used to catalyze the conversion of methanol to gasoline.
    2. The conversion of glucose to a carboxylic acid occurs with catalysis by the enzyme glucose oxidase.
    3. Metallic rhodium is used to the conversion of carbon monoxide and water to carbon dioxide and hydrogen.
11. Complete the following table to describe some key differences between homogeneous and heterogeneous catalysis.

	Homogeneous	Heterogeneous
number of phases		
ease of separation from product		
ease of recovery of catalyst		

12. To increase the rate of a reaction, a scientist decided to use a catalyst. Unexpectedly, the scientist discovered that the catalyst decreased the yield of the desired product, rather than increasing it. What might have happened?

Answer

1.
2.
3.
4.
5.
6.
7.
8.
9.
10.
11.

	Homogeneous	Heterogeneous
number of phases	single phase	at least two phases
ease of separation from product	difficult	easy
ease of recovery of catalyst	difficult	easy

12.

Numerical Problems

Please be sure you are familiar with the topics discussed in Essential Skills 2 (Section 7.7) before proceeding to the Numerical Problems.

1. Classify each chemical reaction according to the types listed in Table 11.6.1
    1. $12FeCl_2(s) + 3O_2(g) \rightarrow 8FeCl_3(s) + 2Fe_2O_3(s)$
    2. $CaCl_2(aq) + K_2SO_4(aq) \rightarrow CaSO_4(s) + 2KCl(aq)$
    3. $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$
    4. $Br_2(l) + C_2H_4(g) \rightarrow BrCH_2CH_2Br(l)$
2. Classify each chemical reaction according to the types listed in Table 11.6.1
    1. $4FeO(s) + O_2(g) \rightarrow 2Fe_2O_3(s)$
    2. $Ca_3(PO_4)_2(s) + 3H_2SO_4(aq) \rightarrow 3CaSO_4(s) + 2H_3PO_4(aq)$
    3. $HNO_3(aq) + KOH(aq) \rightarrow KNO_3(aq) + H_2O(l)$
    4. ethane(g) + oxygen(g) → carbon dioxide(g) + water(g)
3. Assign oxidation states to the atoms in each compound or ion.
    1. $(NH_4)_2S$
    2. the phosphate ion
    3. $[AlF_6]^{3-}$

4. CuS
5. HCO_3^-
6. NH_4^+
7. H_2SO_4
8. formic acid
9. *n*-butanol

4. Assign oxidation states to the atoms in each compound or ion.

1. ClO_2
2. HO_2^-
3. sodium bicarbonate
4. MnO_2
5. PCl_5
6. $[Mg(H_2O)_6]^{2+}$
7. N_2O_4
8. butanoic acid
9. methanol

5. Balance this chemical equation:

$NaHCO_3(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + CO_2(g) + H_2O(l)$

What type of reaction is this? Justify your answer.

6. Assign oxidation states to the atoms in each compound.

1. iron(III) nitrate
2. Al_2O_3
3. potassium sulfate
4. Cr_2O_3
5. sodium perchlorate
6. Cu_2S
7. hydrazine (N_2H_4)
8. NO_2
9. *n*-pentanol

7. Assign oxidation states to the atoms in each compound.

1. calcium carbonate
2. NaCl
3. CO_2
4. potassium dichromate
5. $KMnO_4$
6. ferric oxide
7. $Cu(OH)_2$
8. Na_2SO_4
9. *n*-hexanol

8. For each redox reaction, determine the identities of the oxidant, the reductant, the species oxidized, and the species reduced.

1. $H_2(g) + I_2(s) \rightarrow 2HI(g)$
2. $2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$
3. $2F_2(g) + 2NaOH(aq) \rightarrow OF_2(g) + 2NaF(aq) + H_2O(l)$

9. For each redox reaction, determine the identities of the oxidant, the reductant, the species oxidized, and the species reduced.

1. $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$

2. $SiCl_4(l) + 2Mg(s) \rightarrow 2MgCl_2(s) + Si(s)$
3. $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

10. Balance each chemical equation. Then identify the oxidant, the reductant, the species oxidized, and the species reduced. (Δ indicates that the reaction requires heating.)
    1. $H_2O(g) + CO(g) \rightarrow CO_2(g) + H_2(g)$
    2. the reaction of aluminum oxide, carbon, and chlorine gas at 900ºC to produce aluminum chloride and carbon monoxide
    3. $HgO(s) \rightarrow Hg(l) + O_2(g)$
11. Balance each chemical equation. Then identify the oxidant, the reductant, the species oxidized, and the species reduced. (Δ indicates that the reaction requires heating.)
    1. the reaction of water and carbon at 800ºC to produce hydrogen and carbon monoxide
    2. $Mn(s) + S_8(s) + CaO(s) \rightarrow CaS(s) + MnO(s)$
    3. the reaction of ethylene and oxygen at elevated temperature in the presence of a silver catalyst to produce ethylene oxide

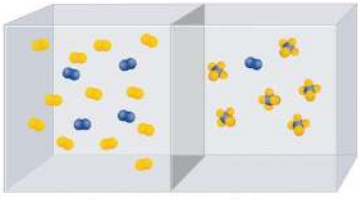


Ethylene oxide

    4. $ZnS(s) + H_2SO_4(aq) + O_2(g) \rightarrow ZnSO_4(aq) + S_8(s) + H_2O(l)$
12. Silver is tarnished by hydrogen sulfide, an atmospheric contaminant, to form a thin layer of dark silver sulfide (Ag_2S) along with hydrogen gas.
    1. Write a balanced chemical equation for this reaction.
    2. Which species has been oxidized and which has been reduced?
    3. Assuming 2.2 g of Ag has been converted to silver sulfide, construct a table showing the reaction in terms of the number of atoms in the reactants and products, the moles of reactants and products, the grams of reactants and products, and the molecules of reactants and products.
13. The following reaction is used in the paper and pulp industry:

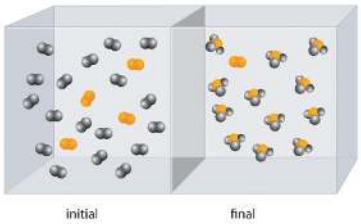
    $Na_2SO_4(aq) + C(s) + NaOH(aq) \rightarrow Na_2CO_3(aq) + Na_2S(aq) + H_2O(l)$

    1. Balance the chemical equation.
    2. Identify the oxidant and the reductant.
    3. How much carbon is needed to convert 2.8 kg of sodium sulfate to sodium sulfide?
    4. If the yield of the reaction were only 78%, how many kilograms of sodium carbonate would be produced from 2.80 kg of sodium sulfate?
    5. If 240 g of carbon and 2.80 kg of sodium sulfate were used in the reaction, what would be the limiting reactant (assuming an excess of sodium hydroxide)?
14. The reaction of A_2 (blue) with B_2 (yellow) is shown below. The initial reaction mixture is shown on the left and the mixture after the reaction has gone to completion is shown on the right.



    1. Write a balanced chemical equation for the reaction.
    2. Which is the limiting reactant in the initial reaction mixture?
    3. How many moles of the product AB_4 could you obtain from a mixture of 0.020 mol A_2 and 0.060 mol B_2?

15. The reaction of X_4 (orange) with Y_2 (black) is shown below. The initial reaction mixture is shown on the left and the mixture after the reaction has gone to completion is shown on the right.



    1. Write a balanced chemical equation for the reaction.
    2. Which is the limiting reactant in the initial reaction mixture?
    3. How many moles of the product XY_3 could you obtain from a mixture of 0.100 mol X_4 and 0.300 mol Y_2?

16. Methyl butyrate, an artificial apple flavor used in the food industry, is produced by the reaction of butanoic acid with methanol in the presence of an acid catalyst (H^+):

$$CH_3CH_2CH_2COOH\,(l) + CH_3OH\,(l) \xrightarrow{H^+} CH_3CH_2CH_2CO_2CH_3\,(l) + H_2O\,(l) \qquad \text{(Chapter 11.6.9)}$$

    1. Given 7.8 g of butanoic acid, how many grams of methyl butyrate would be synthesized, assuming 100% yield?
    2. The reaction produced 5.5 g of methyl butyrate. What was the percent yield?
    3. Is the catalyst used in this reaction heterogeneous or homogeneous?

17. In the presence of a platinum catalyst, hydrogen and bromine react at elevated temperatures (300°C) to form hydrogen bromide (heat is indicated by Δ):

$$H_{2(g)} + Br_2\,(l) \xrightarrow[\Delta]{Pt} 2HBr\,(g) \qquad \text{(Chapter 11.6.10)}$$

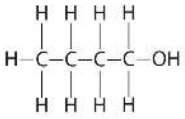
    Given the following, calculate the mass of hydrogen bromide produced:

    1. 8.23×10^{22} molecules of H_2
    2. 6.1×10^3 mol of H_2
    3. 1.3×10^5 g of H_2
    4. Is the catalyst used in this reaction heterogeneous or homogeneous?

Answers

1. 1. redox reaction
    2. exchange
    3. acid–base
    4. condensation
2.
3. 1. S, −2; N, −3; H, +1
    2. P, +5; O, −2
    3. F, −1; Al, +3
    4. S, −2; Cu, +2
    5. H, +1; O, −2; C, +4
    6. H, +1; N, −3
    7. H, +1; O, −2; S, +6
    8. H, +1, O, −2; C, +2

9. butanol:



O,−2; H, +1

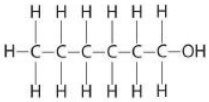
From left to right: C, −3–2–2–1

4.

5. $2NaHCO_3(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2CO_2(g) + 2H_2O(l)$ acid–base reaction

6.

7. 1. Ca, +2; O, −2; C, +4
   2. Na, +1; Cl, −1
   3. O, −2; C, +4
   4. K, +1; O, −2; Cr, +6
   5. K, +1; O, −2; Mn, +7
   6. O, −2; Fe, +3
   7. O, −2; H, +1; Cu, +2
   8. O, −2; S, +6
   9. Hexanol



O,−2; H, +1 From left to right: C: −3, −2, −2, −2, −2, −1

8.

9. 1. Na is the reductant and is oxidized. Cl_2 is the oxidant and is reduced.
   2. Mg is the reductant and is oxidized. Si is the oxidant and is reduced.
   3. H_2O_2 is both the oxidant and reductant. One molecule is oxidized, and one molecule is reduced.

10.

11. 1. $H_2O(g) + C(s) \rightarrow H_2(g) + CO(g)$

    C is the reductant and is oxidized. H_2O is the oxidant and is reduced.

    2. $8Mn(s) + S_8(s) + 8CaO(s) \rightarrow 8CaS(s) + 8MnO(s)$

    Mn is the reductant and is oxidized. The S_8 is the oxidant and is reduced.

    3. $2C_2H_4(g) + O_2(g) >\rightarrow 2C_2H_4O(g)$

    Ethylene is the reductant and is oxidized. O_2 is the oxidant and is reduced.

    4. $8ZnS(s) + 8H_2SO_4(aq) + 4O_2(g) \rightarrow 8ZnSO_4(aq) + S_8(s) + 8H_2O(l)$

    Sulfide in ZnS is the reductant and is oxidized. O_2 is the oxidant and is reduced.

12.

13. 1. $Na_2SO_4 + 2C + 4NaOH \rightarrow 2Na_2CO_3 + Na_2S + 2H_2O$
    2. The sulfate ion is the oxidant, and the reductant is carbon.
    3. 470 g
    4. 3300 g
    5. carbon

14.
15.
16.
17. 1. 22.1 g
    2. 9.9×10^5 g
    3. 1.0×10^7 g
    4. heterogeneous

Contributors

- Anonymous

Modified by Joshua Halpern, Scott Sinex and Scott Johnson

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Chapter 11.7: End of Chapter Material

Application Problems

Problems marked with a ♦ involve multiple concepts.

1. Hydrogen sulfide is a noxious and toxic gas produced from decaying organic matter that contains sulfur. A lethal concentration in rats corresponds to an inhaled dose of 715 molecules per million molecules of air. How many molecules does this correspond to per mole of air? How many moles of hydrogen sulfide does this correspond to per mole of air?
2. Bromine, sometimes produced from brines (salt lakes) and ocean water, can be used for bleaching fibers and silks. How many moles of bromine atoms are found in 8.0 g of molecular bromine (Br_2)?
3. Paris yellow is a lead compound that is used as a pigment; it contains 16.09% chromium, 19.80% oxygen, and 64.11% lead. What is the empirical formula of Paris yellow?
4. A particular chromium compound used for dyeing and waterproofing fabrics has the elemental composition 18.36% chromium, 13.81% potassium, 45.19% oxygen, and 22.64% sulfur. What is the empirical formula of this compound?
5. Compounds with aluminum and silicon are commonly found in the clay fractions of soils derived from volcanic ash. One of these compounds is *vermiculite*, which is formed in reactions caused by exposure to weather. Vermiculite has the following formula: $Ca_{0.7}[Si_{6.6}Al_{1.4}]Al_4O_{20}(OH)_4$. (The content of calcium, silicon, and aluminum are not shown as integers because the relative amounts of these elements vary from sample to sample.) What is the mass percent of each element in this sample of vermiculite?
6. ♦ Pheromones are chemical signals secreted by a member of one species to evoke a response in another member of the same species. One honeybee pheromone is an organic compound known as an alarm pheromone, which smells like bananas. It induces an aggressive attack by other honeybees, causing swarms of angry bees to attack the same aggressor. The composition of this alarm pheromone is 64.58% carbon, 10.84% hydrogen, and 24.58% oxygen by mass, and its molecular mass is 130.2 amu.
   a. Calculate the empirical formula of this pheromone.
   b. Determine its molecular formula.
   c. Assuming a honeybee secretes 1.00×10^{-11} g of pure pheromone, how many molecules of pheromone are secreted?
7. Amoxicillin is a prescription drug used to treat a wide variety of bacterial infections, including infections of the middle ear and the upper and lower respiratory tracts. It destroys the cell walls of bacteria, which causes them to die. The elemental composition of amoxicillin is 52.59% carbon, 5.24% hydrogen, 11.50% nitrogen, 21.89% oxygen, and 8.77% sulfur by mass. What is its empirical formula?
8. Monosodium glutamate (MSG; molar mass = 169 g/mol), is used as a flavor enhancer in food preparation. It is known to cause headaches and chest pains in some individuals, the so-called Chinese food syndrome. Its composition was found to be 35.51% carbon, 4.77% hydrogen, 8.28% nitrogen, and 13.59% sodium by mass. If the “missing” mass is oxygen, what is the empirical formula of MSG?
9. Ritalin is a mild central nervous system stimulant that is prescribed to treat attention deficit disorders and narcolepsy (an uncontrollable desire to sleep). Its chemical name is methylphenidate hydrochloride, and its empirical formula is $C_{14}H_{20}ClNO_2$. If you sent a sample of this compound to a commercial laboratory for elemental analysis, what results would you expect for the mass percentages of carbon, hydrogen, and nitrogen?
10. Fructose, a sugar found in fruit, contains only carbon, oxygen, and hydrogen. It is used in ice cream to prevent a sandy texture. Complete combustion of 32.4 mg of fructose in oxygen produced 47.6 mg of CO_2 and 19.4 mg of H_2O. What is the empirical formula of fructose?
11. Coniine, the primary toxin in hemlock, contains only carbon, nitrogen, and hydrogen. When ingested, it causes paralysis and eventual death. Complete combustion of 28.7 mg of coniine produced 79.4 mg of CO_2 and 34.4 mg of H_2O. What is the empirical formula of the coniine?

12. Copper and tin alloys (bronzes) with a high arsenic content were presumably used by Bronze Age metallurgists because bronze produced from arsenic-rich ores had superior casting and working properties. The compositions of some representative bronzes of this type are as follows:

Origin	% Composition	
	Cu	As
Dead Sea	87.0	12.0
Central America	90.7	3.8

If ancient metallurgists had used the mineral As_2S_3 as their source of arsenic, how much As_2S_3 would have been required to process 100 g of cuprite (Cu_2O) bronzes with these compositions?

13. ♦ The phrase *mad as a hatter* refers to mental disorders caused by exposure to mercury(II) nitrate in the felt hat manufacturing trade during the 18th and 19th centuries. An even greater danger to humans, however, arises from alkyl derivatives of mercury.

    a. Give the empirical formula of mercury(II) nitrate.
    b. One alkyl derivative, dimethylmercury, is a highly toxic compound that can cause mercury poisoning in humans. How many molecules are contained in a 5.0 g sample of dimethylmercury?
    c. What is the percentage of mercury in the sample?

14. Magnesium carbonate, aluminum hydroxide, and sodium bicarbonate are commonly used as antacids. Give the empirical formulas and determine the molar masses of these compounds. Based on their formulas, suggest another compound that might be an effective antacid.

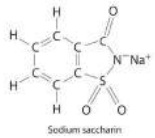
15. ♦ Nickel(II) acetate, lead(II) phosphate, zinc nitrate, and beryllium oxide have all been reported to induce cancers in experimental animals.

    a. Give the empirical formulas for these compounds.
    b. Calculate their formula masses.
    c. Based on the location of cadmium in the periodic table, would you predict that cadmium chloride might also induce cancer?

16. ♦ Methane, the major component of natural gas, is found in the atmospheres of Jupiter, Saturn, Uranus, and Neptune.

    a. What is the structure of methane?
    b. Calculate the molecular mass of methane.
    c. Calculate the mass percentage of both elements present in methane.

17. Sodium saccharin, which is approximately 500 times sweeter than sucrose, is frequently used as a sugar substitute. What are the percentages of carbon, oxygen, and sulfur in this artificial sweetener?



Sodium saccharin

18. Lactic acid, found in sour milk, dill pickles, and sauerkraut, has the functional groups of both an alcohol and a carboxylic acid. The empirical formula for this compound is CH_2O, and its molar mass is 90 g/mol. If this compound were sent to a laboratory for elemental analysis, what results would you expect for carbon, hydrogen, and oxygen content?

19. The compound 2-nonenal is a cockroach repellant that is found in cucumbers, watermelon, and carrots. Determine its molecular mass.



2-Nonenal

20. You have obtained a 720 mg sample of what you believe to be pure fructose, although it is possible that the sample has been contaminated with formaldehyde. Fructose and formaldehyde both have the empirical formula CH_2O. Could you use the results from combustion analysis to determine whether your sample is pure?

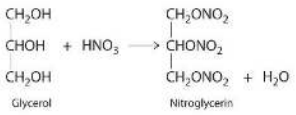
21. ♦ The booster rockets in the space shuttles used a mixture of aluminum metal and ammonium perchlorate for fuel. Upon ignition, this mixture can react according to the chemical equation

$$Al\,(s) + NH_4ClO_4\,(s) \rightarrow Al_2O_3\,(s) + AlCl_3\,(g) + NO\,(g) + H_2O\,(g) \quad \text{(Chapter 11.7.1)}$$

Balance the equation and construct a table showing how to interpret this information in terms of the following:

a. numbers of individual atoms, molecules, and ions
b. moles of reactants and products
c. grams of reactants and products
d. numbers of molecules of reactants and products given 1 mol of aluminum metal

22. ♦ One of the byproducts of the manufacturing of soap is glycerol. In 1847, it was discovered that the reaction of glycerol with nitric acid produced nitroglycerin according to the following unbalanced chemical equation:



Nitroglycerine is both an explosive liquid and a blood vessel dilator that is used to treat a heart condition known as angina.

a. Balance the chemical equation and determine how many grams of nitroglycerine would be produced from 15.00 g of glycerol.
b. If 9.00 g of nitric acid had been used in the reaction, which would be the limiting reactant?
c. What is the theoretical yield in grams of nitroglycerin?
d. If 9.3 g of nitroglycerin was produced from 9.0 g of nitric acid, what would be the percent yield?
e. Given the data in part d, how would you rate the success of this reaction according to the criteria mentioned in this chapter?
f. Derive a general expression for the theoretical yield of nitroglycerin in terms of *x* grams of glycerol.

23. ♦ A significant weathering reaction in geochemistry is hydration–dehydration. An example is the transformation of hematite (Fe_2O_3) to ferrihydrite ($Fe_{10}O_{15}{\cdot}9H_2O$) as the relative humidity of the soil approaches 100%:

$$Fe_2O_3\,(s) + H_2O\,(l) \rightarrow Fe_{10}O_{15} \cdot 9H_2O\,(s) \quad \text{(Chapter 11.7.2)}$$

This reaction occurs during advanced stages of the weathering process.

1. Balance the chemical equation.
2. Is this a redox reaction? Explain your answer.
3. If 1 tn of hematite rock weathered in this manner, how many kilograms of ferrihydrite would be formed?

24. ♦ Hydrazine (N_2H_4) is used not only as a rocket fuel but also in industry to remove toxic chromates from waste water according to the following chemical equation:

$$4CrO_4^{2-}(aq) + 3N_2H_4\,(l) + 4H_2O\,(l) \rightarrow 4Cr(OH)_3\,(s) + 3N_2\,(g) + 8OH^-(aq) \quad \text{(Chapter 11.7.3)}$$

Identify the species that is oxidized and the species that is reduced. What mass of water is needed for the complete reaction of 15.0 kg of hydrazine? Write a general equation for the mass of chromium(III) hydroxide [$Cr(OH)_3$] produced from *x* grams of hydrazine.

25. ♦ *Corrosion* is a term for the deterioration of metals through chemical reaction with their environment. A particularly difficult problem for the archaeological chemist is the formation of CuCl, an unstable compound that is formed by the corrosion of copper and its alloys. Although copper and bronze objects can survive burial for centuries without significant deterioration, exposure to air can cause cuprous chloride to react with atmospheric oxygen to form Cu_2O and cupric chloride. The cupric chloride then reacts with the free metal to produce cuprous chloride. Continued reaction of oxygen and water with cuprous chloride causes "bronze disease," which consists of spots of a pale green, powdery deposit of $[CuCl_2{\cdot}3Cu(OH)_2{\cdot}H_2O]$ on the surface of the object that continues to grow. Using this series of reactions described, complete and balance the following equations, which together result in bronze disease:

Equation 1: ___ + O_2 → ___ + ___

Equation 2: ___ + Cu → ___

Equation 3: $\underset{bronzedisease}{\text{___} + O_2 + H_2O \rightarrow CuCl_2 \cdot 3Cu(OH)_2 \cdot H_2) + CuCl_2}$

a. Which species are the oxidants and the reductants in each equation?
b. If 8.0% by mass of a 350.0 kg copper statue consisted of CuCl, and the statue succumbed to bronze disease, how many pounds of the powdery green hydrate would be formed?
c. What factors could affect the rate of deterioration of a recently excavated bronze artifact?

26. ♦ Iron submerged in seawater will react with dissolved oxygen, but when an iron object, such as a ship, sinks into the seabed where there is little or no free oxygen, the iron remains fresh until it is brought to the surface. Even in the seabed, however, iron can react with salt water according to the following unbalanced chemical equation:

$$Fe(s) + NaCl(aq) + H_2O(l) \rightarrow FeCl_2(s) + NaOH(aq) + H_2(g) \quad \text{(Chapter 11.7.4)}$$

The ferrous chloride and water then form hydrated ferrous chloride according to the following equation:

$$FeCl_2(s) + 2H_2O(l) \rightarrow FeCl_2 \cdot 2H_2O(s) \quad \text{(Chapter 11.7.5)}$$

When the submerged iron object is removed from the seabed, the ferrous chloride dihydrate reacts with atmospheric moisture to form a solution that seeps outward, producing a characteristic "sweat" that may continue to emerge for many years. Oxygen from the air oxidizes the solution to ferric resulting in the formation of what is commonly referred to as rust (ferric oxide):

$$FeCl_2(aq) + O_2(g) \rightarrow FeCl_3(aq) + Fe_2O_3(s) \quad \text{(Chapter 11.7.6)}$$

The rust layer will continue to grow until arrested.

a. Balance each chemical equation.
b. Given a 10.0 tn ship of which 2.60% is now rust, how many kilograms of iron were converted to $FeCl_2$, assuming that the ship was pure iron?
c. What mass of rust in grams would result?
d. What is the overall change in the oxidation state of iron for this process?
e. In the first equation given, what species has been reduced? What species has been oxidized?

27. ♦ The glass industry uses lead oxide in the production of fine crystal glass, such as crystal goblets. Lead oxide can be formed by the following reaction:

$$PbS(s) + O_2(g) \rightarrow PbO(s) + SO_2(g) \quad \text{(Chapter 11.7.7)}$$

Balance the equation and determine what has been oxidized and what has been reduced. How many grams of sulfur dioxide would be produced from 4.0×10^3 g of lead sulfide? Discuss some potential environmental hazards that stem from this reaction.

28. ♦ The Deacon process is one way to recover Cl_2 on-site in industrial plants where the chlorination of hydrocarbons produces HCl. The reaction uses oxygen to oxidize HCl to chlorine, as shown.

$$HCl\,(g) + O_2\,(g) \rightarrow Cl_2\,(g) + H_2O\,(g) \qquad \text{(Chapter 11.7.8)}$$

The reaction is frequently carried out in the presence of NO as a catalyst.

a. Balance the chemical equation.
b. Which compound is the oxidant, and which is the reductant?
c. If 26 kg of HCl was produced during a chlorination reaction, how many kilograms of water would result from the Deacon process?

29. In 1834, Eilhardt Mitscherlich of the University of Berlin synthesized benzene (C_6H_6) by heating benzoic acid (C_6H_5COOH) with calcium oxide according to this balanced chemical equation:

$$C_6H_5COOH\,(s) + CaO\,(s) \xrightarrow{\Delta} C_6H_6\,(l) + CaCO_3\,(s) \qquad \text{(Chapter 11.7.9)}$$

(Heating is indicated by the symbol Δ.) How much benzene would you expect from the reaction of 16.9 g of benzoic acid and 18.4 g of calcium oxide? Which is the limiting reactant? How many grams of benzene would you expect to obtain from this reaction, assuming a 73% yield?

30. Aspirin ($C_9H_8O_4$) is synthesized by the reaction of salicylic acid ($C_7H_6O_3$) with acetic anhydride ($C_4H_6O_3$) according to the following equation:

$$C_7H_6O_3\,(s) + C_4H_6O_3\,(l) \rightarrow C_9H_8O_4\,(s) + H_2O\,(l) \qquad \text{(Chapter 11.7.10)}$$

Balance the equation and find the limiting reactant given 10.0 g of acetic anhydride and 8.0 g of salicylic acid. How many grams of aspirin would you expect from this reaction, assuming an 83% yield?

31. ♦ Hydrofluoric acid etches glass because it dissolves silicon dioxide, as represented in the following chemical equation:

$$SiO_2\,(s) + HF\,(aq) \rightarrow SiF_6^{2-}\,(aq) + H^+\,(aq) + H_2O\,(l) \qquad \text{(Chapter 11.7.11)}$$

a. Balance the equation.
b. How many grams of silicon dioxide will react with 5.6 g of HF?
c. How many grams of HF are needed to remove 80% of the silicon dioxide from a 4.0 kg piece of glass? (Assume that the glass is pure silicon dioxide.)

32. ♦ Lead sulfide and hydrogen peroxide react to form lead sulfate and water. This reaction is used to clean oil paintings that have blackened due to the reaction of the lead-based paints with atmospheric hydrogen sulfide.

1. Write the balanced chemical equation for the oxidation of lead sulfide by hydrogen peroxide.
2. What mass of hydrogen peroxide would be needed to remove 3.4 g of lead sulfide?
3. If the painting had originally been covered with 5.4 g of lead sulfide and you had 3.0 g of hydrogen peroxide, what percent of the lead sulfide could be removed?

33. ♦ It has been suggested that diacetylene (C_4H_2, HC≡C–C≡CH) may be the ozone of the outer planets. As the largest hydrocarbon yet identified in planetary atmospheres, diacetylene shields planetary surfaces from ultraviolet radiation and is itself reactive when exposed to light. One reaction of diacetylene is an important route for the formation of higher hydrocarbons, as shown in the following chemical equations:

$$\begin{aligned} &C_4H_2\,(g) + C_4H_2\,(g) \\ &\rightarrow C_8H_3\,(g) + H\,(g)\; C_8H_3\,(g) + C_4H_2\,(g) \\ &\rightarrow C_{10}H_3\,(g) + C_2H_2\,(g) \end{aligned} \qquad \text{(Chapter 11.7.12)}$$

Consider the second reaction.

a. Given 18.4 mol of C_8H_3 and 1000 g of C_4H_2, which is the limiting reactant?

b. Given 2.8×10^{24} molecules of C_8H_3 and 250 g of C_4H_2, which is the limiting reactant?
c. Given 385 g of C_8H_3 and 200 g of C_4H_2, which is in excess? How many grams of excess reactant would remain?
d. Suggest why this reaction might be of interest to scientists.

34. ♦ Glucose ($C_6H_{12}O_6$) can be converted to ethanol and carbon dioxide using certain enzymes. As alcohol concentrations are increased, however, catalytic activity is inhibited, and alcohol production ceases.

a. Write a balanced chemical equation for the conversion of glucose to ethanol and carbon dioxide.
b. Given 12.6 g of glucose, how many grams of ethanol would be produced, assuming complete conversion?
c. If 4.3 g of ethanol had been produced, what would be the percent yield for this reaction?
d. Is a heterogeneous catalyst or a homogeneous catalyst used in this reaction?
e. You have been asked to find a way to increase the rate of this reaction given stoichiometric quantities of each reactant. How would you do this?

35. Early spacecraft developed by the National Aeronautics and Space Administration for its manned missions used capsules that had a pure oxygen atmosphere. This practice was stopped when a spark from an electrical short in the wiring inside the capsule of the Apollo 1 spacecraft ignited its contents. The resulting explosion and fire killed the three astronauts on board within minutes. What chemical steps could have been taken to prevent this disaster?

Answers

1. 4.31×10^{20} molecules, 7.15×10^{-4}
2.
3. $PbCrO_4$
4.
5. To two decimal places, the percentages are: H: 0.54%; O: 51.39%; Al: 19.50%; Si: 24.81%; Ca: 3.75%
6.
7. $C_{16}H_{19}O_5N_3S$
8.
9.
10.
11.
12.
13. 1. $Hg(NO_3)_2$
    2. 1.3×10^{22} molecules
    3. 86.96% mercury by mass.
14.
15. 1. $Ni(O_2CCH_3)_2$; $Pb_3(PO_4)_2$; $Zn(NO_3)_2$; BeO
    2. To four significant figures, the values are: $Ni(O_2CCH_3)_2$, 176.8 amu; $Pb_3(PO_4)_2$, 811.5 amu; $Zn(NO_3)_2$, 189.4 amu; BeO, 25.01 amu.
    3. Yes.
16.
17. C, 40.98%; O, 23.39%; S, 15.63%
18.
19. 140.22 amu
20.
21. $3Al(s) + 3NH_4ClO_4(s) \rightarrow Al_2O_3(s) + AlCl_3(g) + 3NO(g) + 6H_2O(g)$

	3Al	$3NH_4ClO_4$	Al_2O_3
a.	3 atoms	30 atoms, 6 ions	5 atoms
b.	3 mol	3 mol	1 mol
c.	81 g	352 g	102 g
d.	6×10^{23}	6×10^{23}	2×10^{23}

	$AlCl_3$	3NO	$6H_2O$
a.	4 atoms, 1 molecule	6 atoms, 3 molecules	18 atoms, 6 molecules
b.	1 mol	3 mol	6 mol
c.	133 g	90 g	108 g
d.	2×10^{23}	6×10^{23}	1.2×10^{22}

22.

23. 1. $5Fe_2O_3 + 9H_2O \rightarrow Fe_{10}O_{15} \cdot 9H_2O$
    2. No.
    3. 1090 kg

24.

25. Equation 1: $8CuCl + O_2 \rightarrow 2Cu_2O + 4CuCl_2$

    Equation 2: $CuCl_2 + Cu \rightarrow 2CuCl$ Equation 3: $12CuCl + 3O_2 + 8H_2O \rightarrow 2[CuCl_2\ 3Cu(OH)_2\ H_2O] + 4CuCl_2$

    1. Equation 1: Oxygen is the oxidant, and CuCl is the reductant. Equation 2: Copper is the reductant, and copper(II) chloride is the oxidant. Equation 3: Copper(I) chloride is the reductant, and oxygen is the oxidant.
    2. 46 pounds
    3. temperature, humidity, and wind (to bring more O_2 into contact with the statue)

26.

27. $2PbS(s) + 3O_2(g) \rightarrow 2PbO(s) + 2SO_2(g)$ Sulfur in PbS has been oxidized, and oxygen has been reduced. 1.1×10^3 g SO_2 is produced. Lead is a toxic metal. Sulfur dioxide reacts with water to make acid rain.

28.

29. 10.8 g benzene; limiting reactant is benzoic acid; 7.9 g of benzene

30.

31. 1. $SiO_2 + 6HF \rightarrow SiF_6^{2-} + 2H^+ + 2H_2O$
    2. 2.8 g
    3. 6400 g HF

32.

33. 1. C_8H_3
    2. C_8H_3
    3. C_4H_2; 6.0 g
    4. Complex molecules are essential for life. Reactions that help block UV may have implications regarding life on other planets.

34.

35. The disaster occurred because organic compounds are highly flammable in a pure oxygen atmosphere. Using a mixture of 20% O_2 and an inert gas such as N_2 or He would have prevented the disaster.

Contributors

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CHAPTER OVERVIEW

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- Chapter 12.1: Preparing Solutions
- Chapter 12.2: Stoichiometry of Reactions in Solution
- Chapter 12.3: Ionic Equations
- Chapter 12.4: Precipitation Reactions
- Chapter 12.5: Acid Base Reactions
- Chapter 12.6: The Chemistry of Acid Rain
- Chapter 12.7: Oxidation-Reduction Reactions
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Chapter 12.1: Preparing Solutions

Learning Objective

- To describe the concentrations of solutions quantitatively.

In Section 9.3 we described various ways of characterizing the concentration of solution, molarity (M), molality (m), percent concentrations and mole fraction (X). The quantity of solute that is dissolved in a particular quantity of solvent or solution. of a solution describes the quantity of a solute that is contained in a particular quantity of solvent or solution. Knowing the concentration of solutes is important in controlling the stoichiometry of reactants for reactions that occur in solution. This section describes how solutions can be prepared from stock solution of known concentration

The Preparation of Solutions

To prepare a solution that contains a specified concentration of a substance, it is necessary to dissolve the desired number of moles of solute in enough solvent to give the desired final volume of solution.

$$Molarity of solution = dfrac moles of soluteVolume of solution$$

Figure 12.1.1 illustrates this procedure for a solution of cobalt(II) chloride dihydrate in ethanol. Note that the volume of the *solvent* is not specified. Because the solute occupies space in the solution, the volume of the solvent needed is almost always *less* than the desired volume of solution. For example, if the desired volume were 1.00 L, it would be incorrect to add 1.00 L of water to 342 g of sucrose because that would produce more than 1.00 L of solution. As shown in Figure 12.1.2, for some substances this effect can be significant, especially for concentrated solutions.



Figure 12.1.1 Preparation of a Solution of Known Concentration Using a Solid Solute

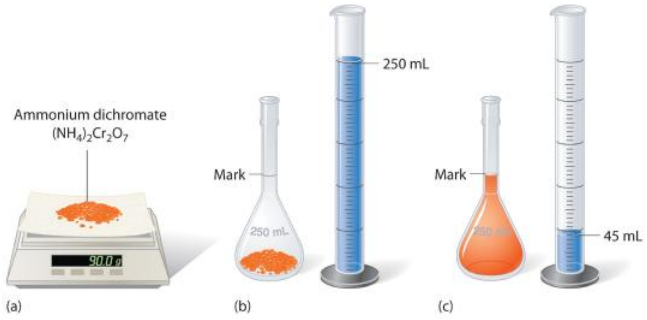


Figure 12.1.2 Preparation of 250 mL of a Solution of $(NH_4)_2Cr_2O_7$ in Water

The solute occupies space in the solution, so less than 250 mL of water are needed to make 250 mL of solution.

Example 12.1.1

The solution in Figure 12.1.1 contains 10.0 g of cobalt(II) chloride dihydrate, $CoCl_2 \cdot 2H_2O$, in enough ethanol to make exactly 500 mL of solution. What is the molar concentration of $CoCl_2 \cdot 2H_2O$?

Given: mass of solute and volume of solution

Asked for: concentration (M)

Strategy:

To find the number of moles of $CoCl_2 \cdot 2H_2O$, divide the mass of the compound by its molar mass. Calculate the molarity of the solution by dividing the number of moles of solute by the volume of the solution in liters.

Solution:

The molar mass of $CoCl_2 \cdot 2H_2O$ is 165.87 g/mol. Therefore,

$$moles\ CoCl_2 \cdot 2H_2O = \left(\frac{10.0\ \cancel{g}}{165.87\ \cancel{g}/mol}\right) = 0.0603\ mol$$

The volume of the solution in liters is

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

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

$$molarity = \frac{0.0603\ mol}{0.500\ L} = 0.121\ M = CoCl_2 \cdot H_2O$$

Exercise

The solution shown in Figure 12.1.2 contains 90.0 g of $(NH_4)_2Cr_2O_7$ in enough water to give a final volume of exactly 250 mL. What is the molar concentration of ammonium dichromate?

Answer: $(NH_4)_2Cr_2O_7$ = 1.43 M

To prepare a particular volume of a solution that contains a specified concentration of a solute, we first need to calculate the number of moles of solute in the desired volume of solution using the relationship shown in Equation 12.1.1. We then convert the number of moles of solute to the corresponding mass of solute needed. This procedure is illustrated in Example 12.1.2.

Example 12.1.2

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

Given: molarity, volume, and molar mass of solute

Asked for: mass of solute

Strategy:

A Calculate the number of moles of glucose contained in the specified volume of solution by multiplying the volume of the solution by its molarity.

B Obtain the mass of glucose needed by multiplying the number of moles of the compound by its molar mass.

Solution:

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

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

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

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

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

Exercise

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

Answer: 2.3 g NaCl

A solution of a desired concentration can also be prepared by diluting a small volume of a more concentrated solution with additional solvent. A stock solution is a commercially prepared solution of known concentration and is often used for this purpose. Diluting a stock solution is preferred because the alternative method, weighing out tiny amounts of solute, is difficult to carry out with a high degree of accuracy. Dilution is also used to prepare solutions from substances that are sold as concentrated aqueous solutions, such as strong acids.

The procedure for preparing a solution of known concentration from a stock solution is shown in Figure 12.1.3. It requires calculating the number of moles of solute desired in the final volume of the more dilute solution and then calculating the volume of the stock solution that contains this amount of solute. Remember that diluting a given quantity of stock solution with solvent does *not* change the number of moles of solute present. The relationship between the volume and concentration of the stock solution and the volume and concentration of the desired diluted solution is therefore

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

where the subscripts *s* and *d* indicate the stock and dilute solutions, respectively. Example 5 demonstrates the calculations involved in diluting a concentrated stock solution.

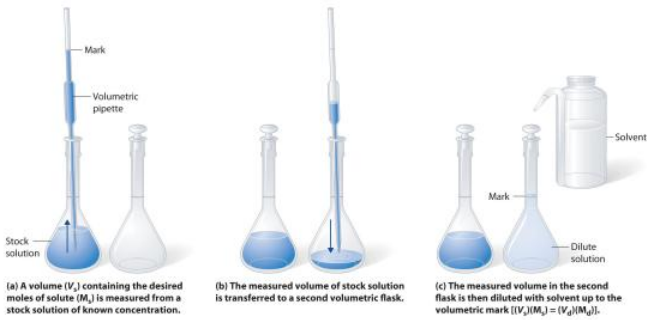


Figure 12.1.3 Preparation of a Solution of Known Concentration by Diluting a Stock Solution *(a) A volume (V_s) containing the desired moles of solute (M_s) is measured from a stock solution of known concentration. (b) The measured volume of stock solution is transferred to a second volumetric flask. (c) The measured volume in the second flask is then diluted with solvent up to the volumetric mark [$(V_s)(M_s) = (V_d)(M_d)$].*

Example 12.1.3

What volume of a 3.00 M glucose stock solution is necessary to prepare 2500 mL of the D5W solution in Example 4?

Given: volume and molarity of dilute solution

Asked for: volume of stock solution

Strategy:

A Calculate the number of moles of glucose contained in the indicated volume of dilute solution by multiplying the volume of the solution by its molarity.

B To determine the volume of stock solution needed, divide the number of moles of glucose by the molarity of the stock solution.

Solution:

A The D5W solution in Example 4 was 0.310 M glucose. We begin by using Equation 12.1.2 to calculate the number of moles of glucose contained in 2500 mL of the solution:

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

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

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

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

We could also have solved this problem in a single step by solving Equation 12.1.2 for V_s and substituting the appropriate values:

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

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

Exercise

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

Answer: 16 mL

Ion Concentrations in Solution

In Section 9.3 we calculated that a solution containing 90.00 g of ammonium dichromate in a final volume of 250 mL has a concentration of 1.43 M. Let's consider in more detail exactly what that means. Ammonium dichromate is an ionic compound that contains two NH_4^+ ions and one $Cr_2O_7^{2-}$ ion per formula unit. Like other ionic compounds, it is a strong electrolyte that dissociates in aqueous solution to give hydrated NH_4^+ and $Cr_2O_7^{2-}$ ions:

$$(NH_4)_2Cr_2O_7(s) \xrightarrow{H_2O(l)} 2NH_4^+(aq) + Cr_2O_7^{2-}(aq)$$

Thus 1 mol of ammonium dichromate formula units dissolves in water to produce 1 mol of $Cr_2O_7^{2-}$ anions and 2 mol of NH_4^+ cations (see Figure 12.1.4).

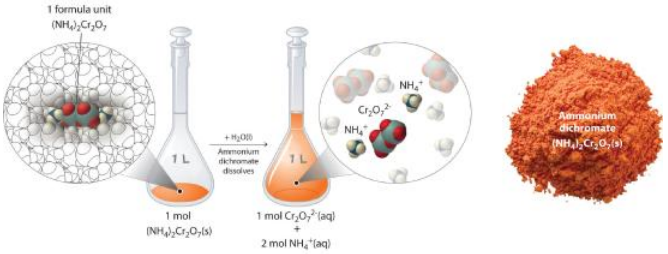


Figure 12.1.4 Dissolution of 1 mol of an Ionic Compound *In this case, dissolving 1 mol of $(NH_4)_2Cr_2O_7$ produces a solution that contains 1 mol of $Cr_2O_7^{2-}$ ions and 2 mol of NH_4^+ ions. (Water molecules are omitted from a molecular view of the solution for clarity.)*

When we carry out a chemical reaction using a solution of a salt such as ammonium dichromate, we need to know the concentration of each ion present in the solution. If a solution contains 1.43 M $(NH_4)_2Cr_2O_7$, then the concentration of $Cr_2O_7^{2-}$ must also be 1.43 M because there is one $Cr_2O_7^{2-}$ ion per formula unit. However, there are two NH_4^+ ions per formula unit, so the concentration of NH_4^+ ions is 2 × 1.43 M = 2.86 M. Because each formula unit of $(NH_4)_2Cr_2O_7$ produces *three* ions when dissolved in water ($2NH_4^+ + 1Cr_2O_7^{2-}$), the *total* concentration of ions in the solution is 3 × 1.43 M = 4.29 M.

Example 12.1.4

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

1. 0.21 M NaOH
2. 3.7 M $(CH_3)CHOH$
3. 0.032 M $In(NO_3)_3$

Given: molarity

Asked for: concentrations

Strategy:

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

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

Solution:

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

   $$NaOH(s) \xrightarrow{H_2O(l)} Na^+(aq) + OH^-(aq)$$

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

2. **A** The formula $(CH_3)_2CHOH$ represents 2-propanol (isopropyl alcohol) and contains the –OH group, so it is an alcohol. Recall from Section 9.1 that alcohols are covalent compounds that dissolve in water to give solutions of neutral molecules. Thus alcohols are nonelectrolytes.

   B The only solute species in solution is therefore $(CH_3)_2CHOH$ molecules, so $[(CH_3)_2CHOH] = 3.7$ M.

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

   $$In(NO_3)_3(s) \xrightarrow{H_2O(l)} In^{3+}(aq) + 3NO_3^-(aq)$$

   B One formula unit of $In(NO_3)_3$ produces one In^{3+} ion and three NO_3^- ions, so a 0.032 M $In(NO_3)_3$ solution contains 0.032 M In^{3+} and 3 × 0.032 M = 0.096 M NO_3^-—that is, $[In^{3+}] = 0.032$ M and $[NO_3^-] = 0.096$ M.

Exercise

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

1. 0.0012 M $Ba(OH)_2$
2. 0.17 M Na_2SO_4
3. 0.50 M $(CH_3)_2CO$, commonly known as acetone



Acetone
$(CH_3)_2CO$

Answer:

1. $[Ba^{2+}] = 0.0012$ M; $[OH^-] = 0.0024$ M
2. $[Na^+] = 0.34$ M; $[SO_4^{2-}] = 0.17$ M
3. $[(CH_3)_2CO] = 0.50$ M

Key Equations

relationship between volume and concentration of stock and dilute solutions

Equation 12.1.2: $(V_s)(M_s) = moles\ of\ solute = (V_d)(M_d)$

Summary

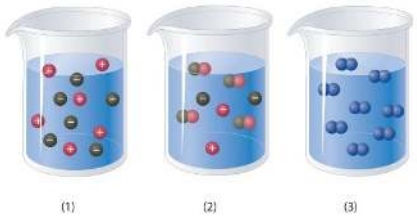
The **concentration** of a substance is the quantity of solute present in a given quantity of solution. Concentrations are usually expressed as **molarity**, the number of moles of solute in 1 L of solution. Solutions of known concentration can be prepared either by dissolving a known mass of solute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

Key Takeaway

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

Conceptual Problems

1. Which of the representations best corresponds to a 1 M aqueous solution of each compound? Justify your answers.
    1. NH_3
    2. HF
    3. $CH_3CH_2CH_2OH$
    4. Na_2SO_4



2. Which of the representations shown in Problem 1 best corresponds to a 1 M aqueous solution of each compound? Justify your answers.
    1. CH_3CO_2H
    2. NaCl
    3. Na_2S
    4. Na_3PO_4
    5. acetaldehyde
3. Would you expect a 1.0 M solution of $CaCl_2$ to be a better conductor of electricity than a 1.0 M solution of NaCl? Why or why not?
4. An alternative way to define the concentration of a solution is *molality*, abbreviated *m*. Molality is defined as the number of moles of solute in 1 kg of *solvent*. How is this different from molarity? Would you expect a 1 M solution of sucrose to be more or less concentrated than a 1 m solution of sucrose? Explain your answer.
5. What are the advantages of using solutions for quantitative calculations?

Answer

1.
2.
3. of the amount of a substance required for a reaction is too small to be weighed accurately, the use of a solution of the substance, in which the solute is dispersed in a much larger mass of solvent, allows chemists to measure the quantity of the substance more accurately.
4.
5.

Numerical Problems

1. Calculate the number of grams of solute in 1.000 L of each solution.
    1. 0.2593 M $NaBrO_3$
    2. 1.592 M KNO_3
    3. 1.559 M acetic acid
    4. 0.943 M potassium iodate
2. Calculate the number of grams of solute in 1.000 L of each solution.
    1. 0.1065 M BaI_2
    2. 1.135 M Na_2SO_4
    3. 1.428 M NH_4Br
    4. 0.889 M sodium acetate
3. If all solutions contain the same solute, which solution contains the greater mass of solute?
    1. 1.40 L of a 0.334 M solution or 1.10 L of a 0.420 M solution

2. 25.0 mL of a 0.134 M solution or 10.0 mL of a 0.295 M solution
3. 250 mL of a 0.489 M solution or 150 mL of a 0.769 M solution

4. Complete the following table for 500 mL of solution.

Compound	Mass (g)	Moles	Concentration (M)
calcium sulfate	4.86		
acetic acid		3.62	
hydrogen iodide dihydrate			1.273
barium bromide	3.92		
glucose			0.983
sodium acetate		2.42	

5. What is the concentration of each species present in the following aqueous solutions?
   1. 0.489 mol of $NiSO_4$ in 600 mL of solution
   2. 1.045 mol of magnesium bromide in 500 mL of solution
   3. 0.146 mol of glucose in 800 mL of solution
   4. 0.479 mol of $CeCl_3$ in 700 mL of solution
6. What is the concentration of each species present in the following aqueous solutions?
   1. 0.324 mol of K_2MoO_4 in 250 mL of solution
   2. 0.528 mol of potassium formate in 300 mL of solution
   3. 0.477 mol of $KClO_3$ in 900 mL of solution
   4. 0.378 mol of potassium iodide in 750 mL of solution
7. What is the molar concentration of each solution?
   1. 8.7 g of calcium bromide in 250 mL of solution
   2. 9.8 g of lithium sulfate in 300 mL of solution
   3. 12.4 g of sucrose ($C_{12}H_{22}O_{11}$) in 750 mL of solution
   4. 14.2 g of iron(III) nitrate hexahydrate in 300 mL of solution
8. What is the molar concentration of each solution?
   1. 12.8 g of sodium hydrogen sulfate in 400 mL of solution
   2. 7.5 g of potassium hydrogen phosphate in 250 mL of solution
   3. 11.4 g of barium chloride in 350 mL of solution
   4. 4.3 g of tartaric acid ($C_4H_6O_6$) in 250 mL of solution
9. Give the concentration of each reactant in the following equations, assuming 20.0 g of each and a solution volume of 250 mL for each reactant.
   1. $BaCl_2(aq) + Na_2SO_4(aq) \rightarrow$
   2. $Ca(OH)_2(aq) + H_3PO_4(aq) \rightarrow$
   3. $Al(NO_3)_3(aq) + H_2SO_4(aq) \rightarrow$
   4. $Pb(NO_3)_2(aq) + CuSO_4(aq) \rightarrow$
   5. $Al(CH_3CO_2)_3(aq) + NaOH(aq) \rightarrow$
10. An experiment required 200.0 mL of a 0.330 M solution of Na_2CrO_4. A stock solution of Na_2CrO_4 containing 20.0% solute by mass with a density of 1.19 g/cm^3 was used to prepare this solution. Describe how to prepare 200.0 mL of a 0.330 M solution of Na_2CrO_4 using the stock solution.

11. Calcium hypochlorite [$Ca(OCl)_2$] is an effective disinfectant for clothing and bedding. If a solution has a $Ca(OCl)_2$ concentration of 3.4 g per 100 mL of solution, what is the molarity of hypochlorite?

11. 0.48 M ClO^-

12. Phenol (C_6H_5OH) is often used as an antiseptic in mouthwashes and throat lozenges. If a mouthwash has a phenol concentration of 1.5 g per 100 mL of solution, what is the molarity of phenol?

13. 1.74×10^{-3} M caffeine

15. If a tablet containing 100 mg of caffeine ($C_8H_{10}N_4O_2$) is dissolved in water to give 10.0 oz of solution, what is the molar concentration of caffeine in the solution?

14. A certain drug label carries instructions to add 10.0 mL of sterile water, stating that each milliliter of the resulting solution will contain 0.500 g of medication. If a patient has a prescribed dose of 900.0 mg, how many milliliters of the solution should be administered?

Answers

1.

Contributors

- Anonymous

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Chapter 12.2: Stoichiometry of Reactions in Solution

Learning Objective

- To balance equations that describe reactions in solution.
- To solve quantitative problems involving the stoichiometry of reactions in solution.

Quantitative calculations involving reactions in solution are carried out in the same manner as we discussed in Chapter 11. Instead of *masses*, however, we use *volumes* of solutions of known concentration to determine the number of moles of reactants. Whether we are dealing with volumes of solutions of reactants or masses of reactants, the coefficients in the balanced chemical equation tell us the number of moles of each reactant needed and the number of moles of each product that can be produced.

Calculating Moles from Volume

An expanded version of the flowchart for stoichiometric calculations illustrated in Figure 11.4.1 is shown in Figure 12.2.1. We can use the balanced chemical equation for the reaction and *either* the masses of solid reactants and products *or* the volumes of solutions of reactants and products to determine the amounts of other species, as illustrated in Example 7, Example 8, and Example 9.

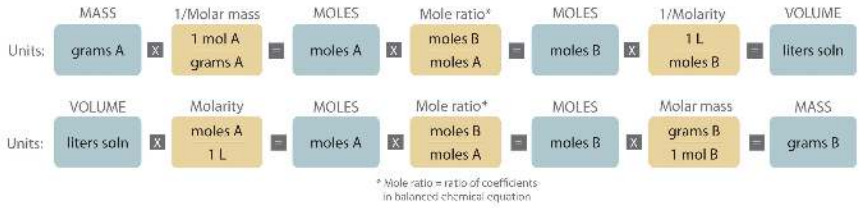


Figure 12.2.1 An Expanded Flowchart for Stoichiometric Calculations *Either the masses or the volumes of solutions of reactants and products can be used to determine the amounts of other species in a balanced chemical equation.*

Note the Pattern

The balanced chemical equation for a reaction and either the masses of solid reactants and products or the volumes of solutions of reactants and products can be used in stoichiometric calculations.

Example 12.2.1

Gold is extracted from its ores by treatment with an aqueous cyanide solution, which causes a reaction that forms the soluble $[Au(CN)_2]^-$ ion. Gold is then recovered by reduction with metallic zinc according to the following equation:

$$Zn(s) + 2[Au(CN)_2]^-(aq) \rightarrow [Zn(CN)_4]^{2-}(aq) + 2Au(s)$$

What mass of gold would you expect to recover from 400.0 L of a 3.30×10^{-4} M solution of $[Au(CN)_2]^-$?

Given: chemical equation and molarity and volume of reactant

Asked for: mass of product

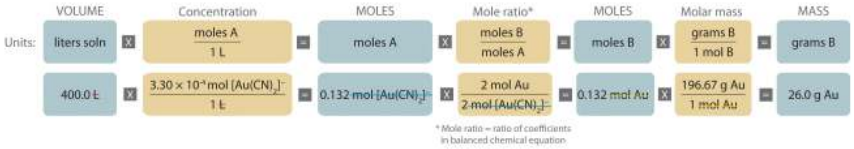
Strategy:

A Check the chemical equation to make sure it is balanced as written; balance if necessary. Then calculate the number of moles of $[Au(CN)_2]^-$ present by multiplying the volume of the solution by its concentration.

B From the balanced chemical equation, use a mole ratio to calculate the number of moles of gold that can be obtained from the reaction. To calculate the mass of gold recovered, multiply the number of moles of gold by its molar mass.

Solution:

A The equation is balanced as written, so we can proceed to the stoichiometric calculation. We can adapt Figure 12.2.1 for this particular problem as follows:



As indicated in the strategy, we start by calculating the number of moles of $[Au(CN)_2]^-$ present in the solution from the volume and concentration of the $[Au(CN)_2]^-$ solution:

$$moles\ [Au(CN)_2]^- = V_L M_{mol/L} \quad \text{(Chapter 12.2.1)}$$

$$= 400.0\ \cancel{L}\left(\frac{3.30 \times 10^{4-}\ mol\ [Au(CN)_2]^-}{1\ \cancel{L}}\right) = 0.132\ mol\ [Au(CN)_2]^- \quad \text{(Chapter 12.2.2)}$$

B Because the coefficients of gold and the $[Au(CN)_2]^-$ ion are the same in the balanced chemical equation, if we assume that Zn(s) is present in excess, the number of moles of gold produced is the same as the number of moles of $[Au(CN)_2]^-$ we started with (i.e., 0.132 mol of Au). The problem asks for the mass of gold that can be obtained, so we need to convert the number of moles of gold to the corresponding mass using the molar mass of gold:

$$mass\ of\ Au = (moles\ Au)(molar\ mass\ Au) \quad \text{(Chapter 12.2.3)}$$

$$= 0.132\ \cancel{mol\ Au}\left(\frac{196.97\ g\ Au}{1\ \cancel{mol\ Au}}\right) = 26.0\ g\ Au \quad \text{(Chapter 12.2.4)}$$

At a 2011 market price of over $1400 per troy ounce (31.10 g), this amount of gold is worth $1170.

$$26.0\ \cancel{g\ Au} \times \frac{1\ \cancel{troy\ oz}}{31.10\ \cancel{g}} \times \frac{\$1400}{1\ \cancel{troy\ oz\ Au}} = \$1170$$

We can also modify the table method using the volume and the molarity to calculate the number of moles

	Zn(s)	+ 2[Au(CN)O_2]$^-$(aq)	→ $[Zn(CN)_4]^{2-}$(aq)	+ 2Au(s)
Volume (L)		400.0		26.0 g
Molarity (g/L)		3.30 x 10^{-4}		MW = 196.97 g
Moles		0.132		0.132
Stoichiometric Coefficients	1	2	1	2
Stoichiometric Equivalents		0.066		0.066

Exercise

What mass of solid lanthanum(III) oxalate nonahydrate $[La_2(C_2O_4)_3{\cdot}9H_2O]$ can be obtained from 650 mL of a 0.0170 M aqueous solution of $LaCl_3$ by adding a stoichiometric amount of sodium oxalate?

Answer: 3.89 g

Limiting Reactants in Solutions

The concept of limiting reactants applies to reactions that are carried out in solution as well as to reactions that involve pure substances. If all the reactants but one are present in excess, then the amount of the limiting reactant may be calculated as illustrated in Example 8.

Example 12.2.2

Because the consumption of alcoholic beverages adversely affects the performance of tasks that require skill and judgment, in most countries it is illegal to drive while under the influence of alcohol. In almost all US states, a blood alcohol level of 0.08% by volume is considered legally drunk. Higher levels cause acute intoxication (0.20%), unconsciousness (about 0.30%), and even

death (about 0.50%). The Breathalyzer is a portable device that measures the ethanol concentration in a person's breath, which is directly proportional to the blood alcohol level. The reaction used in the Breathalyzer is the oxidation of ethanol by the dichromate ion:

$$3CH_3CH_2OH(aq) + \underset{yellow-orange}{2Cr_2O_7^{2-}}(aq) + 16H^+(aq) \xrightarrow[H_2SO_4(aq)]{Ag^+} 3CH_3CO_2H(aq) + \underset{green}{4Cr^{3+}}(aq) + 11H_2O(l)$$

When a measured volume (52.5 mL) of a suspect's breath is bubbled through a solution of excess potassium dichromate in dilute sulfuric acid, the ethanol is rapidly absorbed and oxidized to acetic acid by the dichromate ions. In the process, the chromium atoms in some of the $Cr_2O_7^{2-}$ ions are reduced from Cr^{6+} to Cr^{3+}. In the presence of Ag^+ ions that act as a catalyst, the reaction is complete in less than a minute. Because the $Cr_2O_7^{2-}$ ion (the reactant) is yellow-orange and the Cr^{3+} ion (the product) forms a green solution, the amount of ethanol in the person's breath (the limiting reactant) can be determined quite accurately by comparing the color of the final solution with the colors of standard solutions prepared with known amounts of ethanol.

A typical Breathalyzer ampul contains 3.0 mL of a 0.25 mg/mL solution of $K_2Cr_2O_7$ in 50% H_2SO_4 as well as a fixed concentration of $AgNO_3$ (typically 0.25 mg/mL is used for this purpose). How many grams of ethanol must be present in 52.5 mL of a person's breath to convert all the Cr^{6+} to Cr^{3+}?

Given: volume and concentration of one reactant

Asked for: mass of other reactant needed for complete reaction

Strategy:

A Calculate the number of moles of $Cr_2O_7^{2-}$ ion in 1 mL of the Breathalyzer solution by dividing the mass of $K_2Cr_2O_7$ by its molar mass.

B Find the total number of moles of $Cr_2O_7^{2-}$ ion in the Breathalyzer ampul by multiplying the number of moles contained in 1 mL by the total volume of the Breathalyzer solution (3.0 mL).

C Use the mole ratios from the balanced chemical equation to calculate the number of moles of C_2H_5OH needed to react completely with the number of moles of $Cr_2O_7^{2-}$ ions present. Then find the mass of C_2H_5OH needed by multiplying the number of moles of C_2H_5OH by its molar mass.

Solution:

A In any stoichiometry problem, the first step is always to calculate the number of moles of each reactant present. In this case, we are given the mass of $K_2Cr_2O_7$ in 1 mL of solution, which we can use to calculate the number of moles of $K_2Cr_2O_7$ contained in 1 mL:

$$\frac{moles\ K_2Cr_2O_7}{1\ mL} = \frac{(0.25\ \cancel{mg}\ K_2Cr_2O_7)}{mL}\left(\frac{1\ \cancel{g}}{1000\ \cancel{mg}}\right)\left(\frac{1\ mol}{294.18\ \cancel{g}\ K_2Cr_2O_7}\right) = 8.5 \times 10^{-7}\ moles$$

Using the table method

	$3CH_3CH_2OH(aq)$	$+ 2Cr_2O_7^{2-}(aq)$	$16H^+(aq)$	$\rightarrow 3CH_3CO_2H(aq)$	$4Cr^{3+}(aq)$	$+ 11H_2O(l)$
Volume (mL)		3 mL				
Density (mg/mL)		0.25 mg/mL				
Mass	1.76×10^{-4} g	0.75×10^{-3} g				
MW	46.07	294.18				
moles	3.82×10^{-6}	2.55×10^{-6}				
Stoichiometric Coefficients	3	2	16	3	4	11
Stoichiometric Equivalents	1.27×10^{-6}	1.27×10^{-6}				

OR

B Because 1 mol of $K_2Cr_2O_7$ produces 1 mol of $Cr_2O_7^{2-}$ when it dissolves, each milliliter of solution contains 8.5×10^{-7} mol of $Cr_2O_7^{2-}$. The total number of moles of $Cr_2O_7^{2-}$ in a 3.0 mL Breathalyzer ampul is thus

$$moles\ Cr_2O_7^{2-} = \left(\frac{8.5 \times 10^{-7}\ mol}{1\ \cancel{mL}}\right)(3.0\ \cancel{mL}) = 2.6 \times 10^{-6}\ mol\ Cr_2O_7^{2-}$$

C The balanced chemical equation tells us that 3 mol of C_2H_5OH is needed to consume 2 mol of $Cr_2O_7^{2-}$ ion, so the total number of moles of C_2H_5OH required for complete reaction is

$$moles\ of\ C_2H_5OH = (2.6 \times 10^{-6}\ \cancel{mol\ Cr_2O_7^{2-}})\left(\frac{3\ mol\ C_2H_5OH}{2\ \cancel{mol\ Cr_2O_7^{2-}}}\right) = 3.9 \times 10^{-6}\ mol\ C_2H_5OH$$

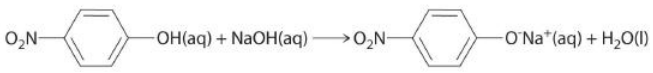
As indicated in the strategy, this number can be converted to the mass of C_2H_5OH using its molar mass:

$$mass\ C_2H_5OH = (3.9 \times 10^{-6}\ \cancel{mol\ C_2H_5OH})\left(\frac{46.07\ g}{\cancel{mol\ C_2H_5OH}}\right) = 1.8 \times 10^{-4}\ g\ C_2H_5OH$$

Thus 1.8×10^{-4} g or 0.18 mg of C_2H_5OH must be present. Experimentally, it is found that this value corresponds to a blood alcohol level of 0.7%, which is usually fatal.

Exercise

The compound *para*-nitrophenol (molar mass = 139 g/mol) reacts with sodium hydroxide in aqueous solution to generate a yellow anion via the reaction



para-Nitrophenol Yellow

Because the amount of *para*-nitrophenol is easily estimated from the intensity of the yellow color that results when excess NaOH is added, reactions that produce *para*-nitrophenol are commonly used to measure the activity of enzymes, the catalysts in biological systems. What volume of 0.105 M NaOH must be added to 50.0 mL of a solution containing 7.20×10^{-4} g of *para*-nitrophenol to ensure that formation of the yellow anion is complete?

Answer: 4.93×10^{-5} L or 49.3 µL

In Example 12.2.1 and Example 12.2.2, the identity of the limiting reactant has been apparent: $[Au(CN)_2]^-$, $LaCl_3$, ethanol, and *para*-nitrophenol. When the limiting reactant is not apparent, we can determine which reactant is limiting by comparing the molar amounts of the reactants with their coefficients in the balanced chemical equation, just as we did in Section 11.4. The only difference is that now we use the volumes and concentrations of solutions of reactants rather than the masses of reactants to calculate the number of moles of reactants, as illustrated in Example 12.2.4

Example 12.2.4

When aqueous solutions of silver nitrate and potassium dichromate are mixed, an exchange reaction occurs, and silver dichromate is obtained as a red solid. The overall chemical equation for the reaction is as follows:

$$2AgNO_3(aq) + K_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + 2KNO_3(aq)$$

What mass of $Ag_2Cr_2O_7$ is formed when 500 mL of 0.17 M $K_2Cr_2O_7$ are mixed with 250 mL of 0.57 M $AgNO_3$?

Given: balanced chemical equation and volume and concentration of each reactant

Asked for: mass of product

Strategy:

A Calculate the number of moles of each reactant by multiplying the volume of each solution by its molarity.

B Determine which reactant is limiting by dividing the number of moles of each reactant by its stoichiometric coefficient in the balanced chemical equation.

C Use mole ratios to calculate the number of moles of product that can be formed from the limiting reactant. Multiply the number of moles of the product by its molar mass to obtain the corresponding mass of product.

Solution:

Using the Table method

	$2AgNO_3(aq)$	$+ K_2Cr_2O_7(aq)$	$\rightarrow Ag_2Cr_2O_7(aq)$	$2KNO_3(aq)$
Volume (L)	0.250	0.500 L	Mass 30.g	
Molarity (moles/L)	0.57 M	0.17 M	MW 431.72 g	
moles	0.140	0.085	0.070	
Stoichiometric Coefficients	2	1	1	2
Stoichiometric Equivalents	0.070	~~0.085~~	0.070	

A The balanced chemical equation tells us that 2 mol of $AgNO_3(aq)$ reacts with 1 mol of $K_2Cr_2O_7(aq)$ to form 1 mol of $Ag_2Cr_2O_7(s)$ (Figure 12.2.2). The first step is to calculate the number of moles of each reactant in the specified volumes:

$$moles\ K_2Cr_2O_7 = 500\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.17\ mol\ K_2Cr_2O_7}{1\ \cancel{L}}\right) = 0.085\ mol\ K_2Cr_2O_7$$

$$moles\ AgNO_3 = 250\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.57\ mol\ AgNO_3}{1\ \cancel{L}}\right) = 0.14\ mol\ AgNO_3$$

B Now we can determine which reactant is limiting by dividing the number of moles of each reactant by its stoichiometric coefficient:

$$K_2Cr_2O_7: \frac{0.085\ mol}{1\ mol} = 0.085$$

$$AgNO_3: \frac{0.14\ mol}{2\ mol} = 0.070$$

Because 0.070 < 0.085, we know that $AgNO_3$ is the limiting reactant.

C Each mole of $Ag_2Cr_2O_7$ formed requires 2 mol of the limiting reactant ($AgNO_3$), so we can obtain only 0.14/2 = 0.070 mol of $Ag_2Cr_2O_7$. Finally, we convert the number of moles of $Ag_2Cr_2O_7$ to the corresponding mass:

$$mass\ of\ Ag_2Cr_2O_7 = 0.070\ \cancel{mol}\left(\frac{431.72\ g}{1\ \cancel{mol}}\right) = 30\ g\ Ag_2Cr_2O_7$$

Figure 12.2.2 What Happens at the Molecular Level When Solutions of $AgNO_3$ and $K_2Cr_2O_7$ Are Mixed



The Ag^+ and $Cr_2O_7^{2-}$ ions form a red precipitate of solid $Ag_2Cr_2O_7$, while the K^+ and NO_3^- ions remain in solution. (Water molecules are omitted from molecular views of the solutions for clarity.)

Exercise

Aqueous solutions of sodium bicarbonate and sulfuric acid react to produce carbon dioxide according to the following equation:

$$2NaHCO_3(aq) + H_2SO_4(aq) \rightarrow 2CO_2(g) + Na_2SO_4(aq) + 2H_2O(l)$$

If 13.0 mL of 3.0 M H_2SO_4 are added to 732 mL of 0.112 M $NaHCO_3$, what mass of CO_2 is produced?

Answer: 3.4 g

Summary

Quantitative calculations that involve the stoichiometry of reactions in solution use volumes of solutions of known concentration instead of masses of reactants or products. The coefficients in the balanced chemical equation tell how many moles of reactants are needed and how many moles of product can be produced.

Key Takeaway

- Either the masses or the volumes of solutions of reactants and products can be used to determine the amounts of other species in the balanced chemical equation.

Conceptual Problems

1. What information is required to determine the mass of solute in a solution if you know the molar concentration of the solution?
2. Is it possible for one reactant to be limiting in a reaction that does not go to completion?

Numerical Problems

1. Refer to the Breathalyzer test described in Example 8. How much ethanol must be present in 89.5 mL of a person’s breath to consume all the potassium dichromate in a Breathalyzer ampul containing 3.0 mL of a 0.40 mg/mL solution of potassium dichromate?
2. Phosphoric acid and magnesium hydroxide react to produce magnesium phosphate and water. If 45.00 mL of 1.50 M phosphoric acid are used in the reaction, how many grams of magnesium hydroxide are needed for the reaction to go to completion?
3. Barium chloride and sodium sulfate react to produce sodium chloride and barium sulfate. If 50.00 mL of 2.55 M barium chloride are used in the reaction, how many grams of sodium sulfate are needed for the reaction to go to completion?
4. How many grams of sodium phosphate are obtained in solution from the reaction of 75.00 mL of 2.80 M sodium carbonate with a stoichiometric amount of phosphoric acid? A second product is water; what is the third product? How many grams of the third product are obtained?
5. How many grams of ammonium bromide are produced from the reaction of 50.00 mL of 2.08 M iron(II) bromide with a stoichiometric amount of ammonium sulfide? What is the second product? How many grams of the second product are produced?
6. Lead(II) nitrate and hydroiodic acid react to produce lead(II) iodide and nitric acid. If 3.25 g of lead(II) iodide were obtained by adding excess HI to 150.0 mL of lead(II) nitrate, what was the molarity of the lead(II) nitrate solution?

7. Silver nitrate and sodium chloride react to produce sodium nitrate and silver chloride. If 2.60 g of AgCl was obtained by adding excess NaCl to 100 mL of $AgNO_3$, what was the molarity of the silver nitrate solution?

Contributors

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Chapter 12.3: Ionic Equations

Learning Objective

- To understand what ionic reactions are.
- To understand which ions participate in ionic reactions

The chemical equations discussed in Chapter 11.3 showed the identities of the reactants and the products and gave the stoichiometries of the reactions, but they told us very little about what was occurring in solution. In contrast, equations that show only the hydrated species focus our attention on the chemistry that is taking place and allow us to see similarities between reactions that might not otherwise be apparent.

Let's consider the reaction of silver nitrate with potassium dichromate. As you learned in Example 9, when aqueous solutions of silver nitrate and potassium dichromate are mixed, silver dichromate forms as a red solid. The overall chemical equationA chemical equation that shows all the reactants and products as undissociated, electrically neutral compounds. for the reaction shows each reactant and product as undissociated, electrically neutral compounds:

$$2AgNO_3(aq) + K_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + 2KNO_3(aq)$$

Although Equation 12.3.1 gives the identity of the reactants and the products, it does not show the identities of the actual species in solution. Because ionic substances such as $AgNO_3$ and $K_2Cr_2O_7$ are strong electrolytes, they dissociate completely in aqueous solution to form ions. In contrast, because $Ag_2Cr_2O_7$ is not very soluble, it separates from the solution as a solid. To find out what is actually occurring in solution, it is more informative to write the reaction as a complete ionic equation showing which ions and molecules are hydrated and which are present in other forms and phases:

$$2Ag^+(aq) + 2NO_3^-(aq) + 2K^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s) + 2K^+(aq) + 2NO_3^-(aq)$$

Note that $K^+(aq)$ and $NO_3^-(aq)$ ions are present on both sides of the equation, and their coefficients are the same on both sides. These ions are called spectator ionsIons that do not participate in the actual reaction. because they do not participate in the actual reaction. Canceling the spectator ions gives the net ionic equation which shows only those species that participate in the chemical reaction:

$$2Ag^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s)$$

Both mass and charge must be conserved in chemical reactions because the numbers of electrons and protons do not change. For charge to be conserved, the sum of the charges of the ions multiplied by their coefficients must be the same on both sides of the equation. In Equation 12.3.3, the charge on the left side is 2(+1) + 1(−2) = 0, which is the same as the charge of a neutral $Ag_2Cr_2O_7$ formula unit.

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

$$2AgF(aq) + (NH_4)_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + 2NH_4F(aq)$$

The complete ionic equation for this reaction is as follows:

$$2Ag^+(aq) + 2F^-(aq) + 2NH_4^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s) + 2NH_4^+(aq) + 2F^-(aq)$$

Because two $NH_4^+(aq)$ and two $F^-(aq)$ ions appear on both sides of Equation 12.3.5, they are spectator ions. They can therefore be canceled to give the net ionic equation (Equation 12.3.6), which is identical to Equation 12.3.3:

$$2Ag^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow Ag_2Cr_2O_7(s)$$

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

Example 12.3.1

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

Given: reactants and products

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

Strategy:

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

Solution:

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

$$Ba(NO_3)_2(aq) + Na_3PO_4(aq) \rightarrow Ba_3(PO_4)_2(s) + NaNO_3(aq)$$

Because the product is $Ba_3(PO_4)_2$, which contains three Ba^{2+} ions and two PO_4^{3-} ions per formula unit, we can balance the equation by inspection:

$$3Ba(NO_3)_2(aq) + 2Na_3PO_4(aq) \rightarrow Ba_3(PO_4)_2(s) + 6NaNO_3(aq)$$

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

$$3Ba^{2+}(aq) + 6NO_3^-(aq) + 6Na^+(aq) + 2PO_4^{3-}(aq) \rightarrow Ba_3(PO_4)_2(s) + 6Na^+(aq) + 6NO_3^-(aq)$$

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

$$3Ba^{2+}(aq) + 2PO_4^{3-}(aq) \rightarrow Ba_3(PO_4)_2(s)$$

Exercise

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

Answer:

overall chemical equation: $3AgF(aq) + Na_3PO_4(aq) \rightarrow Ag_3PO_4(s) + 3NaF(aq)$

complete ionic equation: $3Ag^+(aq) + 3F^-(aq) + 3Na^+(aq) + PO_4^{3-}(aq) \rightarrow Ag_3PO_4(s) + 3Na^+(aq) + 3F^-(aq)$

net ionic equation: $3Ag^+(aq) + PO_4^{3-}(aq) \rightarrow Ag_3PO_4(s)$

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

The most important step in analyzing an unknown reaction is to *write down all the species—whether molecules or dissociated ions—that are actually present in the solution* (not forgetting the solvent itself) so that you can assess which species are most likely to react with one another. The easiest way to make that kind of prediction is to attempt to place the reaction into one of several familiar classifications, refinements of the five general kinds of reactions introduced in Chapter 11.6 (acid–base, exchange, condensation, cleavage, and oxidation–reduction reactions). In the sections that follow, we discuss three of the most important kinds of reactions that occur in aqueous solutions: precipitation reactions (also known as exchange reactions), acid–base reactions, and oxidation–reduction reactions.

Summary

The chemical equation for a reaction in solution can be written in three ways. The **overall chemical equation** shows all the substances present in their undissociated forms; the **complete ionic equation** shows all the substances present in the form in which they actually exist in solution; and the **net ionic equation** is derived from the complete ionic equation by omitting all **spectator**

ions, ions that occur on both sides of the equation with the same coefficients. Net ionic equations demonstrate that many different combinations of reactants can give the same net chemical reaction.

Key Takeaway

- A complete ionic equation consists of the net ionic equation and spectator ions.

Conceptual Problem

1. What information can be obtained from a complete ionic equation that cannot be obtained from the overall chemical equation?

Contributors

- Anonymous

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Chapter 12.4: Precipitation Reactions

Learning Objective

- To identify a precipitation reaction
- To predict solubility of ionix compounds.

A precipitation reaction A subclass of an exchange reaction that yields an insoluble product (a precipitate) when two solutions are mixed. is a reaction that yields an insoluble product—a precipitate The insoluble product that forms in a precipitation reaction.—when two solutions are mixed. In Section 12.3, we described a precipitation reaction in which a colorless solution of silver nitrate was mixed with a yellow-orange solution of potassium dichromate to give a reddish precipitate of silver dichromate:

$$AgNO_3(aq) + K_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + KNO_3(aq)$$

This equation has the general form of an exchange reaction:

$$AC + BD \rightarrow \underset{insoluble}{AD} + BC$$

Thus precipitation reactions are a subclass of exchange reactions that occur between ionic compounds when one of the products is insoluble. Because both components of each compound change partners, such reactions are sometimes called *double-displacement reactions*. Two important uses of precipitation reactions are to isolate metals that have been extracted from their ores and to recover precious metals for recycling.

Note the Pattern

Precipitation reactions are a subclass of exchange reactions.

Predicting Solubilities

Table 12.4.1 gives guidelines for predicting the solubility of a wide variety of ionic compounds. To determine whether a precipitation reaction will occur, we identify each species in the solution and then refer to Table 12.4.1 to see which, if any, combination(s) of cation and anion are likely to produce an insoluble salt. In doing so, it is important to recognize that *soluble* and *insoluble* are relative terms that span a wide range of actual solubilities. We will discuss solubilities quantitatively later on, where you will learn that very small amounts of the constituent ions remain in solution even after precipitation of an "insoluble" salt. For our purposes, however, we will assume that precipitation of an insoluble salt is complete.

Table 12.4.1 Guidelines for Predicting the Solubility of Ionic Compounds in Water

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

Just as important as predicting the product of a reaction is knowing when a chemical reaction will *not* occur. Simply mixing solutions of two different chemical substances does *not* guarantee that a reaction will take place. For example, if 500 mL of a 1.0 M aqueous NaCl solution is mixed with 500 mL of a 1.0 M aqueous KBr solution, the final solution has a volume of 1.00 L and contains 0.50 M Na^+(aq), 0.50 M Cl^-(aq), 0.50 M K^+(aq), and 0.50 M Br^-(aq). As you will see in the following sections, none of these species reacts with any of the others. When these solutions are mixed, the only effect is to dilute each solution with the other (Figure 12.4.1).

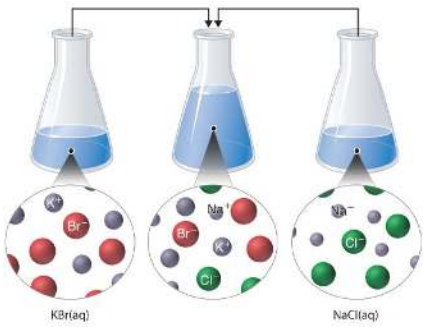


Figure 12.4.1 The Effect of Mixing Aqueous KBr and NaCl Solutions *Because no net reaction occurs, the only effect is to dilute each solution with the other. (Water molecules are omitted from molecular views of the solutions for clarity.)*

Example 12.4.1

Using the information in Table 12.4.1 predict what will happen in each case involving strong electrolytes. Write the net ionic equation for any reaction that occurs.

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

Given: reactants

Asked for: reaction and net ionic equation

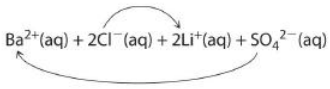
Strategy:

A Identify the ions present in solution and write the products of each possible exchange reaction.

B Refer to Table 12.4.1 to determine which, if any, of the products is insoluble and will therefore form a precipitate. If a precipitate forms, write the net ionic equation for the reaction.

Solution:

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



   B We now need to decide whether either of these products is insoluble. Table 12.4.1 shows that LiCl is soluble in water (rules 1 and 4), but $BaSO_4$ is not soluble in water (rule 5). Thus $BaSO_4$ will precipitate according to the net ionic equation

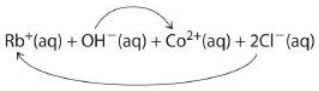
$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$

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



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

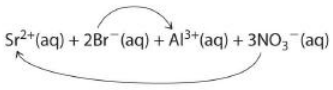
2. **A** Rubidium hydroxide and cobalt(II) chloride are strong electrolytes, so when aqueous solutions of these compounds are mixed, the resulting solution initially contains Rb^+, OH^-, Co^{2+}, and Cl^- ions. The possible products of an exchange reaction are rubidium chloride and cobalt(II) hydroxide):



   B According to Table 12.4.1 RbCl is soluble (rules 1 and 4), but $Co(OH)_2$ is not soluble (rule 5). Hence $Co(OH)_2$ will precipitate according to the following net ionic equation:

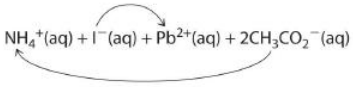
$$Co^{2+}(aq) + 2OH^-(aq) \rightarrow Co(OH)_2(s)$$

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



B According to Table 12.4.1 both $AlBr_3$ (rule 4) and $Sr(NO_3)_2$ (rule 2) are soluble. Thus no net reaction will occur.

4. **A** According to Table 12.4.1 lead acetate is soluble (rule 3). Thus solid lead acetate dissolves in water to give Pb^{2+} and $CH_3CO_2^-$ ions. Because the solution also contains NH_4^+ and I^- ions, the possible products of an exchange reaction are ammonium acetate and lead(II) iodide:



B According to Table 12.4.1 ammonium acetate is soluble (rules 1 and 3), but PbI_2 is insoluble (rule 4). Thus $Pb(C_2H_3O_2)_2$ will dissolve, and PbI_2 will precipitate. The net ionic equation is as follows:

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

Exercise

Using the information in Table 12.4.1 predict what will happen in each case involving strong electrolytes. Write the net ionic equation for any reaction that occurs.

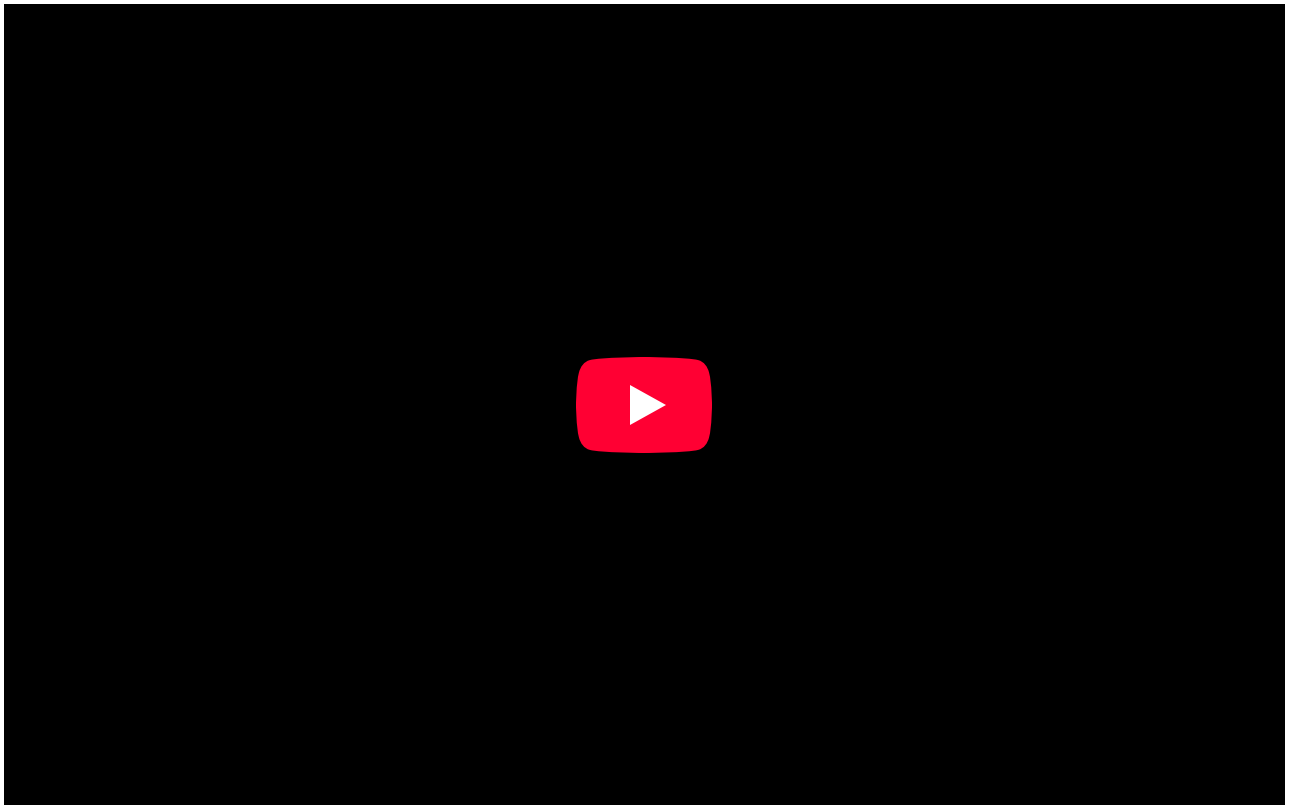
1. An aqueous solution of strontium hydroxide is added to an aqueous solution of iron(II) chloride.
2. Solid potassium phosphate is added to an aqueous solution of mercury(II) perchlorate.
3. Solid sodium fluoride is added to an aqueous solution of ammonium formate.
4. Aqueous solutions of calcium bromide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

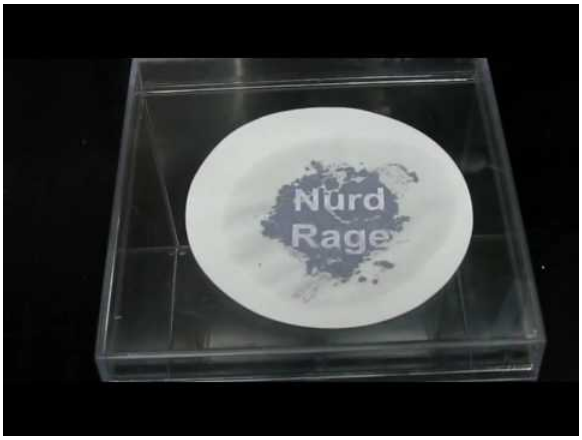
Answer:

1. $Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$
2. $2PO_4^{3-}(aq) + 3Hg^{2+}(aq) \rightarrow Hg_3(PO_4)_2(s)$
3. $NaF(s)$ dissolves; no net reaction
4. $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$

Precipitation Reactions in Photography

Precipitation reactions can be used to recover silver from solutions used to develop conventional photographic film. Although largely supplanted by digital photography, conventional methods are often used for artistic purposes. Silver bromide is an off-white solid that turns black when exposed to light, which is due to the formation of small particles of silver metal. Black-and-white photography uses this reaction to capture images in shades of gray, with the darkest areas of the film corresponding to the areas that received the most light. The first step in film processing is to enhance the black/white contrast by using a developer to increase the amount of black. The developer is a reductant: because silver atoms catalyze the reduction reaction, grains of silver bromide that have already been partially reduced by exposure to light react with the reductant much more rapidly than unexposed grains.





Darkening of silver chloride crystals by exposure to light. The video from NurdRage shows how to prepare silver chloride and by exposing it to strong light how to take a negative image.

After the film is developed, any unexposed silver chloride must be removed by a process called “fixing”; otherwise, the entire film would turn black with additional exposure to light. The photographic procedure is summarized in Figure 12.4.2. The negative image is then projected onto paper coated with silver halides, and the developing and fixing processes are repeated to give a positive image. (Color photography works in much the same way, with a combination of silver halides and organic dyes superimposed in layers.) “Instant photo” operations can generate more than a hundred gallons of dilute silver waste solution per day. Recovery of silver from thiosulfate fixing solutions involves first removing the thiosulfate by oxidation and then precipitating Ag^+ ions with excess chloride ions.

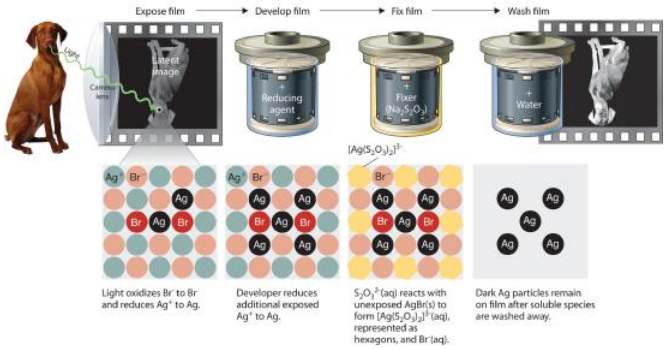


Figure 12.4.2 Outline of the Steps Involved in Producing a Black-and-White Photograph

Example 12.4.2

A silver recovery unit can process 1500 L of photographic silver waste solution per day. Adding excess solid sodium chloride to a 500 mL sample of the waste (after removing the thiosulfate as described previously) gives a white precipitate that, after filtration and drying, consists of 3.73 g of AgCl. What mass of NaCl must be added to the 1500 L of silver waste to ensure that all the Ag^+ ions precipitate?

Given: volume of solution of one reactant and mass of product from a sample of reactant solution

Asked for: mass of second reactant needed for complete reaction

Strategy:

A Write the net ionic equation for the reaction. Calculate the number of moles of AgCl obtained from the 500 mL sample and then determine the concentration of Ag^+ in the sample by dividing the number of moles of AgCl formed by the volume of solution.

B Determine the total number of moles of Ag^+ in the 1500 L solution by multiplying the Ag^+ concentration by the total volume.

C Use mole ratios to calculate the number of moles of chloride needed to react with Ag^+. Obtain the mass of NaCl by multiplying the number of moles of NaCl needed by its molar mass.

Solution:

We can use the data provided to determine the concentration of Ag^+ ions in the waste, from which the number of moles of Ag^+ in the entire waste solution can be calculated. From the net ionic equation, we can determine how many moles of Cl^- are needed, which in turn will give us the mass of NaCl necessary.

A The first step is to write the net ionic equation for the reaction:

$$Cl^-(aq) + Ag^+(aq) \rightarrow AgCl(s)$$

We know that 500 mL of solution produced 3.73 g of AgCl. We can convert this value to the number of moles of AgCl as follows:

$$moles\ AgCl = \frac{grams\ AgCl}{molar\ mass\ AgCl} = 3.73\ \cancel{g\ AgCl}\left(\frac{1\ mol\ AgCl}{143.32\ \cancel{g\ AgCl}}\right) = 0.0260\ mol\ AgCl$$

Therefore, the 500 mL sample of the solution contained 0.0260 mol of Ag^+. The Ag^+ concentration is determined as follows:

$$[Ag^+] = \frac{moles\ Ag^+}{liters\ soln} = \frac{0.0260\ mol\ AgCl}{0.500\ L} = 0.0520\ M$$

B The total number of moles of Ag^+ present in 1500 L of solution is as follows:

$$moles\ Ag^+ = 1500\ \cancel{L}\left(\frac{0.520\ mol}{1\ \cancel{L}}\right) = 78.1\ mol\ Ag^+$$

C According to the net ionic equation, one Cl^- ion is required for each Ag^+ ion. Thus 78.1 mol of NaCl are needed to precipitate the silver. The corresponding mass of NaCl is

$$mass\ NaCl = 78.1\ \cancel{mol\ NaCl}\left(\frac{58.44\ g\ NaCl}{1\ \cancel{mol\ NaCl}}\right) = 4560\ g\ NaCl = 4.56\ kg\ NaCl$$

Note that 78.1 mol of AgCl correspond to 8.43 kg of metallic silver, which is worth about $7983 at 2011 prices ($32.84 per troy ounce). Silver recovery may be economically attractive as well as ecologically sound, although the procedure outlined is becoming nearly obsolete for all but artistic purposes with the growth of digital photography.

Exercise

Because of its toxicity, arsenic is the active ingredient in many pesticides. The arsenic content of a pesticide can be measured by oxidizing arsenic compounds to the arsenate ion (AsO_4^{3-}), which forms an insoluble silver salt (Ag_3AsO_4). Suppose you are asked to assess the purity of technical grade sodium arsenite ($NaAsO_2$), the active ingredient in a pesticide used against termites. You dissolve a 10.00 g sample in water, oxidize it to arsenate, and dilute it with water to a final volume of 500 mL. You then add excess $AgNO_3$ solution to a 50.0 mL sample of the arsenate solution. The resulting precipitate of Ag_3AsO_4 has a mass of 3.24 g after drying. What is the percentage by mass of $NaAsO_2$ in the original sample?

Answer: 91.0%

Summary

In a **precipitation reaction**, a subclass of exchange reactions, an insoluble material (a **precipitate**) forms when solutions of two substances are mixed. To predict the product of a precipitation reaction, all species initially present in the solutions are identified, as are any combinations likely to produce an insoluble salt.

Key Takeaway

- Predicting the solubility of ionic compounds in water can give insight into whether or not a reaction will occur.

Conceptual Problems

1. Predict whether mixing each pair of solutions will result in the formation of a precipitate. If so, identify the precipitate.
    1. $FeCl_2(aq) + Na_2S(aq)$
    2. $NaOH(aq) + H_3PO_4(aq)$
    3. $ZnCl_2(aq) + (NH_4)_2S(aq)$
2. Predict whether mixing each pair of solutions will result in the formation of a precipitate. If so, identify the precipitate.
    1. $KOH(aq) + H_3PO_4(aq)$
    2. $K_2CO_3(aq) + BaCl_2(aq)$
    3. $Ba(NO_3)_2(aq) + Na_2SO_4(aq)$
3. Which representation best corresponds to an aqueous solution originally containing each of the following?
    1. 1 M NH_4Cl
    2. 1 M NaO_2CCH_3
    3. 1 M NaOH + 1 M HCl
    4. 1 M $Ba(OH)_2$ + 1 M H_2SO_4

    
4. Which representation in Problem 3 best corresponds to an aqueous solution originally containing each of the following?
    1. 1 M CH_3CO_2H + 1 M NaOH
    2. 1 M NH_3 + 1 M HCl
    3. 1 M Na_2CO_3 + 1 M H_2SO_4
    4. 1 M $CaCl_2$ + 1 M H_3PO_4

Answer

1.
2.
3. 1. 1
    2. 1

3. 1
4. 2

4.

Numerical Problems

1. What mass of precipitate would you expect to obtain by mixing 250 mL of a solution containing 4.88 g of Na_2CrO_4 with 200 mL of a solution containing 3.84 g of $AgNO_3$? What is the final nitrate ion concentration?
2. Adding 10.0 mL of a dilute solution of zinc nitrate to 246 mL of 2.00 M sodium sulfide produced 0.279 g of a precipitate. How many grams of zinc(II) nitrate and sodium sulfide were consumed to produce this quantity of product? What was the concentration of each ion in the original solutions? What is the concentration of the sulfide ion in solution after the precipitation reaction, assuming no further reaction?

Answer

1. 3.75 g Ag_2CrO_4; 5.02×10^{-2} M nitrate
2.

Contributors

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Chapter 12.5: Acid Base Reactions

Template:HideTOC

Learning Objective

Learning Objective

- To know the characteristic properties of acids and bases.

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

Definitions of Acids and Bases

In Chapter 10, we defined **acids** as substances that dissolve in water to produce H^+ ions, whereas **bases** were defined as substances that dissolve in water to produce OH^- ions. In fact, this is only one possible set of definitions. Although the general properties of acids and bases have been known for more than a thousand years, the definitions of *acid* and *base* have changed dramatically as scientists have learned more about them. In ancient times, an acid was any substance that had a sour taste (e.g., vinegar or lemon juice), caused consistent color changes in dyes derived from plants (e.g., turning blue litmus paper red), reacted with certain metals to produce hydrogen gas and a solution of a salt containing a metal cation, and dissolved carbonate salts such as limestone ($CaCO_3$) with the evolution of carbon dioxide. In contrast, a base was any substance that had a bitter taste, felt slippery to the touch, and caused color changes in plant dyes that differed diametrically from the changes caused by acids (e.g., turning red litmus paper blue). Although these definitions were useful, they were entirely descriptive.



The Arrhenius Definition of Acids and Bases

The first person to define acids and bases in detail was the Swedish chemist Svante Arrhenius (1859–1927; Nobel Prize in Chemistry, 1903). According to the *Arrhenius definition*, an acid is a substance like hydrochloric acid that dissolves in water to produce H^+ ions (protons; Equation 12.5.1), and a base is a substance like sodium hydroxide that dissolves in water to produce hydroxide (OH^-) ions (Equation 12.5.2):

$$\underset{\text{an Arrhenius acid}}{HCl_{(g)}} \xrightarrow{H_2O_{(l)}} H^+_{(aq)} + Cl^-_{(aq)}$$

$$\underset{\text{an Arrhenius base}}{NaOH_{(s)}} \xrightarrow{H_2O_{(l)}} Na^+_{(aq)} + OH^-_{(aq)}$$

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

1. First, because acids and bases were defined in terms of ions obtained from water, the Arrhenius concept applied only to substances in aqueous solution.
2. Second, and more important, the Arrhenius definition predicted that *only* substances that dissolve in water to produce H^+ and OH^- ions should exhibit the properties of acids and bases, respectively. For example, according to the Arrhenius definition, the reaction of ammonia (a base) with gaseous HCl (an acid) to give ammonium chloride (Equation 12.5.3) is not an acid–base reaction because it does not involve H^+ and OH^-:

$$NH_{3\,(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)} \tag{12.5.3}$$

The Brønsted–Lowry Definition of Acids and Bases

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

According to Brønsted and Lowry, an acid is any substance that can donate a proton, and a base is any substance that can accept a proton. The Brønsted–Lowry definition of an acid is essentially the same as the Arrhenius definition, except that it is not restricted to aqueous solutions. The Brønsted–Lowry definition of a base, however, is far more general because the hydroxide ion is just one of many substances that can accept a proton. Ammonia, for example, reacts with a proton to form NH_4^+, so in Equation 12.5.3, NH_3 is a Brønsted–Lowry base and HCl is a Brønsted–Lowry acid. Because of its more general nature, the Brønsted–Lowry definition is used throughout this text unless otherwise specified.

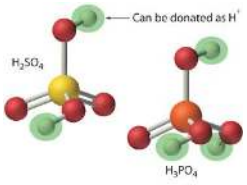
Polyprotic Acids

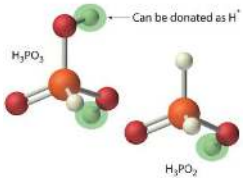
Acids differ in the number of protons they can donate. For example, monoprotic acids are compounds that are capable of donating a single proton per molecule. Monoprotic acids include HF, HCl, HBr, HI, HNO_3, and HNO_2. All carboxylic acids that contain a single $-CO_2H$ group, such as acetic acid (CH_3CO_2H), are monoprotic acids, dissociating to form RCO_2^- and H^+. A compound that can donate more than one proton per molecule is a polyprotic acid. For example, H_2SO_4 can donate two H^+ ions in separate steps, so it is a diprotic acid and H_3PO_4, which is capable of donating three protons in successive steps, is a triprotic acid , (Equation 12.5.4, Equation 12.5.5, and Equation 12.5.6):

$$H_3PO_4(l) \overset{H_2O(l)}{\rightleftharpoons} H^+(aq) + H_2PO_4^-(aq) \tag{12.5.4}$$

$$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq) \tag{12.5.5}$$

$$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq) \tag{12.5.6}$$





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

Strengths of Acids and Bases

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

In practice, only a few strong acids are commonly encountered: HCl, HBr, HI, HNO_3, $HClO_4$, and H_2SO_4 (H_3PO_4 is only moderately strong). The most common strong bases are ionic compounds that contain the hydroxide ion as the anion; three examples are NaOH, KOH, and $Ca(OH)_2$. Common weak acids include HCN, H_2S, HF, oxoacids such as HNO_2 and HClO, and carboxylic acids such as acetic acid. The ionization reaction of acetic acid is as follows:

$$CH_3CO_2H(l) \overset{H_2O(l)}{\rightleftharpoons} H^+(aq) + CH_3CO_2^-(aq) \tag{12.5.7}$$

Although acetic acid is *very* soluble in water, almost all of the acetic acid in solution exists in the form of neutral molecules (less than 1% dissociates). Sulfuric acid is unusual in that it is a strong acid when it donates its first proton (Equation 12.5.8) but a weak acid when it donates its second proton (Equation 12.5.9) as indicated by the single and double arrows, respectively:

$$\underset{\text{strong acid}}{H_2SO_4(l)} \xrightarrow{H_2O(l)} H^+(aq) + HSO_4^-(aq) \tag{12.5.8}$$

$$\underset{\text{weak acid}}{HSO_4^-(aq)} \rightleftharpoons H^+(aq) + SO_4^{2-}(aq) \tag{12.5.9}$$

Consequently, an aqueous solution of sulfuric acid contains $H^+_{(aq)}$ ions and a mixture of $HSO^-_{4\,(aq)}$ and $SO^{2-}_{4\,(aq)}$ ions, but no H_2SO_4 molecules.

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

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \tag{12.5.10}$$

Most of the ammonia (>99%) is present in the form of $NH_3(g)$. Amines, which are organic analogues of ammonia, are also weak bases, as are ionic compounds that contain anions derived from weak acids (such as S^{2-}).

Table 12.5.1 lists some common strong acids and bases. Acids other than the six common strong acids are almost invariably weak acids. The only common strong bases are the hydroxides of the alkali metals and the heavier alkaline earths (Ca, Sr, and Ba); any other bases you encounter are most likely weak. Remember that *there is no correlation between solubility and whether a substance is a strong or a weak electrolyte!* Many weak acids and bases are extremely soluble in water.

Note the Pattern

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

Table 12.5.1 Common Strong Acids and Bases

Strong Acids		Strong Bases	
Hydrogen Halides	Oxoacids	Group 1 Hydroxides	Hydroxides of the Heavier Group 2 Elements
HCl	HNO_3	LiOH	$Ca(OH)_2$
HBr	H_2SO_4	NaOH	$Sr(OH)_2$
HI	$HClO_4$	KOH	$Ba(OH)_2$
		RbOH	
		CsOH	

Example 12.5.1

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

1. $CH_3CH_2CO_2H$
2. CH_3OH
3. $Sr(OH)_2$
4. $CH_3CH_2NH_2$
5. $HBrO_4$

Given: compound

Asked for: acid or base strength

Strategy:

A Determine whether the compound is organic or inorganic.

B If inorganic, determine whether the compound is acidic or basic by the presence of dissociable H^+ or OH^- ions, respectively. If organic, identify the compound as a weak base or a weak acid by the presence of an amine or a carboxylic acid group, respectively. Recall that all polyprotic acids except H_2SO_4 are weak acids.

Solution:

1. **A** This compound is propionic acid, which is organic. **B** It contains a carboxylic acid group analogous to that in acetic acid, so it must be a weak acid.
2. **A** CH_3OH is methanol, an organic compound that contains the −OH group. **B** As a covalent compound, it does not dissociate to form the OH^- ion. Because it does not contain a carboxylic acid ($-CO_2H$) group, methanol also cannot dissociate to form H^+ (aq) ions. Thus we predict that in aqueous solution methanol is neither an acid nor a base.
3. **A** $Sr(OH)_2$ is an inorganic compound that contains one Sr^{2+} and two OH^- ions per formula unit. **B** We therefore expect it to be a strong base, similar to $Ca(OH)_2$.
4. **A** $CH_3CH_2NH_2$ is an amine (ethylamine), an organic compound in which one hydrogen of ammonia has been replaced by an R group. **B** Consequently, we expect it to behave similarly to ammonia (Equation 12.5.7), reacting with water to produce small amounts of the OH^- ion. Ethylamine is therefore a weak base.
5. **A** $HBrO_4$ is perbromic acid, an inorganic compound. **B** It is not listed in Table 12.5.1 as one of the common strong acids, but that does not necessarily mean that it is a weak acid. If you examine the periodic table, you can see that Br lies directly below Cl in group 17. We might therefore expect that $HBrO_4$ is chemically similar to $HClO_4$, a strong acid—and, in fact, it is.

Exercise

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

1. $Ba(OH)_2$
2. HIO_4
3. $CH_3CH_2CH_2CO_2H$
4. $(CH_3)_2NH$
5. CH_2O

Answer:

1. strong base
2. strong acid
3. weak acid
4. weak base
5. none of these; formaldehyde is a neutral molecule

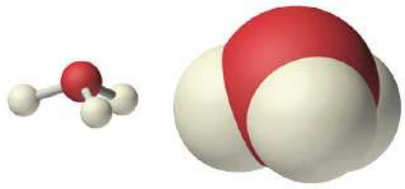
The Hydronium Ion

Because isolated protons are *very* unstable and hence very reactive, an acid never simply “loses” an H^+ ion. Instead, the proton is always transferred to another substance, which acts as a base in the Brønsted–Lowry definition. Thus in every acid–base reaction,

one species acts as an acid and one species acts as a base. Occasionally, the same substance performs both roles, as you will see later. When a strong acid dissolves in water, the proton that is released is transferred to a water molecule that acts as a proton acceptor or base, as shown for the dissociation of sulfuric acid:

$$\underset{\text{acid (proton donor)}}{H_2SO_4(l)} + \underset{\text{base (proton acceptor)}}{H_2O(l)} \rightarrow \underset{\text{acid}}{H_3O^+(aq)} + \underset{\text{base}}{HSO_4^-(aq)} \tag{12.5.11}$$

Technically, therefore, it is imprecise to describe the dissociation of a strong acid as producing $H^+_{(aq)}$ ions, as we have been doing. The resulting H_3O^+ ion is a more accurate representation of $H^+_{(aq)}$. For the sake of brevity, however, in discussing acid dissociation reactions, we often show the product as $H^+_{(aq)}$ (as in Equation 12.5.7) with the understanding that the product is actually the$H_3O^+_{(aq)}$ ion.



Hydronium ion,
H_3O^+

Conversely, bases that do not contain the hydroxide ion accept a proton from water, so small amounts of OH^- are produced, as in the following:

$$\underset{\text{base}}{NH_3(g)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons \underset{\text{acid}}{NH_4^+(aq)} + \underset{\text{base}}{OH^-(aq)}$$

Again, the double arrow indicates that the reaction does not go to completion but rather reaches a state of equilibrium. In this reaction, water acts as an acid by donating a proton to ammonia, and ammonia acts as a base by accepting a proton from water. Thus water can act as either an acid or a base by donating a proton to a base or by accepting a proton from an acid. Substances that can behave as both an acid and a base are said to be amphotericWhen substances can behave as both an acid and a base..

The products of an acid–base reaction are also an acid and a base. In Equation 12.5.11, for example, the products of the reaction are the hydronium ion, here an acid, and the hydrogen sulfate ion, here a weak base. In Equation 12.5.12, the products are NH_4^+, an acid, and OH^-, a base. The product NH_4^+ is called the conjugate acid and the product OH^- is called the conjugate base. Thus all acid–base reactions actually involve two conjugate acid–base pairs. All acid–base reactions involve two conjugate acid–base pairs, the Brønsted–Lowry acid and the base it forms after donating its proton, and the Brønsted–Lowry base and the acid it forms after accepting a proton.; in Equation 12.5.12, they are NH_4^+/NH_3 and H_2O/OH^-.

Neutralization Reactions

A neutralization reaction is one in which an acid and a base react in stoichiometric amounts to produce water and a salt, the general term for any ionic substance that does not have OH^- as the anion or H^+ as the cation. If the base is a metal hydroxide, then the general formula for the reaction of an acid with a base is described as follows: *Acid plus base yields water plus salt*. For example, the reaction of equimolar amounts of HBr and NaOH to give water and a salt (NaBr) is a neutralization reaction:

$$\underset{\text{acid}}{HBr(aq)} + \underset{\text{base}}{NaOH(aq)} \rightarrow \underset{\text{water}}{H_2O(l)} + \underset{\text{salt}}{NaBr(aq)} \tag{12.5.13}$$

Note the Pattern

Acid plus base yields water plus salt.

If we write the complete ionic equation for the reaction in Equation 12.5.13, we see that $Na^+_{(aq)}$ and $Br^-_{(aq)}$ are spectator ions and are not involved in the reaction:

$$H^+(aq) + \cancel{Br^-(aq)} + \cancel{Na^+(aq)} + OH^-(aq) \rightarrow H_2O(l) + \cancel{Na^+(aq)} + \cancel{Br^-(aq)}$$

The overall reaction is therefore simply the combination of H^+(aq) and OH^-(aq) to produce H_2O, as shown in the net ionic equation:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

The net ionic equation for the reaction of any strong acid with any strong base is identical to Equation 12.5.15.

The strengths of the acid and the base generally determine whether the reaction goes to completion. The reaction of *any* strong acid with *any* strong base goes essentially to completion, as does the reaction of a strong acid with a weak base, and a weak acid with a strong base. Examples of the last two are as follows:

$$\underset{\text{strong acid}}{HCl(aq)} + \underset{\text{weak base}}{NH_3(aq)} \rightarrow \underset{\text{salt}}{NH_4Cl(aq)}$$

$$\underset{\text{weak acid}}{CH_3CO_2H(aq)} + \underset{\text{strong base}}{NaOH(aq)} \rightarrow \underset{\text{salt}}{CH_3CO_2Na(aq)} + H_2O(l)$$

Sodium acetate is written with the organic component first followed by the cation, as is usual for organic salts. Most reactions of a weak acid with a weak base also go essentially to completion. One example is the reaction of acetic acid with ammonia:

$$\underset{\text{weak acid}}{CH_3CO_2H(aq)} + \underset{\text{weak base}}{NH_3(aq)} \rightarrow \underset{\text{salt}}{CH_3CO_2NH_4(aq)}$$

An example of an acid–base reaction that does not go to completion is the reaction of a weak acid or a weak base with water, which is both an extremely weak acid and an extremely weak base.

Note the Pattern

Except for the reaction of a weak acid or a weak base with water, acid–base reactions essentially go to completion.

In some cases, the reaction of an acid with an anion derived from a weak acid (such as HS^-) produces a gas (in this case, H_2S). Because the gaseous product escapes from solution in the form of bubbles, the reverse reaction cannot occur. Therefore, these reactions tend to be forced, or driven, to completion. Examples include reactions in which an acid is added to ionic compounds that contain the HCO_3^-, CN^-, or S^{2-} anions, all of which are driven to completion (Figure 12.5.1):

$$HCO_3^-(aq) + H^+(aq) \rightarrow H_2CO_3(aq)$$

$$H_2CO_3(aq) \rightarrow CO_2(g) + H_2O(l)$$

$$CN^-(aq) + H^+(aq) \rightarrow HCN(g)$$

$$S^{2-}(aq) + H^+(aq) \rightarrow HS^-(aq)$$

$$HS^-(aq) + H^+(aq) \rightarrow H_2S(g)$$

The reactions in Equation 12.5.21 are responsible for the rotten egg smell that is produced when metal sulfides come in contact with acids.

Example 12.5.2

Calcium propionate is used to inhibit the growth of molds in foods, tobacco, and some medicines. Write a balanced chemical equation for the reaction of aqueous propionic acid ($CH_3CH_2CO_2H$) with aqueous calcium hydroxide [$Ca(OH)_2$] to give calcium propionate. Do you expect this reaction to go to completion, making it a feasible method for the preparation of calcium propionate?

Given: reactants and product

Asked for: balanced chemical equation and whether the reaction will go to completion

Strategy:

Write the balanced chemical equation for the reaction of propionic acid with calcium hydroxide. Based on their acid and base strengths, predict whether the reaction will go to completion.

Solution:

Propionic acid is an organic compound that is a weak acid, and calcium hydroxide is an inorganic compound that is a strong base. The balanced chemical equation is as follows:

$$2CH_3CH_2CO_2H(aq) + Ca(OH)_2(aq) \rightarrow (CH_3CH_2CO_2)_2Ca(aq) + 2H_2O(l)$$

The reaction of a weak acid and a strong base will go to completion, so it is reasonable to prepare calcium propionate by mixing solutions of propionic acid and calcium hydroxide in a 2:1 mole ratio.

Exercise

Write a balanced chemical equation for the reaction of solid sodium acetate with dilute sulfuric acid to give sodium sulfate.

Answer: $2CH_3CO_2Na(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2CH_3CO_2H(aq)$



Stomach acid. *An antacid tablet reacts with 0.1 M HCl (the approximate concentration found in the human stomach).*

One of the most familiar and most heavily advertised applications of acid–base chemistry is *antacids*, which are bases that neutralize stomach acid. The human stomach contains an approximately 0.1 M solution of hydrochloric acid that helps digest foods. If the protective lining of the stomach breaks down, this acid can attack the stomach tissue, resulting in the formation of an *ulcer*. Because one factor that is believed to contribute to the formation of stomach ulcers is the production of excess acid in the stomach, many individuals routinely consume large quantities of antacids. The active ingredients in antacids include sodium bicarbonate and potassium bicarbonate ($NaHCO_3$ and $KHCO_3$; Alka-Seltzer); a mixture of magnesium hydroxide and aluminum hydroxide [$Mg(OH)_2$ and $Al(OH)_3$; Maalox, Mylanta]; calcium carbonate ($CaCO_3$; Tums); and a complex salt, dihydroxyaluminum sodium carbonate [$NaAl(OH)_2CO_3$; original Rolaids]. Each has certain advantages and disadvantages. For example, $Mg(OH)_2$ is a powerful laxative (it is the active ingredient in milk of magnesia), whereas $Al(OH)_3$ causes constipation. When mixed, each tends to counteract the unwanted effects of the other. Although all antacids contain both an anionic base (OH^-, CO_3^{2-}, or HCO_3^-) and an appropriate cation, they differ substantially in the amount of active ingredient in a given mass of product.

Example 12.5.3

Assume that the stomach of someone suffering from acid indigestion contains 75 mL of 0.20 M HCl. How many Tums tablets are required to neutralize 90% of the stomach acid, if each tablet contains 500 mg of $CaCO_3$? (Neutralizing all of the stomach acid is not desirable because that would completely shut down digestion.)

Given: volume and molarity of acid and mass of base in an antacid tablet

Asked for: number of tablets required for 90% neutralization

Strategy:

A Write the balanced chemical equation for the reaction and then decide whether the reaction will go to completion.

B Calculate the number of moles of acid present. Multiply the number of moles by the percentage to obtain the quantity of acid that must be neutralized. Using mole ratios, calculate the number of moles of base required to neutralize the acid.

C Calculate the number of moles of base contained in one tablet by dividing the mass of base by the corresponding molar mass. Calculate the number of tablets required by dividing the moles of base by the moles contained in one tablet.

Solution:

A We first write the balanced chemical equation for the reaction:

$$2HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + H_2CO_3(aq)$$

Each carbonate ion can react with 2 mol of H^+ to produce H_2CO_3, which rapidly decomposes to H_2O and CO_2. Because HCl is a strong acid and CO_3^{2-} is a weak base, the reaction will go to completion.

B Next we need to determine the number of moles of HCl present:

$$75\ \cancel{mL}\left(\frac{1\ \cancel{L}}{1000\ \cancel{mL}}\right)\left(\frac{0.20\ mol\ HCl}{\cancel{L}}\right) = 0.015\ mol\ HCl$$

Because we want to neutralize only 90% of the acid present, we multiply the number of moles of HCl by 0.90:

$$(0.015\ mol\ HCl)(0.90) = 0.014\ mol\ HCl$$

We know from the stoichiometry of the reaction that each mole of $CaCO_3$ reacts with 2 mol of HCl, so we need

$$moles\ CaCO_3 = 0.014\ \cancel{mol\ HCl}\left(\frac{1\ mol\ CaCO_3}{2\ \cancel{mol\ HCl}}\right) = 0.0070\ mol\ CaCO_3$$

C Each Tums tablet contains

$$\left(\frac{500\ \cancel{mg\ CaCO_3}}{1\ Tums\ tablet}\right)\left(\frac{1\ \cancel{g}}{1000\ \cancel{mg\ CaCO_3}}\right)\left(\frac{1\ mol\ CaCO_3}{100.1\ \cancel{g}}\right) = 0.00500\ mol\ CaCO_3$$

Thus we need $\dfrac{0.0070\ \cancel{mol\ CaCO_3}}{0.00500\ \cancel{mol\ CaCO_3}} = 1.4$ Tums tablets.

Exercise

Assume that as a result of overeating, a person's stomach contains 300 mL of 0.25 M HCl. How many Rolaids tablets must be consumed to neutralize 95% of the acid, if each tablet contains 400 mg of $NaAl(OH)_2CO_3$? The neutralization reaction can be written as follows:

$$NaAl(OH)_2CO_3(s) + 4HCl(aq) \rightarrow AlCl_3(aq) + NaCl(aq) + CO_2(g) + 3H_2O(l)$$

Answer: 6.4 tablets

The pH Scale

One of the key factors affecting reactions that occur in dilute solutions of acids and bases is the concentration of H^+ and OH^- ions. The pH scale provides a convenient way of expressing the hydrogen ion (H^+) concentration of a solution and enables us to describe acidity or basicity in quantitative terms.

Pure liquid water contains extremely low but measurable concentrations of H_3O^+(aq) and OH^-(aq) ions produced via an *autoionization reaction*, in which water acts simultaneously as an acid and as a base:

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

The concentration of hydrogen ions in pure water is only 1.0×10^{-7} M at 25°C. Because the autoionization reaction produces both a proton and a hydroxide ion, the OH^- concentration in pure water is also 1.0×10^{-7} M. Pure water is a neutral solution in which $[H^+] = [OH^-] = 1.0 \times 10^{-7}$ M.

The pH scale describes the hydrogen ion concentration of a solution in a way that avoids the use of exponential notation; pH is defined as the negative base-10 logarithm of hydrogen ion *activity*. As you will learn in a more advanced course, the activity of a substance in solution is related to its concentration. For dilute solutions such as those we are discussing, the activity and the concentration are approximately the same.

$$pH = -log[H^+]$$

Conversely,

$$[H^+] = 10^{-pH}$$

Because the hydrogen ion concentration is 1.0×10^{-7} M in pure water at 25°C, the pH of pure liquid water (and, by extension, of any neutral solution) is

$$pH = -log[1.0 \times 10^{-7}] = 7.00$$

Adding an acid to pure water increases the hydrogen ion concentration and decreases the hydroxide ion concentration because a neutralization reaction occurs, such as that shown in Equation 12.5.15. Because the negative exponent of $[H^+]$ becomes smaller as $[H^+]$ increases, the pH *decreases* with increasing $[H^+]$. For example, a 1.0 M solution of a strong monoprotic acid such as HCl or HNO_3 has a pH of 0.00:

$$pH = -log[1.0] = 0.00$$

Note the Pattern

pH decreases with increasing $[H^+]$.

Conversely, adding a base to pure water increases the hydroxide ion concentration and decreases the hydrogen ion concentration. Because the autoionization reaction of water does not go to completion, neither does the neutralization reaction. Even a strongly basic solution contains a detectable amount of H^+ ions. For example, a 1.0 M OH^- solution has $[H^+] = 1.0 \times 10^{-14}$ M. The pH of a 1.0 M NaOH solution is therefore

$$pH = -log[1.0 \times 10^{-14}] = 14.00$$

For practical purposes, the pH scale runs from pH = 0 (corresponding to 1 M H^+) to pH 14 (corresponding to 1 M OH^-), although pH values less than 0 or greater than 14 are possible.

We can summarize the relationships between acidity, basicity, and pH as follows:

- If pH = 7.0, the solution is neutral.
- If pH < 7.0, the solution is acidic.
- If pH > 7.0, the solution is basic.

It is important to recognize that the pH scale is a continuum, there is no sharp change in concentrations as pH changes between acidic and basic or visa versa. Acidic solutions simply have more $[H^+]$ than OH^- and the situation is reversed for basic solutions. Keep in mind that the pH scale is logarithmic, so a change of 1.0 in the pH of a solution corresponds to a *tenfold* change in the hydrogen ion concentration and a change of 0.1 pH would be an approximately 30% change. The foods and consumer products we encounter daily represent a wide range of pH values, as shown in Figure 12.5.2.

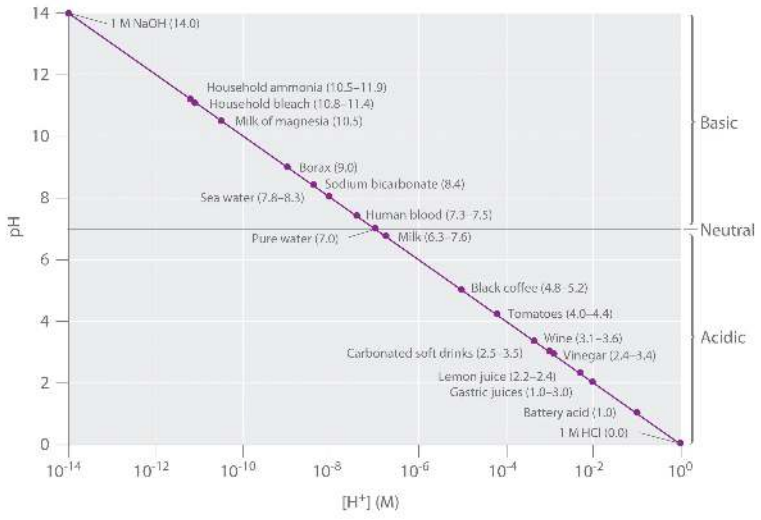


Figure 12.5.2 A Plot of pH versus $[H^+]$ for Some Common Aqueous Solutions *Although many substances exist in a range of pH values (indicated in parentheses), they are plotted using typical values.*

Example 12.5.4

1. What is the pH of a 2.1×10^{-2} M aqueous solution of $HClO_4$?
2. The pH of a vinegar sample is 3.80. What is its hydrogen ion concentration?

Given: molarity of acid or pH

Asked for: pH or $[H^+]$

Strategy:

Using the balanced chemical equation for the acid dissociation reaction and Equation 12.5.25 or 12.5.24, determine $[H^+]$ and convert it to pH or vice versa.

Solution:

1. $HClO_4$ (perchloric acid) is a strong acid, so it dissociates completely into H^+ ions and ClO_4^- ions:

$$HClO_4(l) \rightarrow H^+(aq) + ClO_4^-(aq)$$

The H^+ ion concentration is therefore the same as the perchloric acid concentration. The pH of the perchloric acid solution is thus

$$pH = -log[H^+] = -log(2.1 \times 10^{-2}) = 1.68$$

The result makes sense: the H^+ ion concentration is between 10^{-1} M and 10^{-2} M, so the pH must be between 1 and 2.

Note: The assumption that $[H^+]$ is the same as the concentration of the acid is valid for *only* strong acids. Because weak acids do *not* dissociate completely in aqueous solution, a more complex procedure is needed to calculate the pH of their solutions.

2. We are given the pH and asked to calculate the hydrogen ion concentration. From Equation 12.5.24,

$$10^{-pH} = [H^+]$$

Thus $[H^+] = 10^{-3.80} = 1.6 \times 10^{-4}\ M$.

Exercise

1. What is the pH of a 3.0×10^{-5} M aqueous solution of HNO_3?
2. What is the hydrogen ion concentration of turnip juice, which has a pH of 5.41?

Answer:

1. $pH = 4.52$
2. $[H^+] = 3.9 \times 10^{-6}\ M$

Tools have been developed that make the measurement of pH simple and convenient (Figure 12.5.3). For example, pH paper consists of strips of paper impregnated with one or more acid–base indicators which are intensely colored organic molecules whose colors change dramatically depending on the pH of the solution. Placing a drop of a solution on a strip of pH paper and comparing its color with standards give the solution's approximate pH. A more accurate tool, the pH meter, uses a glass electrode, a device whose voltage depends on the H^+ ion concentration.

Figure 12.5.3 Two Ways of Measuring the pH of a Solution: pH Paper and a pH Meter

Note that both show that the pH is 1.7, but the pH meter gives a more precise value.

Key Equations

definition of pH

Equation 12.5.23: $pH = -log[H^+]$

Equation 12.5.24: $[H^+] = 10^{-pH}$

Summary

Acid–base reactions require both an acid and a base. In Brønsted–Lowry terms, an **acid** is a substance that can donate a proton (H^+), and a **base** is a substance that can accept a proton. All acid–base reactions contain two acid–base pairs: the reactants and the products. Acids can donate one proton (**monoprotic acids**), two protons (**diprotic acids**), or three protons (**triprotic acids**). Compounds that are capable of donating more than one proton are generally called **polyprotic acids**. Acids also differ in their tendency to donate a proton, a measure of their acid strength. **Strong acids** react completely with water to produce H_3O^+(aq) (the

hydronium ion), whereas **weak acids** dissociate only partially in water. Conversely, **strong bases** react completely with water to produce the hydroxide ion, whereas **weak bases** react only partially with water to form hydroxide ions. The reaction of a strong acid with a strong base is a **neutralization reaction**, which produces water plus a **salt**.

The acidity or basicity of an aqueous solution is described quantitatively using the **pH scale**. The **pH** of a solution is the negative logarithm of the H^+ ion concentration and typically ranges from 0 for strongly acidic solutions to 14 for strongly basic ones. Because of the *autoionization reaction* of water, which produces small amounts of hydronium ions and hydroxide ions, a **neutral solution** of water contains 1×10^{-7} M H^+ ions and has a pH of 7.0. An **indicator** is an intensely colored organic substance whose color is pH dependent; it is used to determine the pH of a solution.

Key Takeaway

- An acidic solution and a basic solution react together in a neutralization reaction that also forms a salt.

Conceptual Problems

1. Why was it necessary to expand on the Arrhenius definition of an acid and a base? What specific point does the Brønsted–Lowry definition address?
2. State whether each compound is an acid, a base, or a salt.
    1. $CaCO_3$
    2. $NaHCO_3$
    3. H_2SO_4
    4. $CaCl_2$
    5. $Ba(OH)_2$
3. State whether each compound is an acid, a base, or a salt.
    1. NH_3
    2. NH_4Cl
    3. H_2CO_3
    4. CH_3COOH
    5. NaOH
4. Classify each compound as a strong acid, a weak acid, a strong base, or a weak base in aqueous solution.
    1. sodium hydroxide
    2. acetic acid
    3. magnesium hydroxide
    4. tartaric acid
    5. sulfuric acid
    6. ammonia
    7. hydroxylamine (NH_2OH)
    8. hydrocyanic acid
5. Decide whether each compound forms an aqueous solution that is strongly acidic, weakly acidic, strongly basic, or weakly basic.
    1. propanoic acid
    2. hydrobromic acid
    3. methylamine
    4. lithium hydroxide
    5. citric acid
    6. sodium acetate
    7. ammonium chloride
    8. barium hydroxide

6. What is the relationship between the strength of an acid and the strength of the conjugate base derived from that acid? Would you expect the $CH_3CO_2^-$ ion to be a strong base or a weak base? Why? Is the hydronium ion a strong acid or a weak acid? Explain your answer.
7. What are the products of an acid–base reaction? Under what circumstances is one of the products a gas?
8. Explain how an aqueous solution that is strongly basic can have a pH, which is a measure of the *acidity* of a solution.

Answer

1.
2.
3.
4.
5. 1. weakly acidic
   2. strongly acidic
   3. weakly basic
   4. strongly basic
   5. weakly acidic
   6. weakly basic
   7. weakly acidic
   8. strongly basic
6.
7.
8.

Numerical Problems

1. Derive an equation to relate the hydrogen ion concentration to the molarity of a solution of a strong monoprotic acid.
2. Derive an equation to relate the hydroxide ion concentration to the molarity of a solution of
   1. a group I hydroxide.
   2. a group II hydroxide.
3. Given the following salts, identify the acid and the base in the neutralization reactions and then write the complete ionic equation:
   1. barium sulfate
   2. lithium nitrate
   3. sodium bromide
   4. calcium perchlorate
4. What is the pH of each solution?
   1. 5.8×10^{-3} mol of HNO_3 in 257 mL of water
   2. 0.0079 mol of HI in 750 mL of water
   3. 0.011 mol of $HClO_4$ in 500 mL of water
   4. 0.257 mol of HBr in 5.00 L of water
5. What is the hydrogen ion concentration of each substance in the indicated pH range?
   1. black coffee (pH 5.10)
   2. milk (pH 6.30–7.60)
   3. tomatoes (pH 4.00–4.40)
6. What is the hydrogen ion concentration of each substance in the indicated pH range?
   1. orange juice (pH 3–4)

2. fresh egg white (pH 7.60–7.80)
3. lemon juice (pH 2.20–2.40)

7. What is the pH of a solution prepared by diluting 25.00 mL of 0.879 M HCl to a volume of 555 mL?
8. Vinegar is primarily an aqueous solution of acetic acid. Commercial vinegar typically contains 5.0 g of acetic acid in 95.0 g of water. What is the concentration of commercial vinegar? If only 3.1% of the acetic acid dissociates to $CH_3CO_2^-$ and H^+, what is the pH of the solution? (Assume the density of the solution is 1.00 g/mL.)
9. If a typical household cleanser is 0.50 M in strong base, what volume of 0.998 M strong monoprotic acid is needed to neutralize 50.0 mL of the cleanser?
10. A 25.00 mL sample of a 0.9005 M solution of HCl is diluted to 500.0 mL. What is the molarity of the final solution? How many milliliters of 0.223 M NaOH are needed to neutralize 25.00 mL of this final solution?
11. If 20.0 mL of 0.10 M NaOH are needed to neutralize 15.0 mL of gastric fluid, what is the molarity of HCl in the fluid? (Assume all the acidity is due to the presence of HCl.) What other base might be used instead of NaOH?
12. Malonic acid ($C_3H_4O_4$) is a diprotic acid used in the manufacture of barbiturates. How many grams of malonic acid are in a 25.00 mL sample that requires 32.68 mL of 1.124 M KOH for complete neutralization to occur? Malonic acid is a dicarboxylic acid; propose a structure for malonic acid.
13. Describe how you would prepare 500 mL of a 1.00 M stock solution of HCl from an HCl solution that is 12.11 M. Using your stock solution, how would you prepare 500 mL of a solution that is 0.012 M in HCl?
14. Given a stock solution that is 8.52 M in HBr, describe how you would prepare a 500 mL solution with each concentration.
    1. 2.50 M
    2. 4.00×10^{-3} M
    3. 0.989 M
15. How many moles of solute are contained in each?
    1. 25.00 mL of 1.86 M NaOH
    2. 50.00 mL of 0.0898 M HCl
    3. 13.89 mL of 0.102 M HBr
16. A chemist needed a solution that was approximately 0.5 M in HCl but could measure only 10.00 mL samples into a 50.00 mL volumetric flask. Propose a method for preparing the solution. (Assume that concentrated HCl is 12.0 M.)
17. Write the balanced chemical equation for each reaction.
    1. perchloric acid with potassium hydroxide
    2. nitric acid with calcium hydroxide
18. Write the balanced chemical equation for each reaction.
    1. solid strontium hydroxide with hydrobromic acid
    2. aqueous sulfuric acid with solid sodium hydroxide
19. A neutralization reaction gives calcium nitrate as one of the two products. Identify the acid and the base in this reaction. What is the second product? If the product had been cesium iodide, what would have been the acid and the base? What is the complete ionic equation for each reaction?

Answers

1. $[H_3O^+] = [HA]$ M
2.
3.
    1. H_2SO_4 and $Ba(OH)_2$; $2H^+ + SO_4^{2-} + Ba^{2+} + 2OH^- \rightarrow 2H_2O + Ba^{2+} + SO_4^{2-}$
    2. HNO_3 and LiOH; $H^+ + NO_3^- + Li^+ + OH^- \rightarrow H_2O + Li^+ + NO_3^-$
    3. HBr and NaOH; $H^+ + Br^- + Na^+ + OH^- \rightarrow H_2O + Na^+ + Br^-$

4. $HClO_4$ and $Ca(OH)_2$; $2H^+ + 2ClO_4^- + Ca^{2+} + 2OH^- \rightarrow 2H_2O + Ca^{2+} + 2ClO_4^-$

4.

5. 1. 7.9×10^{-6} M H^+
   2. 5.0×10^{-7} to 2.5×10^{-8} M H^+
   3. 1.0×10^{-4} to 4.0×10^{-5} M H^+

6.

7. pH = 1.402

8.

9. 25 mL

10.

11. 0.13 M HCl; magnesium carbonate, $MgCO_3$, or aluminum hydroxide, $Al(OH)_3$

12.

13. 1.00 M solution: dilute 41.20 mL of the concentrated solution to a final volume of 500 mL. 0.012 M solution: dilute 12.0 mL of the 1.00 M stock solution to a final volume of 500 mL.

14.

15. 1. 4.65×10^{-2} mol NaOH
    2. 4.49×10^{-3} mol HCl
    3. 1.42×10^{-3} mol HBr

16.

17. 1. $HClO_4 + KOH \rightarrow KClO_4 + H_2O$
    2. $2HNO_3 + Ca(OH)_2 \rightarrow Ca(NO_3)_2 + 2H_2O$

18.

19. The acid is nitric acid, and the base is calcium hydroxide. The other product is water.

$$2HNO_3 + Ca(OH)_2 \rightarrow Ca(NO_3)_2 + 2H_2O$$

The acid is hydroiodic acid, and the base is cesium hydroxide. The other product is water.

$$HI + CsOH \rightarrow CsI + H_2O$$

The complete ionic equations are

$$2H^+ + 2NO_3^- + Ca^{2+} + 2OH^- \rightarrow Ca^{2+} + 2NO_3^- + H_2O$$
$$H^+ + I^- + Cs^+ + OH^- \rightarrow Cs^+ + I^- + H_2O$$

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Chapter 12.6: The Chemistry of Acid Rain

Learning Objective

- To understand the chemistry of acid rain.

Acid–base reactions can have a strong environmental impact. For example, a dramatic increase in the acidity of rain and snow over the past 150 years is dissolving marble and limestone surfaces, accelerating the corrosion of metal objects, and decreasing the pH of natural waters. This environmental problem is called acid rain which is dramatically more acidic because of human activities. and has significant consequences for all living organisms. To understand acid rain requires an understanding of acid–base reactions in aqueous solution.

The term *acid rain* is actually somewhat misleading because even pure rainwater collected in areas remote from civilization is slightly acidic (pH ≈ 5.6) due to dissolved carbon dioxide, which reacts with water to give carbonic acid, a weak acid:

$$CO_2\,(g) + H_2O\,(l) \;\rightleftharpoons\; H_2CO_3\,(aq) \;\rightleftharpoons\; H^+\,(aq) + HCO_3^-\,(aq)$$

The English chemist Robert Angus Smith is generally credited with coining the phrase *acid rain* in 1872 to describe the increased acidity of the rain in British industrial centers (such as Manchester), which was apparently caused by the unbridled excesses of the early Industrial Revolution, although the connection was not yet understood. At that time, there was no good way to measure hydrogen ion concentrations, so it is difficult to know the actual pH of the rain observed by Smith. Typical pH values for rain in the continental United States now range from 4 to 4.5, with values as low as 2.0 reported for areas such as Los Angeles. Recall from Figure 12.6.1 that rain with a pH of 2 is comparable in acidity to lemon juice, and even “normal” rain is now as acidic as tomato juice or black coffee.

What is the source of the increased acidity in rain and snow? Chemical analysis shows the presence of large quantities of sulfate (SO_4^{2-}) and nitrate (NO_3^-) ions, and a wide variety of evidence indicates that a significant fraction of these species come from nitrogen and sulfur oxides produced during the combustion of fossil fuels. At the high temperatures found in both internal combustion engines and lightning discharges, molecular nitrogen and molecular oxygen react to give nitric oxide:

$$N_2\,(g) + O_2\,(g) \;\rightarrow\; 2NO\,(g)$$

Nitric oxide then reacts rapidly with excess oxygen to give nitrogen dioxide, the compound responsible for the brown color of smog:

$$2NO\,(g) + O_2\,(g) \;\rightarrow\; 2NO_2\,(g))$$

When nitrogen dioxide dissolves in water, it forms a 1:1 mixture of nitrous acid and nitric acid:

$$2NO_2\,(g) + H_2O\,(l) \;\rightarrow\; HNO_2\,(aq) + HNO_3\,(aq)$$

Because molecular oxygen eventually oxidizes nitrous acid to nitric acid, the overall reaction is

$$2N_2\,(g) + 5O_2\,(g) + 2H_2O\,(l) \;\rightarrow 4HNO_3(aq)$$

Large amounts of sulfur dioxide have always been released into the atmosphere by natural sources, such as volcanoes, forest fires, and the microbial decay of organic materials, but for most of Earth’s recorded history the natural cycling of sulfur from the atmosphere into oceans and rocks kept the acidity of rain and snow in check. Unfortunately, the burning of fossil fuels seems to have tipped the balance. Many coals contain as much as 5%–6% pyrite (FeS_2) by mass, and fuel oils typically contain at least 0.5% sulfur by mass. Since the mid-19th century, these fuels have been burned on a huge scale to supply the energy needs of our modern industrial society, releasing tens of millions of tons of additional SO_2 into the atmosphere annually. In addition, roasting sulfide ores to obtain metals such as zinc and copper produces large amounts of SO_2 via reactions such as

$$2ZnS\,(s) + 3O_2\,(g) \;\rightarrow 2ZnO\,(s) + 2SO_2\,(g)$$

Regardless of the source, the SO_2 dissolves in rainwater to give sulfurous acid (Equation 12.6.7), which is eventually oxidized by oxygen to sulfuric acid (Equation 12.6.8):

$$SO_2\,(g) + H_2O\,(l) \;\rightarrow H_2SO_3(aq) \tag{12.6.7}$$

$$2H_2SO_3(aq) + O_2\,(g) \;\rightarrow 2H_2SO_4(aq) \tag{12.6.8}$$

Concerns about the harmful effects of acid rain have led to strong pressure on industry to minimize the release of SO_2 and NO. For example, coal-burning power plants now use SO_2 "scrubbers," which trap SO_2 by its reaction with lime (CaO) to produce calcium sulfite dihydrate ($CaSO_3 \cdot 2H_2O$; Figure 12.6.1).

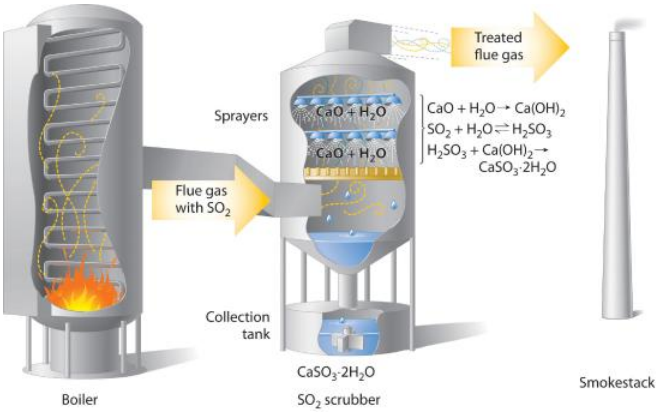


Figure 12.6.1 Schematic Diagram of a Wet Scrubber System *In coal-burning power plants, SO_2 can be removed ("scrubbed") from exhaust gases by its reaction with a lime (CaO) and water spray to produce calcium sulfite dihydrate ($CaSO_3 \cdot 2H_2O$). Removing SO_2 from the gases prevents its conversion to SO_3 and subsequent reaction with rainwater (acid rain). Scrubbing systems are now commonly used to minimize the environmental effects of large-scale fossil fuel combustion.*

The damage that acid rain does to limestone and marble buildings and sculptures is due to a classic acid–base reaction. Marble and limestone both consist of calcium carbonate ($CaCO_3$), a salt derived from the weak acid H_2CO_3. As we saw in Section 12.5 the reaction of a strong acid with a salt of a weak acid goes to completion. Thus we can write the reaction of limestone or marble with dilute sulfuric acid as follows:

$$CaCO_3\,(s) + H_2SO_4(aq) \rightarrow CaSO_4\,(s) + H_2O\,(l) + CO_2\,(g) \tag{12.6.9}$$

Because $CaSO_4$ is sparingly soluble in water, the net result of this reaction is to dissolve the marble or limestone. The Lincoln Memorial in Washington, DC, which was built in 1922, already shows significant damage from acid rain, and many older objects are exhibiting even greater damage (Figure 12.6.2). Metal objects can also suffer damage from acid rain through oxidation–reduction reactions, which are discussed in Section 12.7 .



Figure 12.6.2 Acid Rain Damage to a Statue of George Washington *Both marble and limestone consist of $CaCO_3$, which reacts with acid rain in an acid–base reaction to produce $CaSO_4$. Because $CaSO_4$ is somewhat soluble in water, significant damage to the structure can result.*

The biological effects of acid rain are more complex. As indicated in Figure 8.6.2, biological fluids, such as blood, have a pH of 7–8. Organisms such as fish can maintain their internal pH in water that has a pH in the range of 6.5–8.5. If the external pH is too low, however, many aquatic organisms can no longer maintain their internal pH, so they die. A pH of 4 or lower is fatal for virtually all fish, most invertebrate animals, and many microorganisms. At its worst as a result of acid rain, the pH of some lakes in Europe and

the United States dropped below 4 and surveys suggested that up to 6% of the lakes in the Adirondack Mountains of upstate New York and 4% of the lakes in Sweden and Norway were essentially dead and contain no fish. Neither location contains large concentrations of industry, but New York lies downwind of the industrial Midwest, and Scandinavia is downwind of the most industrialized regions of western Europe. Both regions appear to have borne the brunt of the pollution produced by their upwind neighbors. This problem has been dealt with by regulations limiting emission of sulfur dioxide and nitrogen oxides from coal burning power plants and diesel trucks.

A second major way in which acid rain can cause biological damage is less direct. Trees and many other plants are sensitive to the presence of aluminum and other metals in groundwater. Under normal circumstances, aluminum hydroxide [$Al(OH)_3$], which is present in some soils, is insoluble. At lower pH values, however, $Al(OH)_3$ dissolves via the following reaction:

$$Al(OH)_3\,(s) + 3H^+(aq) \rightarrow Al^{3+}(aq) + 3H_2O\,(l) \tag{12.6.10}$$

The result is increased levels of Al^{3+} ions in groundwater. Because the Al^{3+} ion is toxic to plants, high concentrations can affect plant growth. Acid rain can also weaken the leaves and roots of plants so much that the plants are unable to withstand other stresses. The combination of the two effects caused significant damage to established forests, such as the Black Forest in Germany and the forests of the northeastern United States and Canada and other countries (Figure 12.6.3).



Figure 12.6.3 Acid Rain Damage to a Forest in the Czech Republic*Trees and many other plants are sensitive to aluminum and other metals in groundwater. Acid rain increases the concentration of Al^{3+} in groundwater, thereby adversely affecting plant growth. Large sections of established forests have been severely damaged.*

Summary

Acid rain is rainfall whose pH is less than 5.6, the value typically observed, due to the presence of dissolved carbon dioxide. Acid rain is caused by nitrogen oxides and sulfur dioxide produced by both natural processes and the combustion of fossil fuels. Eventually, these oxides react with oxygen and water to give nitric acid and sulfuric acid.

Key Takeaway

- The damaging effects of acid rain have led to strong pressure on industry to minimize the release of harmful reactants.

Conceptual Problems

1. Why is it recommended that marble countertops not be used in kitchens? Marble is composed mostly of $CaCO_3$.
2. Explain why desulfurization of fossil fuels is an area of intense research.
3. What is the role of NO_x in the formation of acid rain?

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Chapter 12.7: Oxidation-Reduction Reactions

Learning Objective

- To identify oxidation–reduction reactions in solution.
- To balance oxidation–reduction reactions in solution.
- To use the activity series for displacement reactions

We described the defining characteristics of oxidation–reduction, or redox, reactions in Chapter 11.6. Most of the reactions we considered there were relatively simple, and balancing them was straightforward. When oxidation–reduction reactions occur in aqueous solution, however, the equations are more complex and can be more difficult to balance by inspection. Because a balanced chemical equation is the most important prerequisite for solving any stoichiometry problem, we need a method for balancing oxidation–reduction reactions in aqueous solution that is generally applicable. One such method uses *oxidation states*, and a second is referred to as the *half-reaction* method.

Balancing Redox Equations Using Oxidation States

To balance a redox equation using the oxidation state method we conceptually separate the overall reaction into two parts: an oxidation—in which the atoms of one element lose electrons—and a reduction—in which the atoms of one element gain electrons. Consider, for example, the reaction of Cr^{2+}(aq) with manganese dioxide (MnO_2) in the presence of dilute acid. Equation 12.7.1 is the net ionic equation for this reaction before balancing; the oxidation state of each element in each species has been assigned using the procedure described in Section 11.6:

$$\overset{+2}{Cr^{2+}(aq)} + \overset{+4}{\underset{-2}{MnO_2(aq)}} + \overset{+1}{H^+(aq)} \rightarrow \overset{+3}{Cr^{3+}(aq)} + \overset{+2}{Mn^{2+}(aq)} + \overset{+1}{\underset{-2}{H_2O(l)}}$$

Notice that chromium is oxidized from the +2 to the +3 oxidation state, while manganese is reduced from the +4 to the +2 oxidation state. We can write an equation for this reaction that shows only the atoms that are oxidized and reduced:

$$Cr^{2+} + Mn^{4+} \rightarrow Cr^{3+} + Mn^{2+}$$

The oxidation can be written as

$$Cr^{2+} \rightarrow Cr^{3+} + e^-$$

and the reduction as

$$Mn^{4+} + 2e^- \rightarrow Mn^{2+}$$

For the overall chemical equation to be balanced, the number of electrons lost by the reductant must equal the number gained by the oxidant. We must therefore multiply the oxidation and the reduction equations by appropriate coefficients to give us the same number of electrons in both. In this example, we must multiply the oxidation equation by 2 to give

$$2Cr^{2+} \rightarrow 2Cr^{3+} + 2e^-$$

Note the Pattern

In a balanced redox reaction, the number of electrons lost by the reductant equals the number of electrons gained by the oxidant.

The number of electrons lost in the oxidation now equals the number of electrons gained in the reduction:

$$2Cr^{2+} \rightarrow 2Cr^{3+} + 2e^-$$
$$Mn^{4+} + 2e^- \rightarrow Mn^{2+}$$

We then add the equations for the oxidation and the reduction and cancel the electrons on both sides of the equation, using the actual chemical forms of the reactants and products:

$$2Cr^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + \cancel{2e^-}$$

$$\cancel{2e^-} + 2Cr^{2+}(aq) \rightarrow Mn^{2+}(aq)$$

$$2Cr^{2+}(aq) + 2Cr^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + Mn^{2+}(aq)$$

Although the electrons cancel and the metal atoms are balanced, the total charge on the left side of the equation (+4) does not equal the charge on the right side (+8). Because the reaction is carried out in the presence of aqueous acid, we can add H^+ as necessary to either side of the equation to balance the charge. By the same token, if the reaction were carried out in the presence of aqueous base, we could balance the charge by adding OH^- as necessary to either side of the equation to balance the charges. In this case, adding four H^+ ions to the left side of the equation gives

$$2Cr^{2+}(aq) + MnO_2(s) + 4H^+(aq) \rightarrow 2Cr^{3+}(aq) + Mn^{2+}(aq)$$

Although the charges are now balanced, we have two oxygen atoms on the left side of the equation and none on the right. We can balance the oxygen atoms without affecting the overall charge balance by adding H_2O as necessary to either side of the equation. Here, we need to add two H_2O molecules to the right side:

$$2Cr^{2+}(aq) + MnO_2(s) + 4H^+(aq) \rightarrow 2Cr^{3+}(aq) + Mn^{2+}(aq) + 2H_2O(l)$$

Although we did not explicitly balance the hydrogen atoms, we can see by inspection that the overall chemical equation is now balanced. All that remains is to check to make sure that we have not made a mistake. This procedure for balancing reactions is summarized in Table 12.7.1 and illustrated in Example 17.

Table 12.7.1 Procedure for Balancing Oxidation–Reduction Reactions by the Oxidation State Method

1. Write the unbalanced chemical equation for the reaction, showing the reactants and the products.
2. Assign oxidation states to all atoms in the reactants and the products (see Section 3.5) and determine which atoms change oxidation state.
3. Write separate equations for oxidation and reduction, showing (a) the atom(s) that is (are) oxidized and reduced and (b) the number of electrons accepted or donated by each.
4. Multiply the oxidation and reduction equations by appropriate coefficients so that both contain the same number of electrons.
5. Write the oxidation and reduction equations showing the actual chemical forms of the reactants and the products, adjusting the coefficients as necessary to give the numbers of atoms in step 4.
6. Add the two equations and cancel the electrons.
7. Balance the charge by adding H^+ or OH^- ions as necessary for reactions in acidic or basic solution, respectively.
8. Balance the oxygen atoms by adding H_2O molecules to one side of the equation.
9. Check to make sure that the equation is balanced in both atoms and total charges.

Example 12.7.1

Arsenic acid (H_3AsO_4) is a highly poisonous substance that was once used as a pesticide. The reaction of elemental zinc with arsenic acid in acidic solution yields arsine (AsH_3, a highly toxic and unstable gas) and Zn^{2+}(aq). Balance the equation for this reaction using oxidation states:

$$H_3AsO_4(aq) + Zn(s) \rightarrow AsH_3(g) + Zn^{2+}(aq)$$

Given: reactants and products in acidic solution

Asked for: balanced chemical equation using oxidation states

Strategy:

Follow the procedure given in Table 12.7.1 for balancing a redox equation using oxidation states. When you are done, be certain to check that the equation is balanced.

Solution:

1. **Write a chemical equation showing the reactants and the products.** Because we are given this information, we can skip this step.
2. **Assign oxidation states using the procedure described in Section 11.6 and determine which atoms change oxidation state.** The oxidation state of arsenic in arsenic acid is +6, and the oxidation state of arsenic in arsine is −3. Conversely, the oxidation state of zinc in elemental zinc is 0, and the oxidation state of zinc in $Zn^{2+}(aq)$ is +2:

$$[\mathrm{H_3\overset{+5}{As}O_4(aq) + \overset{0}{Zn}(s) \rightarrow \underset{-3}{As}H_3(g) + \overset{+2}{Zn^{2+}}(aq)}]$$

3. **Write separate equations for oxidation and reduction.** The arsenic atom in H_3AsO_4 is reduced from the +5 to the −3 oxidation state, which requires the addition of eight electrons:

$$\textit{Reduction: } As^{5+} + 8e^- \rightarrow \underset{-3}{As^{3-}}$$

Each zinc atom in elemental zinc is oxidized from 0 to +2, which requires the loss of two electrons per zinc atom:

$$\textit{Oxidation: } Zn \rightarrow Zn^{2+} + 2e^-$$

4. **Multiply the oxidation and reduction equations by appropriate coefficients so that both contain the same number of electrons.** The reduction equation has eight electrons, and the oxidation equation has two electrons, so we need to multiply the oxidation equation by 4 to obtain

$$\textit{Reduction } (\times 1): As^{5+} + 8e^- \rightarrow As^{3-} \qquad \text{(Chapter 12.7.1)}$$
$$\textit{Oxidation } (\times 4): 4Zn^0 \rightarrow 4Zn^{2+} + 8e^- \qquad \text{(Chapter 12.7.2)}$$

5. **Write the oxidation and reduction equations showing the actual chemical forms of the reactants and the products, adjusting coefficients as necessary to give the numbers of atoms shown in step 4.** Inserting the actual chemical forms of arsenic and zinc and adjusting the coefficients gives

$$\textit{Reduction: } H_3AsO_4(aq) + 8e^- \rightarrow AsH_3(g) \qquad \text{(Chapter 12.7.3)}$$
$$\textit{Oxidation: } 4Zn(s) \rightarrow 4Zn^{2+}(aq) + 8e^- \qquad \text{(Chapter 12.7.4)}$$

6. *Add the two equations and cancel the electrons.* The sum of the two equations in step 5 is

$$H_3AsO_4(aq) + 4Zn(s) + \cancel{8e^-} \rightarrow AsH_3(g) + 4Zn^{2+}(aq) + \cancel{8e^-}$$

which then yields

$$H_3AsO_4(aq) + 4Zn(s) \rightarrow AsH_3(g) + 4Zn^{2+}(aq)$$

7. *Balance the charge by adding H^+ or OH^- ions as necessary for reactions in acidic or basic solution, respectively.* Because the reaction is carried out in acidic solution, we can add H^+ ions to whichever side of the equation requires them to balance the charge. The overall charge on the left side is zero, and the total charge on the right side is 4 × (+2) = +8. Adding eight H^+ ions to the left side gives a charge of +8 on both sides of the equation:

$$H_3AsO_4(aq) + 4Zn(s) + 8H^+(aq) \rightarrow AsH_3(g) + 4Zn^{2+}(aq)$$

8. *Balance the oxygen atoms by adding H_2O molecules to one side of the equation.* There are 4 O atoms on the left side of the equation. Adding 4 H_2O molecules to the right side balances the O atoms:

$$H_3AsO_4(aq) + 4Zn(s) + 8H^+(aq) \rightarrow AsH_3(g) + 4Zn^{2+}(aq) + 4H_2O(l)$$

Although we have not explicitly balanced H atoms, each side of the equation has 11 H atoms.

9. *Check to make sure that the equation is balanced in both atoms and total charges.* To guard against careless errors, it is important to check that both the total number of atoms of each element and the total charges are the same on both sides of the equation:

$$\textit{Atoms: } 1As + 4Zn + 4O + 11H = 1As + 4Zn + 4O + 11H \qquad \text{(Chapter 12.7.5)}$$
$$\textit{Total charge: } 8(+1) = 4(+2) = +8 \qquad \text{(Chapter 12.7.6)}$$

The balanced chemical equation for the reaction is therefore:

$$H_3AsO_4(aq) + 4Zn(s) + 8H^+(aq) \rightarrow AsH_3(g) + 4Zn^{2+}(aq) + 4H_2O(l)$$

Exercise

Copper commonly occurs as the sulfide mineral CuS. The first step in extracting copper from CuS is to dissolve the mineral in nitric acid, which oxidizes the sulfide to sulfate and reduces nitric acid to NO. Balance the equation for this reaction using oxidation states:

$$CuS(s) + H^+(aq) + NO_3^-(aq) \rightarrow Cu^{2+}(aq) + NO(g) + SO_4^{2-}(aq)$$

Answer: $3CuS(s) + 8H^+(aq) + 8NO_3^-(aq) \rightarrow 3Cu^{2+}(aq) + 8NO(g) + 3SO_4^{2-}(aq) + 4H_2O(l)$

Reactions in basic solutions are balanced in exactly the same manner. To make sure you understand the procedure, consider Example 18.

Example 12.7.2

The commercial solid drain cleaner, Drano, contains a mixture of sodium hydroxide and powdered aluminum. The sodium hydroxide dissolves in standing water to form a strongly basic solution, capable of slowly dissolving organic substances, such as hair, that may be clogging the drain. The aluminum dissolves in the strongly basic solution to produce bubbles of hydrogen gas that agitate the solution to help break up the clogs. The reaction is as follows:

$$Al(s) + H_2O(aq) \rightarrow [Al(OH)_4]^-(aq) + H_2(g)$$

Balance this equation using oxidation states.

Given: reactants and products in a basic solution

Asked for: balanced chemical equation

Strategy:

Follow the procedure given in Table 12.7.1 for balancing a redox reaction using oxidation states. When you are done, be certain to check that the equation is balanced.

Solution:

We will apply the same procedure used in Example 12.7.1 but in a more abbreviated form.

1. The equation for the reaction is given, so we can skip this step.
2. The oxidation state of aluminum changes from 0 in metallic Al to +3 in $[Al(OH)_4]^-$. The oxidation state of hydrogen changes from +1 in H_2O to 0 in H_2. Aluminum is oxidized, while hydrogen is reduced:

$$\overset{0}{Al}(s) + \overset{+1}{H}_2O(aq) \rightarrow [\overset{+3}{Al}(OH)_4]^-(aq) + \overset{0}{H}_2(g)$$

3. $Reduction: Al^0 \rightarrow Al^{3+} + 3e^-$ (Chapter 12.7.7)
   $Oxidation: H^+ + e^- \rightarrow H^0\ (in\ H_2)$ (Chapter 12.7.8)
4. Multiply the reduction equation by 3 to obtain an equation with the same number of electrons as the oxidation equation:

   $Reduction: 3H^+ + 3e^- \rightarrow 3H^0\ (in\ H_2)$ (Chapter 12.7.9)
   $Oxidation: Al^0 \rightarrow Al^{3+} + 3e^-$ (Chapter 12.7.10)
5. Insert the actual chemical forms of the reactants and products, adjusting the coefficients as necessary to obtain the correct numbers of atoms as in step 4. Because a molecule of H_2O contains two protons, in this case, $3H^+$ corresponds to $3/2H_2O$. Similarly, each molecule of hydrogen gas contains two H atoms, so 3H corresponds to $3/2H_2$.

   $Reduction: \frac{3}{2}H_2O + 3e^- \rightarrow \frac{3}{2}H_2$ (Chapter 12.7.11)
   $Oxidation: Al \rightarrow [Al(OH)_4]^- + 3e^-$ (Chapter 12.7.12)
6. Adding the equations and canceling the electrons gives

   $$Al + \frac{3}{2}H_2O + \cancel{3e^-} \rightarrow [Al(OH)_4]^- + \frac{3}{2}H_2 + \cancel{3e^-}$$
   $$Al + \frac{3}{2}H_2O \rightarrow [Al(OH)_4]^- + \frac{3}{2}H_2$$

   To remove the fractional coefficients, multiply both sides of the equation by 2:

   $$2Al + 3H_2O \rightarrow 2[Al(OH)_4]^- + 3H_2$$

7. The right side of the equation has a total charge of −2, whereas the left side has a total charge of 0. Because the reaction is carried out in basic solution, we can balance the charge by adding two OH^- ions to the left side:

$$2Al + 2OH^- + 3H_2O \rightarrow 2[Al(OH)_4]^- + 3H_2$$

8. The left side of the equation contains five O atoms, and the right side contains eight O atoms. We can balance the O atoms by adding three H_2O molecules to the left side:

$$2Al + 2OH^- + 6H_2O \rightarrow 2[Al(OH)_4]^- + 3H_2$$

9. Be sure the equation is balanced:

$$\textit{Atoms}: 2Al + 8O + 14H = 2Al + 8O + 14H \qquad \text{(Chapter 12.7.13)}$$
$$\textit{Total charge}: (2)(0) + (2)(-1) + (6)(0) = (2)(-1) + (3)(0) \qquad \text{(Chapter 12.7.14)}$$
$$-2 = -2$$

10. The balanced chemical equation is therefore

$$2Al(s) + 2OH^-(aq) + 6H_2O(l) \rightarrow 2[Al(OH)_4]^-(aq) + 3H_2(g)$$

Thus 3 mol of H_2 gas are produced for every 2 mol of Al.

Exercise

The permanganate ion reacts with nitrite ion in basic solution to produce manganese(IV) oxide and nitrate ion. Write a balanced chemical equation for the reaction.

Answer: $2MnO_4^-(aq) + 3NO_2^-(aq) + H_2O(l) \rightarrow 2MnO_2(s) + 3NO_3^-(aq) + 2OH^-(aq)$

As suggested in Example 12.7.1 and 12.7.2, a wide variety of redox reactions are possible in aqueous solutions. The identity of the products obtained from a given set of reactants often depends on both the ratio of oxidant to reductant and whether the reaction is carried out in acidic or basic solution, which is one reason it can be difficult to predict the outcome of a reaction. Because oxidation–reduction reactions in solution are so common and so important, however, chemists have developed two general guidelines for predicting whether a redox reaction will occur and the identity of the products:

1. Compounds of elements in high oxidation states (such as ClO_4^-, NO_3^-, MnO_4^-, $Cr_2O_7^{2-}$, and UF_6) tend to act as *oxidants* and *become reduced* in chemical reactions.
2. Compounds of elements in low oxidation states (such as CH_4, NH_3, H_2S, and HI) tend to act as *reductants* and *become oxidized* in chemical reactions.

Note the Pattern

Species in high oxidation states act as oxidants, whereas species in low oxidation states act as reductants.

When an aqueous solution of a compound that contains an element in a high oxidation state is mixed with an aqueous solution of a compound that contains an element in a low oxidation state, an oxidation–reduction reaction is likely to occur.

Redox Reactions of Solid Metals in Aqueous Solution

A widely encountered class of oxidation–reduction reactions is the reaction of aqueous solutions of acids or metal salts with solid metals. An example is the corrosion of metal objects, such as the rusting of an automobile (Figure 12.7.1). Rust is formed from a complex oxidation–reduction reaction involving dilute acid solutions that contain Cl^- ions (effectively, dilute HCl), iron metal, and oxygen. When an object rusts, iron metal reacts with HCl(aq) to produce iron(II) chloride and hydrogen gas:

$$Fe(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2(g)$$

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



Figure 12.7.1 Rust Formation *The corrosion process involves an oxidation–reduction reaction in which metallic iron is converted to $Fe(OH)_3$, a reddish-brown solid.*

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

$$metal + acid \rightarrow salt + hydrogen$$

Some of these reactions have important consequences. For example, it has been proposed that one factor that contributed to the fall of the Roman Empire was the widespread use of lead in cooking utensils and pipes that carried water. Rainwater, as we have seen, is slightly acidic, and foods such as fruits, wine, and vinegar contain organic acids. In the presence of these acids, lead dissolves:

$$Pb(s) + 2H^+(aq) \rightarrow Pb^{2+}(aq) + H_2(g)$$

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

Single-Displacement Reactions

Certain metals are oxidized by aqueous acid, whereas others are oxidized by aqueous solutions of various metal salts. Both types of reactions are called single-displacement reactions, in which the ion in solution is displaced through oxidation of the metal. Two examples of single-displacement reactions are the reduction of iron salts by zinc (Equation 12.7.13) and the reduction of silver salts by copper (Equation 12.7.14 and Figure 12.7.2):

$$Zn(s) + Fe^{2+}(aq) \rightarrow Zn^{2+}(aq) + Fe(s)$$

$$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

The reaction in Equation 12.7.13 is widely used to prevent (or at least postpone) the corrosion of iron or steel objects, such as nails and sheet metal. The process of “galvanizing” consists of applying a thin coating of zinc to the iron or steel, thus protecting it from oxidation as long as zinc remains on the object.



Figure 12.7.2 The Single-Displacement Reaction of Metallic Copper with a Solution of Silver Nitrate *When a copper coil is placed in a solution of silver nitrate, silver ions are reduced to metallic silver on the copper surface, and some of the copper metal*

dissolves. Note the formation of a metallic silver precipitate on the copper coil and a blue color in the surrounding solution due to the presence of aqueous Cu^{2+} ions. Figure used with permission of Wikipedia

The Activity Series

By observing what happens when samples of various metals are placed in contact with solutions of other metals, chemists have arranged the metals according to the relative ease or difficulty with which they can be oxidized in a single-displacement reaction. For example, we saw in Equation 12.7.13 and Equation 12.7.14 that metallic zinc reacts with iron salts, and metallic copper reacts with silver salts. Experimentally, it is found that zinc reacts with both copper salts and silver salts, producing Zn^{2+}. Zinc therefore has a greater tendency to be oxidized than does iron, copper, or silver. Although zinc will not react with magnesium salts to give magnesium metal, magnesium metal will react with zinc salts to give zinc metal:

$$Zn(s) + Mg^{2+}(aq) \not\rightarrow Zn^{2+}(aq) + Mg(s)$$

$$Mg(s) + Zn^{2+}(aq) \rightarrow Mg^{2+}(aq) + Zn(s)$$

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

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

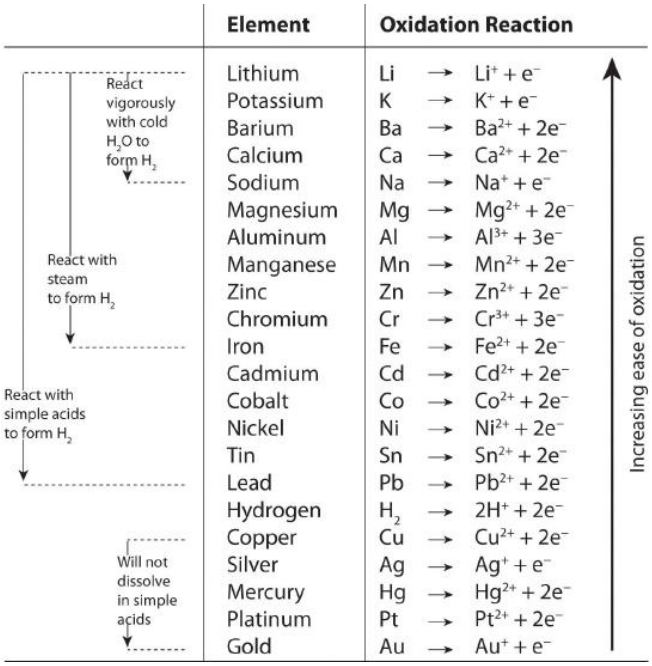


Figure 12.7.3 The Activity Series

When using the activity series to predict the outcome of a reaction, keep in mind that *any element will reduce compounds of the elements below it in the series*. Because magnesium is above zinc in Figure 12.7.3, magnesium metal will reduce zinc salts but not vice versa. Similarly, the precious metals are at the bottom of the activity series, so virtually any other metal will reduce precious metal salts to the pure precious metals. Hydrogen is included in the series, and the tendency of a metal to react with an acid is indicated by its position relative to hydrogen in the activity series. *Only those metals that lie above hydrogen in the activity series dissolve in acids to produce H_2.* Because the precious metals lie below hydrogen, they do not dissolve in dilute acid and therefore

do not corrode readily. Example 19 demonstrates how a familiarity with the activity series allows you to predict the products of many single-displacement reactions. We will return to the activity series when we discuss oxidation–reduction reactions in more detail in Chapter 17.

Example 12.7.3

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

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

Given: reactants

Asked for: overall reaction and net ionic equation

Strategy:

A Locate the reactants in the activity series in Figure 12.7.3 and from their relative positions, predict whether a reaction will occur. If a reaction does occur, identify which metal is oxidized and which is reduced.

B Write the net ionic equation for the redox reaction.

Solution:

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

   $$Al(s) + 3Ag^{+}(aq) \rightarrow Al^{3+}(aq) + 3Ag(s)$$

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

2. **A** Mercury lies below lead in the activity series, so no reaction will occur.

3. **A** Lead is above hydrogen in the activity series, so the lead terminals will be oxidized, and the acid will be reduced to form H_2. **B** From our discussion of solubilities, recall that Pb^{2+} and SO_4^{2-} form insoluble lead(II) sulfate. In this case, the sulfate ions are *not* spectator ions, and the reaction is as follows:

   $$Pb(s) + 2H^{+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + H_2(g)$$

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



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

Exercise

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

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

Answer:

1. *no reaction*
2. $3Zn(s) + 2Cr^{3+}(aq) \rightarrow 3Zn^{2+}(aq) + 2Cr(s)$
3. $2Al(s) + 6CH_3CO_2H(aq) \rightarrow 2Al^{3+}(aq) + 6CH_3CO_2^-(aq) + 3H_2(g)$

Summary

In oxidation–reduction reactions, electrons are transferred from one substance or atom to another. We can balance oxidation–reduction reactions in solution using the **oxidation state method** (Table 12.7.1), in which the overall reaction is separated into an oxidation equation and a reduction equation. **Single-displacement reactions** are reactions of metals with either acids or another metal salt that result in dissolution of the first metal and precipitation of a second (or evolution of hydrogen gas). The outcome of these reactions can be predicted using the **activity series** (Figure 12.7.3, which arranges metals and H_2 in decreasing order of their tendency to be oxidized. Any metal will reduce metal ions below it in the activity series. **Active metals** lie at the top of the activity series, whereas **inert metals** are at the bottom of the activity series.

Key Takeaway

- Oxidation–reduction reactions are balanced by separating the overall chemical equation into an oxidation equation and a reduction equation.

Conceptual Problems

1. Which elements in the periodic table tend to be good oxidants? Which tend to be good reductants?
2. If two compounds are mixed, one containing an element that is a poor oxidant and one with an element that is a poor reductant, do you expect a redox reaction to occur? Explain your answer. What do you predict if one is a strong oxidant and the other is a weak reductant? Why?
3. In each redox reaction, determine which species is oxidized and which is reduced:
    1. $Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$
    2. $Cu(s) + 4HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$
    3. $BrO_3^-(aq) + 2MnO_2(s) + H_2O(l) \rightarrow Br^-(aq) + 2MnO_4^-(aq) + 2H^+(aq)$
4. Single-displacement reactions are a subset of redox reactions. In this subset, what is oxidized and what is reduced? Give an example of a redox reaction that is *not* a single-displacement reaction.
5. Of the following elements, which would you expect to have the greatest tendency to be oxidized: Zn, Li, or S? Explain your reasoning.
6. Of these elements, which would you expect to be easiest to reduce: Se, Sr, or Ni? Explain your reasoning.
7. Which of these metals produces H_2 in acidic solution?
    1. Ag
    2. Cd
    3. Ca
    4. Cu
8. Using the activity series, predict what happens in each situation. If a reaction occurs, write the net ionic equation.
    1. $Mg(s) + Cu^{2+}(aq) \rightarrow$
    2. $Au(s) + Ag^+(aq) \rightarrow$
    3. $Cr(s) + Pb^{2+}(aq) \rightarrow$
    4. $K(s) + H_2O(l) \rightarrow$

5. $Hg(l) + Pb^{2+}(aq) \rightarrow$

Numerical Problems

1. Balance each redox reaction under the conditions indicated.
    1. $CuS(s) + NO_3^-(aq) \rightarrow Cu^{2+}(aq) + SO_4^{2-}(aq) + NO(g)$; acidic solution
    2. $Ag(s) + HS^-(aq) + CrO_4^{2-}(aq) \rightarrow Ag_2S(s) + Cr(OH)_3(s)$; basic solution
    3. $Zn(s) + H_2O(l) \rightarrow Zn^{2+}(aq) + H_2(g)$; acidic solution
    4. $O_2(g) + Sb(s) \rightarrow H_2O_2(aq) + SbO_2^-(aq)$; basic solution
    5. $UO_2^{2+}(aq) + Te(s) \rightarrow U^{4+}(aq) + TeO_4^{2-}(aq)$; acidic solution
2. Balance each redox reaction under the conditions indicated.
    1. $MnO_4^-(aq) + S_2O_3^{2-}(aq) \rightarrow Mn^{2+}(aq) + SO_4^{2-}(aq)$; acidic solution
    2. $Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) \rightarrow Fe^{3+}(aq) + Cr^{3+}(aq)$; acidic solution
    3. $Fe(s) + CrO_4^{2-}(aq) \rightarrow Fe_2O_3(s) + Cr_2O_3(s)$; basic solution
    4. $Cl_2(aq) \rightarrow ClO_3^-(aq) + Cl^-(aq)$; acidic solution
    5. $CO_3^{2-}(aq) + N_2H_4(aq) \rightarrow CO(g) + N_2(g)$; basic solution
3. Using the activity series, predict what happens in each situation. If a reaction occurs, write the net ionic equation; then write the complete ionic equation for the reaction.
    1. Platinum wire is dipped in hydrochloric acid.
    2. Manganese metal is added to a solution of iron(II) chloride.
    3. Tin is heated with steam.
    4. Hydrogen gas is bubbled through a solution of lead(II) nitrate.
4. Using the activity series, predict what happens in each situation. If a reaction occurs, write the net ionic equation; then write the complete ionic equation for the reaction.
    1. A few drops of $NiBr_2$ are dropped onto a piece of iron.
    2. A strip of zinc is placed into a solution of HCl.
    3. Copper is dipped into a solution of $ZnCl_2$.
    4. A solution of silver nitrate is dropped onto an aluminum plate.
5. Dentists occasionally use metallic mixtures called *amalgams* for fillings. If an amalgam contains zinc, however, water can contaminate the amalgam as it is being manipulated, producing hydrogen gas under basic conditions. As the filling hardens, the gas can be released, causing pain and cracking the tooth. Write a balanced chemical equation for this reaction.
6. Copper metal readily dissolves in dilute aqueous nitric acid to form blue $Cu^{2+}(aq)$ and nitric oxide gas.
    1. What has been oxidized? What has been reduced?
    2. Balance the chemical equation.
7. Classify each reaction as an acid–base reaction, a precipitation reaction, or a redox reaction, or state if there is no reaction; then complete and balance the chemical equation:
    1. $Pt^{2+}(aq) + Ag(s) \rightarrow$
    2. $HCN(aq) + NaOH(aq) \rightarrow$
    3. $Fe(NO_3)_3(aq) + NaOH(aq) \rightarrow$
    4. $CH_4(g) + O_2(g) \rightarrow$
8. Classify each reaction as an acid–base reaction, a precipitation reaction, or a redox reaction, or state if there is no reaction; then complete and balance the chemical equation:
    1. $Zn(s) + HCl(aq) \rightarrow$
    2. $HNO_3(aq) + AlCl_3(aq) \rightarrow$
    3. $K_2CrO_4(aq) + Ba(NO_3)_2(aq) \rightarrow$
    4. $Zn(s) + Ni^{2+}(aq) \rightarrow Zn^{2+}(aq) + Ni(s)$

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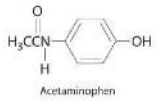
Chapter 12.8: End of Chapter Material

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Application Problems

Please be sure you are familiar with the topics discussed in Essential Skills 3 (Section 8.10) before proceeding to the Application Problems.Problems marked with a ♦ involve multiple concepts.

1. ♦ Acetaminophen (molar mass = 151 g/mol) is an analgesic used as a substitute for aspirin. If a child's dose contains 80.0 mg of acetaminophen/5.00 mL of an ethanol-water solution, what is the molar concentration? Acetaminophen is frequently packaged as an ethanol-water solution rather than as an aqueous one. Why?



Acetaminophen

2. ♦ Lead may have been the first metal ever recovered from its ore by humans. Its cation (Pb^{2+}) forms a precipitate with Cl^- according to the following equation:

$$Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)$$

When $PbCl_2$ is dissolved in hot water, its presence can be confirmed by its reaction with CrO_4^{2-}, with which it forms a yellow precipitate:

$$Pb^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow PbCrO_4(s)$$

The precipitate is used as a rust inhibitor and in pigments.

   a. What type of reaction does each equation represent?
   b. If 100 mL of a Pb^{2+} solution produce 1.65 g of lead chromate, what was the concentration of the lead solution?
   c. What volume of a potassium chromate solution containing 0.503 g of solute per 250.0 mL is needed for this reaction?
   d. If all the $PbCrO_4$ originated from $PbCl_2$, what volume of a 1.463 M NaCl solution was needed for the initial reaction?
   e. Why is there environmental concern over the use of $PbCrO_4$?

3. ♦ Reactions that affect buried marble artifacts present a problem for archaeological chemists. Groundwater dissolves atmospheric carbon dioxide to produce an aqueous solution of carbonic acid:

$$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$$

This weakly acidic carbonic acid solution dissolves marble, converting it to soluble calcium bicarbonate:

$$CaCO_3(s) + H_2CO_3(aq) \rightarrow Ca(HCO_3)_2(aq)$$

Evaporation of water causes carbon dioxide to be driven off, resulting in the precipitation of calcium carbonate:

$$Ca(HCO_3)_2(aq) \rightarrow CaCO_3(s) + H_2O(l) + CO_2(g)$$

The reprecipitated calcium carbonate forms a hard scale, or incrustation, on the surface of the object.

   a. If 8.5 g of calcium carbonate were obtained by evaporating 250 mL of a solution of calcium bicarbonate followed by drying, what was the molarity of the initial calcium bicarbonate solution, assuming complete reaction?
   b. If the overall reaction sequence was 75% efficient, how many grams of carbonic acid were initially dissolved in the 250 mL to produce the calcium bicarbonate?

4. How many Maalox tablets are needed to neutralize 5.00 mL of 0.100 M HCl stomach acid if each tablet contains 200 mg $Mg(OH)_2$ + 200 mg $Al(OH)_3$? Each Rolaids tablet contains 412 mg $CaCO_3$ + 80.0 mg $Mg(OH)_2$. How many Rolaids tablets are needed? Suggest another formula (and approximate composition) for an effective antacid tablet.

5. Citric acid ($C_6H_8O_7$, molar mass = 192.12 g/mol) is a triprotic acid extracted from citrus fruits and pineapple waste that provides tartness in beverages and jellies. How many grams of citric acid are contained in a 25.00 mL sample that requires 38.43 mL of 1.075 M NaOH for neutralization to occur? What is the formula of the calcium salt of this compound?

6. ♦ A method for determining the molarity of a strongly acidic solution has been developed based on the fact that a standard solution of potassium iodide and potassium iodate yields iodine when treated with acid:

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

Starch is used as the indicator in this titration because starch reacts with iodine in the presence of iodide to form an intense blue complex. The amount of iodine produced from this reaction can be determined by subsequent titration with thiosulfate:

$$2S_2O_3^{2+} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

The endpoint is reached when the solution becomes colorless.

   1. The thiosulfate solution was determined to be 1.023 M. If 37.63 mL of thiosulfate solution were needed to titrate a 25.00 mL sample of an acid, what was the H^+ ion concentration of the acid?
   2. If the 25.00 mL sample that was titrated had been produced by dilution of a 10.00 mL sample of acid, what was the molarity of the acid in the original solution?
   3. Why might this be an effective method for determining the molarity of a strong acid, such as H_2SO_4?

7. ♦ Sewage processing occurs in three stages. Primary treatment removes suspended solids, secondary treatment involves biological processes that decompose organic matter, and tertiary treatment removes specific pollutants that arise from secondary treatment (generally phosphates). Phosphate can be removed by treating the HPO_4^{2-} solution produced in the second stage with lime (CaO) to precipitate hydroxyapatite [$Ca_5(PO_4)_3OH$].

   a. Write a balanced chemical equation for the reaction that occurs in the tertiary treatment process.
   b. What has been neutralized in this process?
   c. Four pounds of hydroxyapatite precipitated from the water. What mass of lime was used in the reaction?
   d. Assuming a volume of water of 30 m^3, what was the hydrogen phosphate anion concentration in the water?

8. Calcium hydroxide and calcium carbonate are effective in neutralizing the effects of acid rain on lakes. Suggest other compounds that might be effective in treating lakes. Give a plausible reason to explain why $Ca(OH)_2$ and $CaCO_3$ are used.

9. ♦ Approximately 95% of the chlorine produced industrially comes from the electrolysis of sodium chloride solutions (brine):

$$NaCl(aq) + H_2O(l) \rightarrow Cl_2(g) + H_2(g) + NaOH(aq)$$

Chlorine is a respiratory irritant whose presence is easily detected by its penetrating odor and greenish-yellow color. One use for the chlorine produced is in the manufacture of hydrochloric acid.

   a. In the chemical equation shown, what has been oxidized and what has been reduced?
   b. Write the oxidation and reduction equations for this reaction.
   c. Balance the net ionic equation.
   d. Name another salt that might produce chlorine by electrolysis and give the expected products. Identify those products as gases, liquids, or solids.

10. ♦ The lead/acid battery used in automobiles consists of six cells that produce a 12 V electrical system. During discharge, lead(IV) oxide, lead, and aqueous sulfuric acid react to form lead(II) sulfate and water.

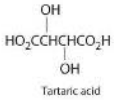
   a. What has been oxidized and what has been reduced?
   b. Write and balance the equation for the reaction.
   c. What is the net ionic equation?
   d. What is the complete ionic equation?
   e. What hazard is associated with handling automobile batteries?

11. The use of iron, which is abundant in Earth's crust, goes back to prehistoric times. In fact, it is believed that the Egyptians used iron implements approximately 5000 years ago. One method for quantifying the iron concentration in a sample involves three steps. The first step is to dissolve a portion of the sample in concentrated hydrochloric acid to produce ferric chloride; the second is to reduce Fe^{3+} to Fe^{2+} using zinc metal; and the third is to titrate Fe^{2+} with permanganate, producing Mn^{2+}(aq) and ferric iron in the form of Fe_2O_3.

   a. Write chemical equations for all three steps.

b. Write the net ionic equations for these three reactions.
c. If 27.64 mL of a 1.032 M solution of permanganate are required to titrate 25.00 mL of Fe^{2+} in the third step, how many grams of Fe were in the original sample?
d. Based on your answer to part c, if the original sample weighed 50.32 g, what was the percentage of iron?

12. Baking powder, which is a mixture of tartaric acid and sodium bicarbonate, is used in baking cakes and bread. Why does bread rise when you use baking powder? What type of reaction is involved?



Tartaric acid

13. An activity series exists for the halogens, which is based on the ease of *reducing* the diatomic halogen molecule (X_2) to X^-. Experimentally, it is found that fluorine is the easiest halogen to reduce (i.e., F_2 is the best oxidant), and iodine is the hardest halogen to reduce (i.e., I_2 is the worst oxidant). Consequently, the addition of any diatomic halogen, Y_2, to solutions containing a halide ion (X^-) that lies below Y in the periodic table will result in the reduction of Y_2 to Y^- and the oxidation of X^-. Describe what you would expect to occur when

a. chlorine is added to an aqueous solution of bromide.
b. iodine crystals are added to a solution of potassium bromide.

Bromide is present in naturally occurring salt solutions called *brines*. Based on your answers, propose an effective method to remove bromide from brine.

14. ♦ Marble is composed of mostly calcium carbonate. Assuming that acid rain contains 4.0×10^{-5} M H_2SO_4, approximately what volume of rain is necessary to dissolve a 250 lb marble statue?

15. ♦ One of the "first-aid" measures used to neutralize lakes whose pH has dropped to critical levels is to spray them with slaked lime ($Ca(OH)_2$) or limestone ($CaCO_3$). (A slower but effective alternative is to add limestone boulders.) How much slaked lime would be needed to neutralize the acid in a lake that contains 4.0×10^{-5} M H_2SO_4 and has a volume of 1.2 cubic miles (5.0×10^{12} L)?

16. The reaction of ethanol with dichromate ion in acidic solution yields acetic acid and $Cr^{3+}(aq)$:

$$Cr_2O_7^{2-}(aq) + CH_3CH_2OH(aq) \rightarrow Cr^{3+}(aq) + CH_3CO_2H(aq)$$

Balance the equation for this reaction using oxidation states. (*Hint*: the oxidation state of carbon in the CH_3 group remains unchanged, as do the oxidation states of hydrogen and oxygen.)

Answers

1. 0.106 M acetaminophen; acetaminophen is an organic compound that is much more soluble in ethanol than water, so using an ethanol/water mixture as the solvent allows a higher concentration of the drug to be used.
2.
3. 1. 0.34 M $Ca(HCO_3)_2$
   2. 7.0 g H_2CO_3
4.
5. 2.646 g citric acid, $Ca_3(C_6H_5O_7)_2$
6.
7. 1. $5CaO + 3HPO_4^{2-} + 2H_2O \rightarrow Ca_5(PO_4)_3OH + 6OH^-$
   2. This is an acid–base reaction, in which the acid is the HPO_4^{2-} ion and the base is CaO. Transferring a proton from the acid to the base produces the PO_4^{3-} ion and the hydroxide ion.
   3. 2.2 lbs (1 kg) of lime
   4. 3.6×10^{-4} M HPO_4^{2-}
8.

9. 1. Chloride is oxidized, and protons are reduced.
   2. Oxidation: $2Cl^- \rightarrow Cl_2 + 2e^-$ Reduction: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
   3. $2Cl^- + 2H_2O \rightarrow Cl_2 + H_2 + 2OH^-$
10.
11.
12.
13.
14.
15.
16.

Contributors

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Modified by Joshua Halpern (Howard University)

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SECTION OVERVIEW

Unit 5: Kinetics and Equilibria

Chapter 13: Chemical Kinetics

- Chapter 13.1: Factors that Affect Reaction Rates
- Chapter 13.2: Reaction Rates and Rate Laws
- Chapter 13.3: Methods of Determining Reaction Order
- Chapter 13.4: Using Graphs to Determine Rate Laws, Rate Constants and Reaction Orders
- Chapter 13.5: Half Lives and Radioactive Decay Kinetics
- Chapter 13.6: Reaction Rates - A Microscopic View
- Chapter 13.7: The Collision Model of Chemical Kinetics
- Chapter 13.8: Catalysis
- Chapter 13.9: End of Chapter Materials

Chapter 14: Chemical Equilibrium

- Chapter 14.1: The Concept of Chemical Equilibrium
- Chapter 14.2: The Equilibrium Constant
- Chapter 14.3: Solving Equilibrium Problems
- Chapter 14.4: Non-equilibrium Conditions
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CHAPTER OVERVIEW

Chapter 13: Chemical Kinetics

- Chapter 13.1: Factors that Affect Reaction Rates
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Chapter 13.1: Factors that Affect Reaction Rates

Learning Objective

- To understand the factors that affect reaction rates.

Although a balanced chemical equation for a reaction describes the quantitative relationships between the amounts of reactants present and the amounts of products that can be formed, it gives us no information about whether or how fast a given reaction will occur. This information is obtained by studying the chemical kinetics of a reaction, which depend on various factors: reactant concentrations, temperature, physical states and surface areas of reactants, and solvent and catalyst properties if either are present. By studying the kinetics of a reaction, chemists gain insights into how to control reaction conditions to achieve a desired outcome.

Concentration Effects

Two substances cannot possibly react with each other unless their constituent particles (molecules, atoms, or ions) come into contact. If there is no contact, the reaction rate will be zero. Conversely, the more reactant particles that collide per unit time, the more often a reaction between them can occur. Consequently, the reaction rate usually increases as the concentration of the reactants increases. One example of this effect is the reaction of sucrose (table sugar) with sulfuric acid, which is shown in Figure 13.1.1.

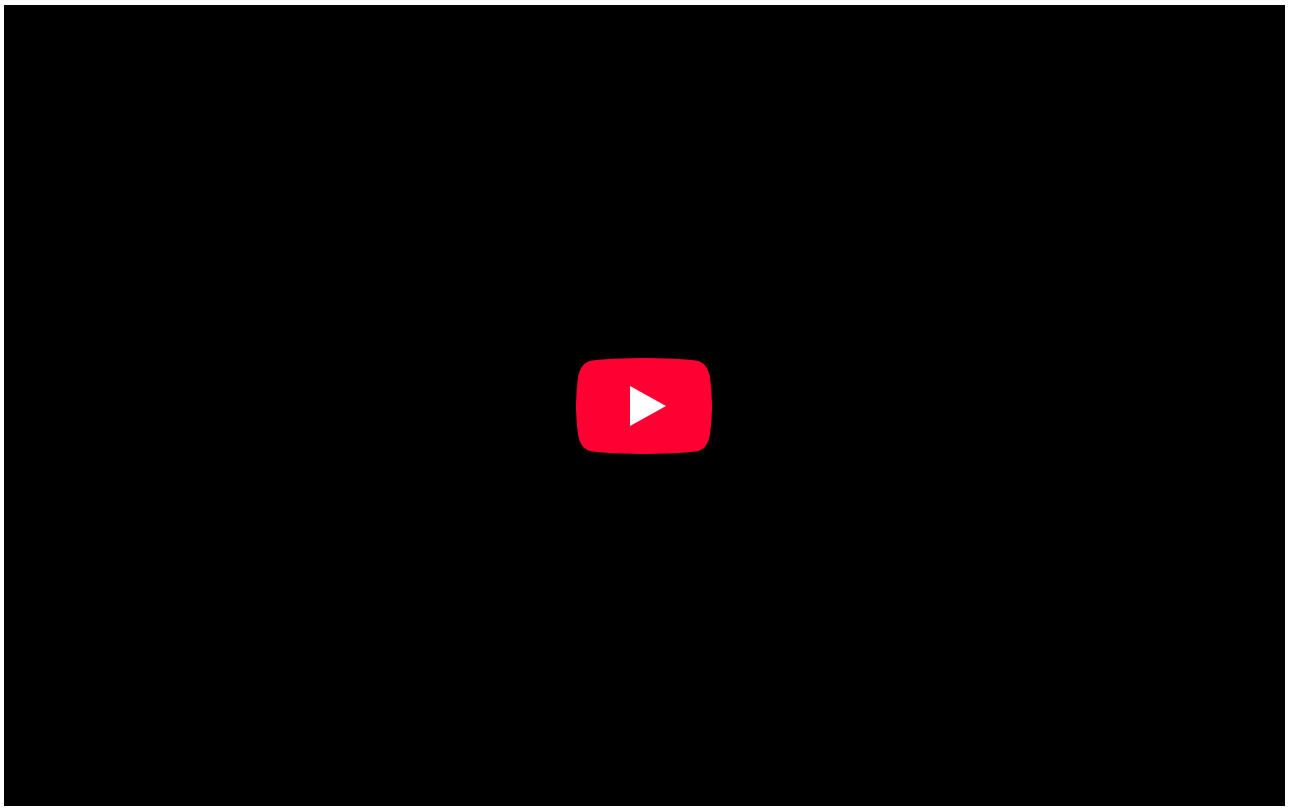




Figure 13.1.1 The Effect of Concentration on Reaction Rates *Mixing sucrose with dilute sulfuric acid in a beaker (a, right) produces a simple solution. Mixing the same amount of sucrose with concentrated sulfuric acid results in a dramatic reaction that eventually produces a column of black porous graphite (c) and an intense smell of burning sugar. Video from UC Berkeley*

Temperature Effects

You learned in Chapter 6 that increasing the temperature of a system increases the average kinetic energy of its constituent particles. As the average kinetic energy increases, the particles move faster, so they collide more frequently per unit time and possess greater energy when they collide. Both of these factors increase the reaction rate. Hence the reaction rate of virtually all reactions increases with increasing temperature. Conversely, the reaction rate of virtually all reactions decreases with decreasing temperature. For example, refrigeration retards the rate of growth of bacteria in foods by decreasing the reaction rates of biochemical reactions that enable bacteria to reproduce. Figure 13.1.2 shows how temperature affects the light emitted by two chemiluminescent light sticks.



Figure 13.1.2 The Effect of Temperature on Reaction Rates *At **high** temperature, the reaction that produces light in a chemiluminescent light stick occurs more rapidly, producing more photons of light per unit time. Consequently, the light glows brighter in hot water (left) than in ice water (right). Video from kriegsman*

In systems where more than one reaction is possible, the same reactants can produce different products under different reaction conditions. For example, in the presence of dilute sulfuric acid and at temperatures around 100°C, ethanol is converted to diethyl ether:

$$2CH_3CH_2OH \xrightarrow{H_2SO_4} CH_3CH_2OCH_2CH_3 + H_2O$$

At 180°C, however, a completely different reaction occurs, which produces ethylene as the major product:

$$CH_3CH_2OH \xrightarrow{H_2SO_4} CH_2CH_2 + H_2O$$

Phase and Surface Area Effects

When two reactants are in the same fluid phase, their particles collide more frequently than when one or both reactants are solids (or when they are in different fluids that do not mix). If the reactants are uniformly dispersed in a single homogeneous solution, then the number of collisions per unit time depends on concentration and temperature, as we have just seen. If the reaction is heterogeneous, however, the reactants are in two different phases, and collisions between the reactants can occur only at interfaces between phases. The number of collisions between reactants per unit time is substantially reduced relative to the homogeneous case, and, hence, so is the reaction rate. The reaction rate of a heterogeneous reaction depends on the surface area of the more condensed phase.

Automobile engines use surface area effects to increase reaction rates. Gasoline is injected into each cylinder, where it combusts on ignition by a spark from the spark plug. The gasoline is injected in the form of microscopic droplets because in that form it has a much larger surface area and can burn much more rapidly than if it were fed into the cylinder as a stream. Similarly, a pile of finely divided flour burns slowly (or not at all), but spraying finely divided flour into a flame produces a vigorous reaction (Figure 13.1.3). Similar phenomena are partially responsible for dust explosions that occasionally destroy grain elevators or coal mines.





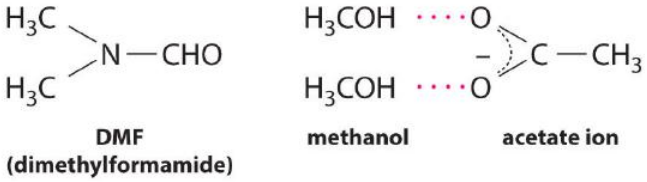
Figure 13.1.3 Burning flour dust *A pile of flour is only scorched by a flame, but when the same flour is sprayed into the flame, it burns rapidly. Peter Wolthers has a series of videos demonstrating combustion reactions that you can watch*

Solvent Effects

The nature of the solvent can also affect the reaction rates of solute particles. For example, a sodium acetate solution reacts with methyl iodide in an exchange reaction to give methyl acetate and sodium iodide.

$$CH_3CO_2Na\,(soln) + CH_3I\,(l) \rightarrow CH_3CO_2CH_3\,(soln) + NaI\,(soln)$$

This reaction occurs 10 million times more rapidly in the organic solvent dimethylformamide [DMF; $(CH_3)_2NCHO$] than it does in methanol (CH_3OH). Although both are organic solvents with similar dielectric constants (36.7 for DMF versus 32.6 for methanol), methanol is able to hydrogen bond with acetate ions, whereas DMF cannot. Hydrogen bonding reduces the reactivity of the oxygen atoms in the acetate ion.



Solvent viscosity is also important in determining reaction rates. In highly viscous solvents, dissolved particles diffuse much more slowly than in less viscous solvents and can collide less frequently per unit time. Thus the reaction rates of most reactions decrease rapidly with increasing solvent viscosity.

Catalyst Effects

You learned in Chapter 11.6 that a catalyst is a substance that participates in a chemical reaction and increases the reaction rate without undergoing a net chemical change itself. Consider, for example, the decomposition of hydrogen peroxide in the presence and absence of different catalysts (Figure 13.1.4). Because most catalysts are highly selective, they often determine the product of a reaction by accelerating only one of several possible reactions that could occur.





Figure 13.1.4 The Effect of Catalysts on Reaction Rates *A solution of hydrogen peroxide (H_2O_2) decomposes in water so slowly that the change is not noticeable. You can store a bottle in your medicine cabinet for a long time without it decomposing. Iodide ion acts as a catalyst for the decomposition of H_2O_2, producing oxygen gas. The solution turns brown because of the reaction of H_2O_2 with I^-, here in a solution of NaI, which generates small amounts of I_3^-.*

The enzyme catalase which is found in liver and potatoes is about 3 *billion* times more effective than iodide as a catalyst on a per molecule basis. Even in the presence of very small amounts of enzyme, the decomposition is vigorous . Most of the bulk chemicals produced in industry are formed with catalyzed reactions. Recent estimates indicate that about 30% of the gross national product of the United States and other industrialized nations relies either directly or indirectly on the use of catalysts.

Summary

Factors that influence the reaction rates of chemical reactions include the concentration of reactants, temperature, the physical state of reactants and their dispersion, the solvent, and the presence of a catalyst.

Key Takeaway

- The reaction rate depends on the concentrations of the reactants, the temperature of the reaction, the phase and surface area of the reactants, the solvent, and the presence or the absence of a catalyst.

Conceptual Problems

1. What information can you obtain by studying the chemical kinetics of a reaction? Does a balanced chemical equation provide the same information? Why or why not?
2. If you were tasked with determining whether to proceed with a particular reaction in an industrial facility, why would studying the chemical kinetics of the reaction be important to you?
3. What is the relationship between each of the following factors and the reaction rate: reactant concentration, temperature of the reaction, physical properties of the reactants, physical and chemical properties of the solvent, and the presence of a catalyst?
4. A slurry is a mixture of a finely divided solid with a liquid in which it is only sparingly soluble. As you prepare a reaction, you notice that one of your reactants forms a slurry with the solvent, rather than a solution. What effect will this have on the reaction rate? What steps can you take to try to solve the problem?
5. Why does the reaction rate of virtually all reactions increase with an increase in temperature? If you were to make a glass of sweetened iced tea the old-fashioned way, by adding sugar and ice cubes to a glass of hot tea, which would you add first?
6. In a typical laboratory setting, a reaction is carried out in a ventilated hood with air circulation provided by outside air. A student noticed that a reaction that gave a high yield of a product in the winter gave a low yield of that same product in the summer, even though his technique did not change and the reagents and concentrations used were identical. What is a plausible explanation for the different yields?
7. A very active area of chemical research involves the development of solubilized catalysts that are not made inactive during the reaction process. Such catalysts are expected to increase reaction rates significantly relative to the same reaction run in the

presence of a heterogeneous catalyst. What is the reason for anticipating that the relative rate will increase?

8. Water has a dielectric constant more than two times greater than that of methanol (80.1 for H_2O and 33.0 for CH_3OH). Which would be your solvent of choice for a substitution reaction between an ionic compound and a polar reagent, both of which are soluble in either methanol or water? Why?

Answers

1. Kinetics gives information on the reaction rate and reaction mechanism; the balanced chemical equation gives only the stoichiometry of the reaction.
2.
3. Reaction rates generally increase with increasing reactant concentration, increasing temperature, and the addition of a catalyst. Physical properties such as high solubility also increase reaction rates. Solvent polarity can either increase or decrease the reaction rate of a reaction, but increasing solvent viscosity generally decreases reaction rates.
4.
5. Increasing the temperature increases the average kinetic energy of molecules and ions, causing them to collide more frequently and with greater energy, which increases the reaction rate. First dissolve sugar in the hot tea, and then add the ice.
6.
7.
8.

Contributors

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Video in 13.1.1 from YouTube by UC Berkeley on YouTube

Video in Figure 13.1.2 from Kriegsman on YouTube

Video in Figure 13.1.3 from Peter Wolthers at the Royal Society on YouTube

Video in Figure 13.1.4 from IST Science on YouTube

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Chapter 13.2: Reaction Rates and Rate Laws

Learning Objective

- To determine the reaction rate.
- To understand the meaning of a rate law.

The factors discussed in Section 13.1 affect the reaction rate of a chemical reaction, which may determine whether a desired product is formed. In this section, we will show you how to quantitatively determine the reaction rate.

Reaction Rates

Reaction rates are usually expressed as the concentration of reactant consumed or the concentration of product formed per unit time. The units are thus moles per liter per unit time, written as M/s, M/min, or M/h. To measure reaction rates, chemists initiate the reaction, measure the concentration of the reactant or product at different times as the reaction progresses, perhaps plot the concentration as a function of time on a graph, and then calculate the *change* in the concentration per unit time.

The progress of a simple reaction (A → B) is shown in Figure 13.2.1 where the beakers are snapshots of the composition of the solution at 10 s intervals. The number of molecules of reactant (A) and product (B) are plotted as a function of time in the graph. Each point in the graph corresponds to one beaker in Figure 13.2.1. The reaction rate is the change in the concentration of either the reactant or the product over a period of time. The concentration of A decreases with time, while the concentration of B increases with time.

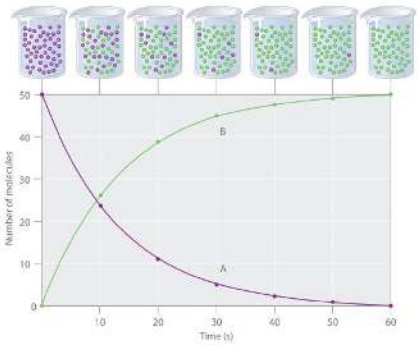


Figure 13.2.1 The Progress of a Simple Reaction (A → B) The mixture initially contains only A molecules (purple). With increasing time, the number of A molecules decreases and more B molecules (green) are formed (top). The graph shows the change in the number of A and B molecules in the reaction as a function of time over a 1 min period (bottom).

$$rate = \frac{d[B]}{dt} = -\frac{d[A]}{dt}$$

Square brackets indicate molar concentrations. We use derivatives to indicate infinitesmal changes with respect to time. On occassion we will use the capital Greek delta (Δ) for a large change over considerable time. Because chemists follow the convention of expressing all reaction rates as positive numbers, however, a negative sign is inserted in front of d[A]/d*t* to convert that expression to a positive number. The reaction rate we would calculate for the reaction A → B using Equation 13.2.1 would be different for each interval. (This is not true for every reaction, as you will see later.) A much greater change occurs in [A] and [B] during the first 10 s interval, for example, than during the last, which means that the reaction rate is fastest at first. This is consistent with the concentration effects described in Section 13.1 because the concentration of A is greatest at the beginning of the reaction.

Note the Pattern

Reaction rates generally decrease with time as reactant concentrations decrease.

Determining the Reaction Rate of Hydrolysis of Aspirin

We can use Equation 13.2.1 to determine the reaction rate of hydrolysis of aspirin, probably the most commonly used drug in the world. (More than 25,000,000 kg are produced annually worldwide.) Aspirin (acetylsalicylic acid) reacts with water (such as water

in body fluids) to give salicylic acid and acetic acid.

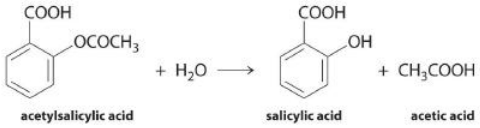


Figure 13.2.2 Because salicylic acid is the actual substance that relieves pain and reduces fever and inflammation, a great deal of research has focused on understanding this reaction and the factors that affect its rate. Data for the hydrolysis of a sample of aspirin are in Table 13.2.1 and are shown in the graph in Figure 13.2.3. These data were obtained by removing samples of the reaction mixture at the indicated times and analyzing them for the concentrations of the reactant (aspirin) and one of the products (salicylic acid).

Table 13.2.1 Data for Aspirin Hydrolysis in Aqueous Solution at pH 7.0 and 37°C*

Time (h)	[Aspirin] (M)	[Salicylic Acid] (M)
0	5.55×10^{-3}	0
2.0	5.51×10^{-3}	0.040×10^{-3}
5.0	5.45×10^{-3}	0.10×10^{-3}
10	5.35×10^{-3}	0.20×10^{-3}
20	5.15×10^{-3}	0.40×10^{-3}
30	4.96×10^{-3}	0.59×10^{-3}
40	4.78×10^{-3}	0.77×10^{-3}
50	4.61×10^{-3}	0.94×10^{-3}
100	3.83×10^{-3}	1.72×10^{-3}
200	2.64×10^{-3}	2.91×10^{-3}
300	1.82×10^{-3}	3.73×10^{-3}

*The reaction at pH 7.0 is very slow. It is *much* faster under acidic conditions, such as those found in the stomach.

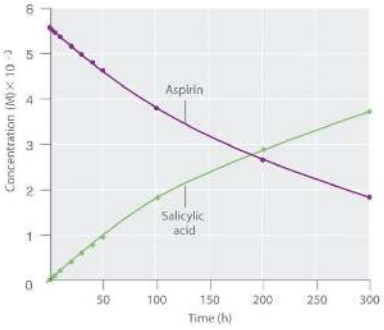


Figure 13.2.3 The Hydrolysis of Aspirin *This graph shows the concentrations of aspirin and salicylic acid as a function of time, based on the hydrolysis data in Table 13.2.1. The time dependence of the concentration of the other product, acetate, is not shown, but based on the stoichiometry of the reaction, it is identical to the data for salicylic acid. Since the difference between points is hours we use Δ[A]/Δt.*

We can calculate the average reaction rateThe reaction rate calculated for a given time interval from the concentrations of either the reactant or one of the products at the beginning of the interval time

$$rate_{(t=0–2.0\ h)} = \frac{[salicylic\ acid]_2 - [salicylic\ acid]_0}{2.0\ h - 0.0\ h}$$
$$= \frac{0.040 \times 10^{-3}\ M - 0.000\ M}{2.0\ h - 0.0\ h} = 2 \times 10^{-5}\ M/h$$

We can also calculate the reaction rate from the concentrations of aspirin at the beginning and the end of the same interval, remembering to insert a negative sign, because its concentration decreases:

$$rate_{(t=0–2.0\ h)} = \frac{[aspirin]_2 - [aspirin]_0}{2.0\ h - 0.0\ h}$$
$$rate_{(t=0–2.0\ h)} = \frac{5.51 \times 10^{-3}\ M - 5.55 \times 10^{-3}\ M}{2.0\ h - 0.0\ h} = 2.0 \times 10^{-5}\ M/h\text{\;h\} \)}$$

If we now calculate the reaction rate during the last interval given in Table 13.2.1 (the interval between 200 h and 300 h after the start of the reaction), we find that the reaction rate is significantly slower than it was during the first interval (t = 0–2.0 h):

$$rate_{(t=200–300\ h)} = \frac{[salicylic\ acid]_{300} - [salicylic\ acid]_{200}}{300\ h - 200\ h}$$
$$= \frac{3.73 \times 10^{-3}\ M - 2.91 \times 10^{-3}\ M}{100;h} = 8.2 \times 10^{-6}\ M/h$$

(You should verify from the data in Table 13.2.1 that you get the same rate using the concentrations of aspirin measured at 200 h and 300 h.)

Calculating the Reaction Rate of Fermentation of Sucrose

In the preceding example, the stoichiometric coefficients in the balanced chemical equation are the same for all reactants and products; that is, the reactants and products all have the coefficient 1. Let us look at a reaction in which the coefficients are *not* all the same: the fermentation of sucrose to ethanol and carbon dioxide.

$$\underset{sucrose}{C_{12}H_{22}O_{11}\,(aq)} + H_2O\,(l) \rightarrow 4C_2H_5OH\,(aq) + \$CO_2\,(g)$$

The coefficients show us that the reaction produces four molecules of ethanol and four molecules of carbon dioxide for every one molecule of sucrose consumed. As before, we can find the reaction rate by looking at the change in the concentration of any reactant or product. In this particular case, however, a chemist would probably use the concentration of either sucrose or ethanol because gases are usually measured as volumes and, as you learned in Chapter 6, the volume of CO_2 gas formed will depend on the total volume of the solution being studied and the solubility of the gas in the solution, not just the concentration of sucrose. The coefficients in the balanced chemical equation tell us that the reaction rate at which ethanol is formed is always four times faster than the reaction rate at which sucrose is consumed:

$$rate = \frac{d\,[C_2H_5OH]}{dt} = -\frac{4d\,[sucrose])}{dt}$$

The concentration of the reactant—in this case sucrose—*decreases* with increasing time, so the value of Δ[sucrose] is negative. Consequently, a minus sign is inserted in front of Δ[sucrose] in Equation 13.2.3 so that the rate of change of the sucrose concentration is expressed as a positive value. Conversely, the ethanol concentration *increases* with increasing time, so its rate of change is automatically expressed as a positive value.

Often the reaction rate is expressed in terms of the reactant or product that has the smallest coefficient in the balanced chemical equation. The smallest coefficient in the sucrose fermentation reaction (Equation 13.2.2) corresponds to sucrose, so the reaction rate is generally defined as follows:

$$rate = -\frac{d\,[sucrose]}{dt} = \frac{1}{4}\left(\frac{d\,[C_2H_5OH]}{dt}\right)$$

Example 13.2.1

Consider the thermal decomposition of gaseous N_2O_5 to NO_2 and O_2 via the following equation:

$$2N_2O_5\,(g) \overset{\Delta}{\rightarrow} 4NO_2\,(g) + O_2\,(g)$$

Write expressions for the reaction rate in terms of the rates of change in the concentrations of the reactant and each product with time.

Given: balanced chemical equation

Asked for: reaction rate expressions

Strategy:

A Choose the species in the equation that has the smallest coefficient. Then write an expression for the rate of change of that species with time.

B For the remaining species in the equation, use molar ratios to obtain equivalent expressions for the reaction rate.

Solution:

A Because O_2 has the smallest coefficient in the balanced chemical equation for the reaction, we define the reaction rate as the rate of change in the concentration of O_2 and write that expression.

B We know from the balanced chemical equation that 2 mol of N_2O_5 must decompose for each 1 mol of O_2 produced and that 4 mol of NO_2 are produced for every 1 mol of O_2 produced. The molar ratios of O_2 to N_2O_5 and to NO_2 are thus 1:2 and 1:4, respectively. This means that we divide the rate of change of $[N_2O_5]$ and $[NO_2]$ by its stoichiometric coefficient to obtain equivalent expressions for the reaction rate. For example, because NO_2 is produced at four times the rate of O_2, we must divide the rate of production of NO_2 by 4. The reaction rate expressions are as follows:

$$rate = \frac{d[O_2]}{dt} = \frac{d[NO_2]}{4dt} = -\frac{d[N_2O_5]}{2dt}$$

Exercise

The key step in the industrial production of sulfuric acid is the reaction of SO_2 with O_2 to produce SO_3.

$$2SO_2\,(g) + O_2\,(g) \rightarrow 2SO_3\,(g)$$

Write expressions for the reaction rate in terms of the rate of change of the concentration of each species.

Answer:

$$rate = -\frac{d[O_2]}{dt} = -\frac{d[SO_2]}{dt} = \frac{d[SO_3]}{2dt}$$

Example 13.2.2

Using the reaction shown in Example 1, calculate the reaction rate from the following data taken at 56°C:

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$			
Time (s)	$[N_2O_5]$ (M)	$[NO_2]$ (M)	$[O_2]$ (M)
240	0.0388	0.0314	0.00792
600	0.0197	0.0699	0.0175

Given: balanced chemical equation and concentrations at specific times

Asked for: reaction rate

Strategy:

A Using the equations in Example 1, subtract the initial concentration of a species from its final concentration and substitute that value into the equation for that species.

B Substitute the value for the time interval into the equation. Make sure your units are consistent.

Solution:

A We are asked to calculate the reaction rate in the interval between t_1 = 240 s and t_2 = 600 s. From Example 1, we see that we can evaluate the reaction rate using any of three expressions:

$$rate = \frac{\Delta [O_2]}{\Delta t} = \frac{\Delta [NO_2]}{4\Delta t} = -\frac{\Delta [N_2O_5]}{2\Delta t}$$

Subtracting the initial concentration from the final concentration of N_2O_5 and inserting the corresponding time interval into the rate expression for N_2O_5,

$$rate = -\frac{\Delta [N_2O_5]}{2\Delta t} = -\frac{[N_2O_5]_{600} - [N_2O_5]_{240}}{2\,(600\ s - 240\ s)}$$

B Substituting actual values into the expression,

$$rate = -\frac{0.197\ M - 0.0388\ M}{2\,(360\ s)}$$

Similarly, we can use NO_2 to calculate the reaction rate:

$$rate = -\frac{\Delta [NO_2]}{4\Delta t} = -\frac{[NO_2]_{600} - [NO_2]_{240}}{4\,(600\ s - 240\ s)} = \frac{0.0699\ M - 0.0314\ M}{4\,(360)} = 2.67 \times 10^{-5}\ M/s$$

If we allow for experimental error, this is the same rate we obtained using the data for N_2O_5, as it should be because the reaction rate should be the same no matter which concentration is used. We can also use the data for O_2:

$$rate = -\frac{\Delta [O_2]}{\Delta t} = -\frac{[O_2]_{600} - [O_2]_{240}}{(600\ s - 240\ s)} = \frac{0.0175\ M - 0.00792\ M}{360\ s} = 2.66 \times 10^{-5}\ M/s$$

Again, this is the same value we obtained from the N_2O_5 and NO_2 data. Thus the reaction rate does not depend on which reactant or product is used to measure it.

Exercise

Using the data in the following table, calculate the reaction rate of SO_2(g) with O_2(g) to give SO_3(g).

$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$			
Time (s)	$[SO_2]$ (M)	$[O_2]$ (M)	$[SO_3]$ (M)
300	0.0270	0.0500	0.0072
720	0.0194	0.0462	0.0148

Answer: 9.0×10^{-6} M/s

Instantaneous Rates of Reaction

So far, we have determined average reaction rates over particular intervals of time. We can also determine the instantaneous rateThe reaction rate of a chemical reaction at any given point in time. of a reaction, which is the reaction rate at any given point in time. As the period of time used to calculate an average rate of a reaction becomes shorter and shorter, the average rate approaches the instantaneous rate. If you have studied calculus, you may recognize that the instantaneous rate of a reaction at a given time corresponds to the slope of a line tangent to the concentration-versus-time curve at that point—that is, the derivative of concentration with respect to time.

Think of the distinction between the instantaneous and average rates of a reaction as being similar to the distinction between the actual speed of a car at any given time on a trip and the average speed of the car for the entire trip. Although you may travel for a long time at 65 mph on an interstate highway during a long trip, there may be times when you travel only 25 mph in construction zones or 0 mph if you stop for meals or gas. Thus your average speed on the trip may be only 50 mph, whereas your instantaneous speed on the interstate at a given moment may be 65 mph. Whether you are able to stop the car in time to avoid an accident depends on your instantaneous speed, not your average speed. There are important differences between the speed of a car during a trip and the speed of a chemical reaction, however. The speed of a car may vary unpredictably over the length of a trip, and the initial part of a trip is often one of the slowest. In a chemical reaction, the initial interval normally has the fastest rate (though this is not always the case), and the reaction rate generally changes smoothly over time.

In chemical kinetics, we generally focus on one particular instantaneous rate, which is the initial reaction rate, $t = 0$. Initial rates are determined by measuring the reaction rate at various times and then extrapolating a plot of rate versus time to $t = 0$.

Rate Laws

In Section 13.1, you learned that reaction rates generally decrease with time because reactant concentrations decrease as reactants are converted to products. You also learned that reaction rates generally increase when reactant concentrations are increased. We now examine the mathematical expressions called rate lawsMathematical expressions that describe the relationships between reactant rates and reactant concentrations in a chemical reaction., which describe the relationships between reactant rates and reactant concentrations. Rate laws are laws as defined in Chapter 1; they are mathematical descriptions of experimentally verifiable data.

Rate laws may be written from either of two different but related perspectives. A differential rate lawA rate law that expresses the reaction rate in terms of changes in the concentration of one or more reactants (Δ[R]) over a specific time interval (Δt) expresses the reaction rate in terms of *changes* in the concentration of one or more reactants (Δ[R]) over a specific time interval (Δ*t*). In contrast, an integrated rate lawA rate law that expresses the reaction rate in terms of the initial concentration $[R]_0$ and the measured concentration of one or more reactants ([R]) after a given amount of time (t) describes the reaction rate in terms of the *initial* concentration ($[R]_0$) and the *measured* concentration of one or more reactants ([R]) after a given amount of time (*t*); we will discuss integrated rate laws in Section 13.3. The integrated rate law can be found by using calculus to integrate the differential rate law. *Whether you use a differential rate law or integrated rate law, always make sure that the rate law gives the proper units for the reaction rate, usually moles per liter per second (M/s).*

Reaction Orders

For a reaction with the general equation

$$aA + bB \rightarrow cC + dD$$

the experimentally determined rate law usually has the following form:

$$rate = k\,[A]^m\,[B]^n$$

The *proportionality constant* (*k*) is called the rate constantA proportionality constant whose value is characteristic of the reaction and the reaction conditions and whose numerical value does not change as the reaction progresses under a given set of conditions., and its value is characteristic of the reaction and the reaction conditions. A given reaction has a particular value of the rate constant under a given set of conditions, such as temperature, pressure, and solvent; varying the temperature or the solvent usually changes the value of the rate constant. The numerical value of *k*, however, does *not* change as the reaction progresses under a given set of conditions.

Thus the reaction rate depends on the rate constant for the given set of reaction conditions and the concentration of A and B raised to the powers *m* and *n*, respectively. The values of *m* and *n* are derived from experimental measurements of the changes in reactant concentrations over time and indicate the reaction orderNumbers that indicate the degree to which the reaction rate depends on the concentration of each reactant., the degree to which the reaction rate depends on the concentration of each reactant; *m* and *n* need not be integers. For example, Equation 13.2.6 tells us that Equation 13.2.5 is *m*th order in reactant A and *n*th order in reactant B. It is important to remember that *n* and *m* are not related to the stoichiometric coefficients *a* and *b* in the balanced chemical equation and must be determined experimentally. The *overall reaction order* is the sum of all the exponents in the rate law: $m + n$.

Note the Pattern

Under a given set of conditions, the value of the rate constant does not change as the reaction progresses.

Although differential rate laws are generally used to describe what is occurring on a molecular level during a reaction, integrated rate laws are used to determine the reaction order and the value of the rate constant from experimental measurements. (We present general forms for integrated rate laws in Section 13.3.) To illustrate how chemists interpret a differential rate law, we turn to the experimentally derived rate law for the hydrolysis of *t*-butyl bromide in 70% aqueous acetone. This reaction produces *t*-butanol according to the following equation:

$$(CH_3)_3CBr\,(soln) + H_2O\,(soln) \rightarrow (CH_3)_3COH\,(soln) + HBr\,(soln)$$

Combining the rate expression in Equation 13.2.1 and Equation 13.2.6 gives us a general expression for the differential rate law:

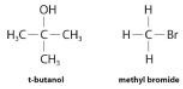
$$rate = -\frac{d[A]}{dt} = k[A]^m[B]^n$$

Inserting the identities of the reactants into Equation 13.2.8 gives the following expression for the differential rate law for the reaction:

$$rate = -\frac{d[(CH_3)_3CBr]}{dt} = k[(CH_3)_3CBr]^m[H_2O]^n$$

Experiments done to determine the rate law for the hydrolysis of *t*-butyl bromide show that the reaction rate is directly proportional to the concentration of $(CH_3)_3CBr$ but is independent of the concentration of water. Thus *m* and *n* in Equation 13.2.9 are 1 and 0, respectively, and

$$rate = k[(CH_3)_3CBr]^1[H_2O]^0 = k[(CH_3)_3CBr]$$



Because the exponent for the reactant is 1, the reaction is *first order* in $(CH_3)_3CBr$. It is *zeroth order* in water because the exponent for $[H_2O]$ is 0. (Recall that anything raised to the zeroth power equals 1.) Thus the overall reaction order is 1 + 0 = 1. What the reaction orders tell us in practical terms is that doubling the concentration of $(CH_3)_3CBr$ doubles the reaction rate of the hydrolysis reaction, halving the concentration of $(CH_3)_3CBr$ halves the reaction rate, and so on. Conversely, increasing or decreasing the concentration of water has *no effect* on the reaction rate. (Again, when you work with rate laws, there is no simple correlation between the stoichiometry of the reaction and the rate law. The values of *k*, *m*, and *n* in the rate law *must* be determined experimentally.) Experimental data show that *k* has the value 5.15×10^{-4} s^{-1} at 25°C. The rate constant has units of reciprocal seconds (s^{-1}) because the reaction rate is defined in units of concentration per unit time (M/s). The units of a rate constant depend on the rate law for a particular reaction.

Under conditions identical to those for the *t*-butyl bromide reaction, the experimentally derived differential rate law for the hydrolysis of methyl bromide (CH_3Br) is as follows:

$$rate = -\frac{d[CH_3Br]}{dt} = k'[CH_3Br]$$

This reaction also has an overall reaction order of 1, but the rate constant in Equation 13..2.11 is approximately 10^6 times smaller than that for *t*-butyl bromide. Thus methyl bromide hydrolyzes about 1 million times more slowly than *t*-butyl bromide, and this information tells chemists how the reactions differ on a molecular level.

Frequently, changes in reaction conditions also produce changes in a rate law. In fact, chemists often change reaction conditions to obtain clues about what is occurring during a reaction. For example, when *t*-butyl bromide is hydrolyzed in an aqueous acetone solution containing OH^- ions rather than in aqueous acetone alone, the differential rate law for the hydrolysis reaction does not change. For methyl bromide, in contrast, the differential rate law becomes rate = $k''[CH_3Br][OH^-]$, with an overall reaction order of 2. Although the two reactions proceed similarly in neutral solution, they proceed very differently in the presence of a base, which again provides clues as to how the reactions differ on a molecular level.

Note the Pattern

Differential rate laws are generally used to describe what is occurring on a molecular level during a reaction, whereas integrated rate laws are used for determining the reaction order and the value of the rate constant from experimental measurements.

Example 13.2.3

We present three reactions and their experimentally determined differential rate laws. For each reaction, give the *units* of the rate constant, give the reaction *order* with respect to each reactant, give the *overall reaction order*, and predict what happens to the reaction rate when the concentration of the first species in each chemical equation is doubled.

1. $2HI(g) \xrightarrow{Pt} H_2(g) + I_2(g) rate = -\frac{1}{2}\frac{d[HI]}{dt} = k[HI]^2$

2. $2N_2O\,(g) \xrightarrow{\Delta} 2N_2\,(g) + O_2\,(g)$
$rate = \frac{1}{2}\frac{d\,[N_2O]}{dt} = k$
3. $cyclopropane\,(g) \xrightarrow{\Delta} propane\,(g)$
$rate = \frac{1}{2}\frac{d\,[cyclopropance]}{dt} = k\,[cyclopropane]$

Given: balanced chemical equations and differential rate laws

Asked for: units of rate constant, reaction orders, and effect of doubling reactant concentration

Strategy:

A Express the reaction rate as moles per liter per second [mol/(L·s), or M/s]. Then determine the units of each chemical species in the rate law. Divide the units for the reaction rate by the units for all species in the rate law to obtain the units for the rate constant.

B Identify the exponent of each species in the rate law to determine the reaction order with respect to that species. Sum all exponents to obtain the overall reaction order.

C Use the mathematical relationships as expressed in the rate law to determine the effect of doubling the concentration of a single species on the reaction rate.

Solution:

1. **A** $[HI]^2$ will give units of (moles per liter)^2. For the reaction rate to have units of moles per liter per second, the rate constant must have reciprocal units [1/(M·s)]:

   $\frac{M}{s} = kM^2 \Rightarrow k = \frac{M/s}{M^2} = \frac{1}{M \cdot s} = M^{-1}s^{-1}$

   B The exponent in the rate law is 2, so the reaction is second order in HI. Because HI is the only reactant and the only species that appears in the rate law, the reaction is also second order overall.

   C If the concentration of HI is doubled, the reaction rate will increase from $k[HI]_0^2$ to $k(2[HI])_0^2 = 4k[HI]_0^2$. The reaction rate will therefore quadruple.

2. **A** Because no concentration term appears in the rate law, the rate constant must have M/s units for the reaction rate to have M/s units.

   B The rate law tells us that the reaction rate is constant and independent of the N_2O concentration. That is, the reaction is zeroth order in N_2O and zeroth order overall.

   C Because the reaction rate is independent of the N_2O concentration, doubling the concentration will have no effect on the reaction rate.

3. **A** The rate law contains only one concentration term raised to the first power. Hence the rate constant must have units of reciprocal seconds (s^{-1}) to have units of moles per liter per second for the reaction rate: $M \cdot s^{-1}$ = M/s.

   B The only concentration in the rate law is that of cyclopropane, and its exponent is 1. This means that the reaction is first order in cyclopropane. Cyclopropane is the only species that appears in the rate law, so the reaction is also first order overall.

   C Doubling the initial cyclopropane concentration will increase the reaction rate from $k[\text{cyclopropane}]_0$ to $2k[\text{cyclopropane}]_0$. This doubles the reaction rate.

Exercise

Given the following two reactions and their experimentally determined differential rate laws: determine the *units* of the rate constant if time is in seconds, determine the reaction *order* with respect to each reactant, give the *overall reaction order*, and predict what will happen to the reaction rate when the concentration of the first species in each equation is doubled.

1. $CH_3N=CH_3N\,(g) \rightarrow C_2H_6\,(g) + N_2\,(g)$
$rate = -\frac{d\,[CH_3N=CH_3N]}{dt} = k\,[CH_3N=CH_3N]$

2. $2NO_2\,(g) + F_2\,(g) \rightarrow 2NO_2F\,(g)$

$$rate = -\frac{d\,[F_2]}{dt} = -\frac{1}{2}\frac{d\,[NO_2]}{dt} = k\,[NO_2]\,[F_2]$$

Answer:

1. s^{-1}; first order in $CH_3N{=}NCH_3$; first order overall; doubling $[CH_3N{=}NCH_3]$ will double the reaction rate.
2. $M^{-1}{\cdot}s^{-1}$; first order in NO_2, first order in F_2; second order overall; doubling $[NO_2]$ will double the reaction rate.

Summary

Reaction rates are reported either as the **average rate** over a period of time or as the **instantaneous rate** at a single time.

The **rate law** for a reaction is a mathematical relationship between the reaction rate and the concentrations of species in solution. Rate laws can be expressed either as a **differential rate law**, describing the change in reactant or product concentrations as a function of time, or as an **integrated rate law**, describing the actual concentrations of reactants or products as a function of time.

The **rate constant** (k) of a rate law is a constant of proportionality between the reaction rate and the reactant concentration. The power to which a concentration is raised in a rate law indicates the **reaction order**, the degree to which the reaction rate depends on the concentration of a particular reactant.

Key Takeaways

- Reaction rates can be determined over particular time intervals or at a given point in time.
- A rate law describes the relationship between reactant rates and reactant concentrations.

Key Equations

general definition of rate for A → B

Equation 13.2.1: $$rate = \frac{d\,[B]}{dt} = -\frac{d\,[A]}{dt}$$

general form of rate law when A and B are reactants

Equation 13.2.6: $$rate = k\,[A]^m\,[B]^n$$

Conceptual Problems

1. Explain why the reaction rate is generally fastest at early time intervals. For the second-order A + B → C, what would the plot of the concentration of C versus time look like during the course of the reaction?
2. Explain the differences between a differential rate law and an integrated rate law. What two components do they have in common? Which form is preferred for obtaining a reaction order and a rate constant? Why?
3. Diffusion-controlled reactions have rates that are determined only by the reaction rate at which two reactant molecules can diffuse together. These reactions are rapid, with second-order rate constants typically on the order of 10^{10} L/(mol·s). Would you expect the reactions to be faster or slower in solvents that have a low viscosity? Why? Consider the reactions $H_3O^+ + OH^- \rightarrow 2H_2O$ and $H_3O^+ + N(CH_3)_3 \rightarrow H_2O + HN(CH_3)_3^+$ in aqueous solution. Which would have the higher rate constant? Why?
4. What information can you get from the reaction order? What correlation does the reaction order have with the stoichiometry of the overall equation?
5. During the hydrolysis reaction $A + H_2O \rightarrow B + C$, the concentration of A decreases much more rapidly in a polar solvent than in a nonpolar solvent. How do you expect this effect to be reflected in the overall reaction order?

Answers

1. Reactant concentrations are highest at the beginning of a reaction. The plot of [C] versus t is a curve with a slope that becomes steadily less positive.
2.
3. Faster in a less viscous solvent because the rate of diffusion is higher; the H_3O^+/OH^- reaction is faster due to the decreased relative size of reactants and the higher electrostatic attraction between the reactants.

4.
5.

Numerical Problems

1. The reaction rate of a particular reaction in which A and B react to make C is as follows:

   $$rate = -\frac{\Delta [A]}{\Delta t} = \frac{1}{2}\frac{d[C]}{dt}$$

   Write a reaction equation that is consistent with this rate law. What is the rate expression with respect to time if 2A are converted to 3C?

2. While commuting to work, a person drove for 12 min at 35 mph, then stopped at an intersection for 2 min, continued the commute at 50 mph for 28 min, drove slowly through traffic at 38 mph for 18 min, and then spent 1 min pulling into a parking space at 3 mph. What was the average rate of the commute? What was the instantaneous rate at 13 min? at 28 min?

3. Why do most studies of chemical reactions use the initial rates of reaction to generate a rate law? How is this initial rate determined? Given the following data, what is the reaction order? Estimate.

Time (s)	[A] (M)
120	0.158
240	0.089
360	0.062

4. Predict how the reaction rate will be affected by doubling the concentration of the first species in each equation.

   1. $C_2H_5I \rightarrow C_2H_4 + HI$: rate = $k[C_2H_5I]$
   2. $SO + O_2 \rightarrow SO_2 + O$: rate = $k[SO][O_2]$
   3. $2CH_3 \rightarrow C_2H_6$: rate = $k[CH_3]^2$
   4. $ClOO \rightarrow Cl + O_2$: rate = k

5. Cleavage of C_2H_6 to produce two $CH_3\cdot$ radicals is a gas-phase reaction that occurs at 700°C. This reaction is first order, with $k = 5.46 \times 10^{-4}\ s^{-1}$. How long will it take for the reaction to go to 15% completion? to 50% completion?

6. Three chemical processes occur at an altitude of approximately 100 km in Earth's atmosphere.

   $$N_2^+ + O_2 \xrightarrow{k_1} N_2 + O_2^+$$

   $$O_2^+ + O \xrightarrow{k_2} O_2 + O^+$$

   $$O^+ + N_2 \xrightarrow{k_3} N + NO^+$$

   Write a rate law for each elementary reaction. If the rate law for the overall reaction were found to be rate = $k[N_2^+][O_2]$, which one of the steps is rate limiting?

7. The oxidation of aqueous iodide by arsenic acid to give I_3^- and arsenous acid proceeds via the following reaction:

   $$H_3AsO_4\,(aq) + 3I^-\,(aq) + 2H^+\,(aq) \overset{k_f}{\rightleftharpoons} H_3AsO_3\,(aq) + I_3^-\,(aq) + H_2O\,(l)$$

   Write an expression for the initial rate of decrease of $[I_3^-]$, $\Delta[I_3^-]/\Delta t$. When the reaction rate of the forward reaction is equal to that of the reverse reaction: $k_f/k_r = [H_3AsO_3][I_3^-]/[H_3AsO_4][I^-]^3[H^+]^2$. Based on this information, what can you say about the nature of the rate-determining steps for the reverse and the forward reactions?

Answer

1.
2.
3.

4.

5. 298 s; 1270 s

6.

7.

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Chapter 13.3: Methods of Determining Reaction Order

Learning Objective

- To know how to determine the reaction order from experimental data.

In the examples in this text, the exponents in the rate law are almost always the positive integers: 1 and 2 or even 0. Thus the reactions are zeroth, first, or second order in each reactant. The common patterns used to identify the reaction order are described in this section, where we focus on characteristic types of differential and integrated rate laws and how to determine the reaction order from experimental data.

Zeroth-Order Reactions

A zeroth-order reactionA reaction whose rate is independent of concentration. is one whose rate is independent of concentration; its differential rate law is rate = k. We refer to these reactions as zeroth order because we could also write their rate in a form such that the exponent of the reactant in the rate law is 0:

$$rate = -\frac{d[A]}{dt} = -k[reactant]^0 = k(1) = k$$

We can integrate this equation with respect to time

$$\int_0^t \frac{d[A]}{dt}dt = \int_0^t d[A]dt = -\int_0^t kdt \tag{13.3.2}$$

$$[A] - [A]_o = kt$$

to develop the integrated rate law for a zeroth order reaction

$$[A] = [A]_o - kt$$

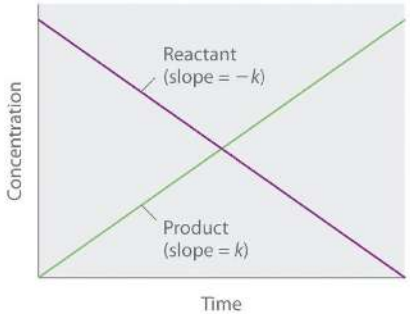


Figure 13.3.1 The graph of a zeroth-order reaction. *The change in concentration of reactant and product with time produces a straight line.*

where $[A]_0$ is the initial concentration of reactant A. (Equation 13.3.4 has the form of the algebraic equation for a straight line, $y = mx + b$, with $y = [A]$, $mx = -kt$, and $b = [A]_0$.) In a zeroth-order reaction, the rate constant must have the same units as the reaction rate, typically moles per liter per second. An important point to remember is that once all of the reactant has been used up [A] = 0 the reaction stops.

Although it may seem counterintuitive for the reaction rate to be independent of the reactant concentration(s), such reactions are rather common. They occur most often when the reaction rate is determined by available surface area. An example is the decomposition of N_2O on a platinum (Pt) surface to produce N_2 and O_2, which occurs at temperatures ranging from 200°C to 400°C:

$$2N_2O\,(g) \xrightarrow{Pt} 2N_2\,(g) + O_2\,(g)$$

Without a platinum surface, the reaction requires temperatures greater than 700°C, but between 200°C and 400°C, the only factor that determines how rapidly N_2O decomposes is the amount of Pt *surface* available (not the *amount* of Pt). As long as there is enough N_2O to react with the entire Pt surface, doubling or quadrupling the N_2O concentration will have no effect on the reaction

rate.At very low concentrations of N_2O, where there are not enough molecules present to occupy the entire available Pt surface, the reaction rate is dependent on the N_2O concentration. The reaction rate is as follows:

$$rate = -\frac{1}{2}\left(\frac{d[N_2O]}{dt}\right) = \frac{1}{2}\left(\frac{d[N_2]}{dt}\right) = \frac{d[O_2]}{dt} = k[N_2O]^0 = k$$

Thus the rate at which N_2O is consumed and the rates at which N_2 and O_2 are produced are independent of concentration. As shown in Figure 13.3.2, the change in the concentrations of all species with time is linear. Most important, the exponent (0) corresponding to the N_2O concentration in the experimentally derived rate law is *not* the same as the reactant's stoichiometric coefficient in the balanced chemical equation (2). For this reaction, as for all others, *the rate law must be determined experimentally*.

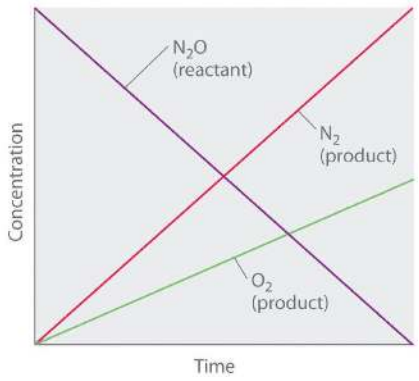


Figure 13.3.2 A Zeroth-Order Reaction *This graph shows the concentrations of reactants and products versus time for the zeroth-order catalyzed decomposition of N_2O to N_2 and O_2 on a Pt surface. The change in the concentrations of all species with time is linear.*

Note the Pattern

If a plot of reactant concentration versus time is linear, then the reaction is zeroth order in that reactant.

A zeroth-order reaction that takes place in the human liver is the oxidation of ethanol (from alcoholic beverages) to acetaldehyde, catalyzed by the enzymeA catalyst that occurs naturally in living organisms and catalyzes biological reactions. alcohol dehydrogenase. At high ethanol concentrations, this reaction is also a zeroth-order reaction. The overall reaction equation is

$$CH_3C{\equiv}N(l) + 2H_2O(l) + H^+(aq) \longrightarrow CH_3\overset{\overset{O}{\|}}{C}OH(aq) + NH_4^+(aq)$$

where NAD^+ (nicotinamide adenine dinucleotide) and NADH (reduced nicotinamide adenine dinucleotide) are the oxidized and reduced forms, respectively, of a species used by all organisms to transport electrons. When an alcoholic beverage is consumed, the ethanol is rapidly absorbed into the blood. Its concentration then decreases at a constant rate until it reaches zero (part (a) in Figure 13.3.3). An average 70 kg person typically takes about 2.5 h to oxidize the 15 mL of ethanol contained in a single 12 oz can of beer, a 5 oz glass of wine, or a shot of distilled spirits (such as whiskey or brandy). The actual rate, however, varies a great deal from person to person, depending on body size and the amount of alcohol dehydrogenase in the liver. The reaction rate does not increase if a greater quantity of alcohol is consumed over the same period of time because the reaction rate is determined only by the amount of enzyme present in the liver.Contrary to popular belief, the caffeine in coffee is ineffective at catalyzing the oxidation of ethanol. When the ethanol has been completely oxidized and its concentration drops to essentially zero, the rate of oxidation also drops rapidly (part (b) in Figure 13.3.3).

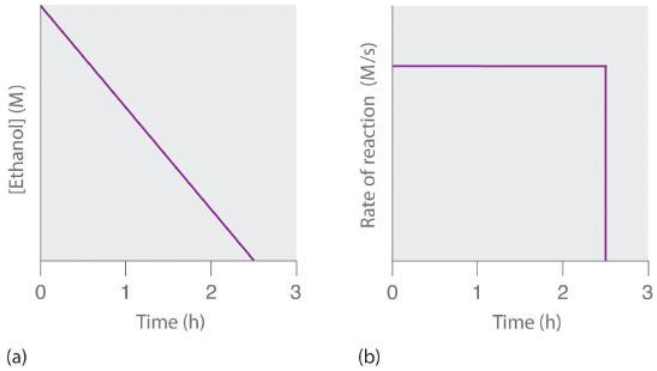


Figure 13.3.3 The Catalyzed Oxidation of Ethanol *(a) The concentration of ethanol in human blood decreases linearly with time, which is typical of a zeroth-order reaction. (b) The rate at which ethanol is oxidized is constant until the ethanol concentration reaches essentially zero, at which point the reaction rate drops to zero.*

These examples illustrate three important points:

1. *In a zeroth-order reaction, the reaction rate does not depend on the reactant concentration.*
2. *A linear change in concentration with time is a clear indication of a zeroth-order reaction.*
3. *When all of the reactant is used up the reaction stops and the rate goes to zero.*

First-Order Reactions

In a first-order reactionA reaction whose rate is directly proportional to the concentration of one reactant., the reaction rate is directly proportional to the concentration of one of the reactants. First-order reactions often have the general form A → products. The differential rate for a first-order reaction is as follows:

$$rate = -\frac{d[A]}{dt} = k[A]^1 = k[A]$$

If the concentration of A is doubled, the reaction rate doubles; if the concentration of A is increased by a factor of 10, the reaction rate increases by a factor of 10, and so forth. Because the units of the reaction rate are always moles per liter per second, the units of a first-order rate constant are reciprocal seconds (s^{-1}).

Integrating Eq 13.3.7

$$\int \frac{d[A]}{dt}dt = \int d[A] = -\int k[A]dt \tag{13.3.8}$$

$$\int_{A_o}^{A} \frac{d[A]}{[A]} = -\int_0^t kdt \tag{13.3.9}$$

yields

$$ln[A] - ln[A]_o = kt$$

and by exponentiating both sides of 13.3.10 we get

$$\frac{[A]}{[A]_o} - kt$$

or multiplying both sides of Equation 13.3.11 by $[A]_o$

$$[A] = [A]_0\, e^{-kt}$$

where $[A]_0$ is the initial concentration of reactant A at $t = 0$; k is the rate constant; and e is the base of the natural logarithms, which has the value 2.718 to three decimal places. Recall that an integrated rate law gives the relationship between reactant concentration and time. Equation 13.3.12. predicts that the concentration of A will decrease in a smooth exponential curve over time. Equation 13.3.10 is an alternative logarithmic expression of the relationship between the concentration of A and t:

Because Equation 13.3.10 has the form of the algebraic equation for a straight line, $y = mx + b$, with $y = \ln[A]$ and $b = \ln[A]_0$, a plot of ln[A] versus t for a first-order reaction should give a straight line with a slope of $-k$ and an intercept of $\ln[A]_0$. Either the differential rate law (Equation 13.3.7) or the integrated rate law (Equation 13.3.10) can be used to determine whether a particular reaction is first order.

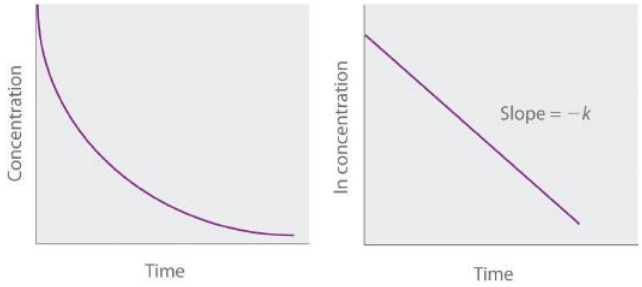


Figure 13.3.4 Graphs of a first-order reaction. *The expected shapes of the curves for plots of reactant concentration versus time (top) and the natural logarithm of reactant concentration versus time (bottom) for a first-order reaction.*

First-order reactions are very common. In this chapter, we have already encountered an example of first-order reactions: the hydrolysis of aspirin (Figure 13.2.3). Another reaction that exhibits apparent first-order kinetics is the hydrolysis of the anticancer drug cisplatin.

Cisplatin, the first "inorganic" anticancer drug to be discovered, is unique in its ability to cause complete remission of the relatively rare but deadly cancers of the reproductive organs in young adults. The structures of cisplatin and its hydrolysis product are as follows:

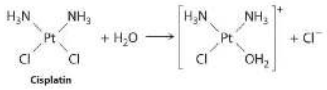


Figure 13.3.5: The hydolysis of cisplatin. *Cisplatin is used to treat cancers. One of the chemical steps is the first order hydrolysis*

Both platinum compounds have four groups arranged in a square plane around a Pt(II) ion. The reaction shown in Figure 13.3.5 is important because cisplatin, the form in which the drug is administered, is *not* the form in which the drug is active. Instead, at least one chloride ion must be replaced by water to produce a species that reacts with deoxyribonucleic acid (DNA) to prevent cell division and tumor growth. Consequently, the kinetics of the reaction in Figure 13.3.5 have been studied extensively to find ways of maximizing the concentration of the active species.

Note the Pattern

If a plot of reactant concentration versus time is not linear but a plot of the natural logarithm of reactant concentration versus time is linear, then the reaction is first order.

The rate law and reaction order of the hydrolysis of cisplatin are determined from experimental data, such as those displayed in Table 13.3.1. The table lists initial rate data for four experiments in which the reaction was run at pH 7.0 and 25°C but with different initial concentrations of cisplatin. Because the reaction rate increases with increasing cisplatin concentration, we know this cannot be a zeroth-order reaction. Comparing Experiments 1 and 2 in Table 13.3.1 shows that the reaction rate doubles [$(1.8 \times 10^{-5}$ M/min) ÷ $(9.0 \times 10^{-6}$ M/min) = 2.0] when the concentration of cisplatin is doubled (from 0.0060 M to 0.012 M). Similarly, comparing Experiments 1 and 4 shows that the reaction rate increases by a factor of 5 [$(4.5 \times 10^{-5}$ M/min) ÷ $(9.0 \times 10^{-6}$ M/min) = 5.0] when the concentration of cisplatin is increased by a factor of 5 (from 0.0060 M to 0.030 M). Because the reaction rate is directly proportional to the concentration of the reactant, the exponent of the cisplatin concentration in the rate law must be 1, so the rate law is rate = k[cisplatin]^1. Thus the reaction is first order. Knowing this, we can calculate the rate constant using the differential rate law for a first-order reaction and the data in any row of Table 13.3.1. For example, substituting the values for Experiment 3 into Equation 13.3.7,

$$\mathbf{3.6 \times 10^{-5}\ M/min = \mathit{k}(0.024\ M)}$$

$$\mathbf{1.5 \times 10^{-3}\ min^{-1} = \mathit{k}}$$

Table 13.3.1 Rates of Hydrolysis of Cisplatin as a Function of Concentration at pH 7.0 and 25°C

Experiment	$[\text{Cisplatin}]_0$ (M)	Initial Rate (M/min)
1	0.0060	9.0×10^{-6}
2	0.012	1.8×10^{-5}
3	0.024	3.6×10^{-5}
4	0.030	4.5×10^{-5}

Knowing the rate constant for the hydrolysis of cisplatin and the rate constants for subsequent reactions that produce species that are highly toxic enables hospital pharmacists to provide patients with solutions that contain only the desired form of the drug.

Example 13.3.1

At high temperatures, ethyl chloride produces HCl and ethylene by the following reaction:

$$CH_3CH_2Cl\,(g) \xrightarrow{\Delta} HCl\,(g) + C_2H_4\,(g)$$

Using the rate data for the reaction at 650°C presented in the following table, calculate the reaction order with respect to the concentration of ethyl chloride and determine the rate constant for the reaction.

Experiment	$[CH_3CH_2Cl]_0$ (M)	Initial Rate (M/s)
1	0.010	1.6×10^{-8}
2	0.015	2.4×10^{-8}
3	0.030	4.8×10^{-8}
4	0.040	6.4×10^{-8}

Given: balanced chemical equation, initial concentrations of reactant, and initial rates of reaction

Asked for: reaction order and rate constant

Strategy:

A Compare the data from two experiments to determine the effect on the reaction rate of changing the concentration of a species.

B Compare the observed effect with behaviors characteristic of zeroth- and first-order reactions to determine the reaction order. Write the rate law for the reaction.

C Use measured concentrations and rate data from any of the experiments to find the rate constant.

Solution:

The reaction order with respect to ethyl chloride is determined by examining the effect of changes in the ethyl chloride concentration on the reaction rate.

A Comparing Experiments 2 and 3 shows that doubling the concentration doubles the reaction rate, so the reaction rate is proportional to $[CH_3CH_2Cl]$. Similarly, comparing Experiments 1 and 4 shows that quadrupling the concentration quadruples the reaction rate, again indicating that the reaction rate is directly proportional to $[CH_3CH_2Cl]$.

B This behavior is characteristic of a first-order reaction, for which the rate law is rate = $k[CH_3CH_2Cl]$.

C We can calculate the rate constant (k) using any row in the table. Selecting Experiment 1 gives the following:

$$\mathbf{1.60 \times 10^{-8}\ M/s = k(0.010\ M)\ 1.6 \times 10^{-6}\ s^{-1} = k}$$

Exercise

Sulfuryl chloride (SO_2Cl_2) decomposes to SO_2 and Cl_2 by the following reaction:

$$\mathbf{SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)}$$

Data for the reaction at 320°C are listed in the following table. Calculate the reaction order with regard to sulfuryl chloride and determine the rate constant for the reaction.

Experiment	$[SO_2Cl_2]_0$ (M)	Initial Rate (M/s)
1	0.0050	1.10×10^{-7}
2	0.0075	1.65×10^{-7}
3	0.0100	2.20×10^{-7}
4	0.0125	2.75×10^{-7}

Answer: first order; $k = 2.2 \times 10^{-5}\ s^{-1}$

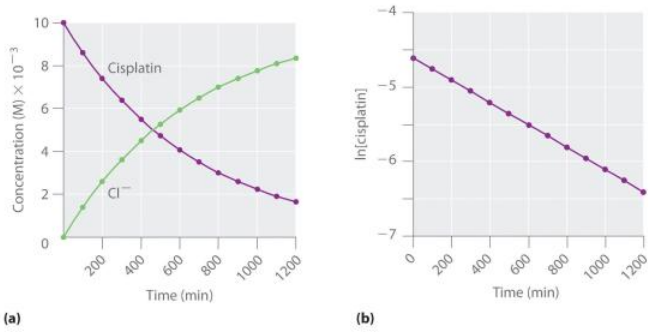


Figure 13.3.6 The Hydrolysis of Cisplatin, a First-Order Reaction *These plots show hydrolysis of cisplatin at pH 7.0 and 25°C as (a) the experimentally determined concentrations of cisplatin and chloride ions versus time and (b) the natural logarithm of the cisplatin concentration versus time. The straight line in (b) is expected for a first-order reaction.*

We can also use the integrated rate law to determine the reaction rate for the hydrolysis of cisplatin. To do this, we examine the change in the concentration of the reactant or the product as a function of time at a single initial cisplatin concentration. Part (a) in Figure 13.3.6 shows plots for a solution that originally contained 0.0100 M cisplatin and was maintained at pH 7 and 25°C. The concentration of cisplatin decreases smoothly with time, and the concentration of chloride ion increases in a similar way. When we plot the natural logarithm of the concentration of cisplatin versus time, we obtain the plot shown in part (b) in Figure 13.3.6. The straight line is consistent with the behavior of a system that obeys a first-order rate law. We can use any two points on the line to calculate the slope of the line, which gives us the rate constant for the reaction. Thus taking the points from part (a) in Figure 13.3.6 for t = 100 min ([cisplatin] = 0.0086 M) and t = 1000 min ([cisplatin] = 0.0022 M),

$$slope = \frac{ln\,[cisplatin]_{1000} - ln\,[cisplatin]_{100}}{1000\ min - 100\ min}$$

$$-k = \frac{ln0.0022 - ln0.0086}{1000\ min - 100\ min} = \frac{-6.12 - (-4.76)}{900\ min} = -1.51 \times 10^{-3} min^{-1}$$

$$k = 1.51 \times 10^{-3}\ min^{-1}$$

The slope is negative because we are calculating the rate of disappearance of cisplatin. Also, the rate constant has units of min^{-1} because the times plotted on the horizontal axes in parts (a) and (b) in Figure 13.3.6 are in minutes rather than seconds.

The reaction order and the magnitude of the rate constant we obtain using the integrated rate law are exactly the same as those we calculated earlier using the differential rate law. This must be true if the experiments were carried out under the same conditions.

Example 13.3.2

Refer back to Example 4. If a sample of ethyl chloride with an initial concentration of 0.0200 M is heated at 650°C, what is the concentration of ethyl chloride after 10 h? How many hours at 650°C must elapse for the concentration to decrease to 0.0050 M? (Recall that we calculated the rate constant for this reaction in Example 4.)

Given: initial concentration, rate constant, and time interval

Asked for: concentration at specified time and time required to obtain particular concentration

Strategy:

A Substitute values for the initial concentration ($[A]_0$) and the calculated rate constant for the reaction (k) into the integrated rate law for a first-order reaction. Calculate the concentration ([A]) at the given time t.

B Given a concentration [A], solve the integrated rate law for time t.

Solution:

The exponential form of the integrated rate law for a first-order reaction (Equation 13.3.12) is $[A] = [A]_0 e^{-kt}$.

A Having been given the initial concentration of ethyl chloride ($[A]_0$) and having calculated the rate constant in Example 4 (k = 1.6 × 10^{-6} s^{-1}), we can use the rate law to calculate the concentration of the reactant at a given time t. Substituting the known values into the integrated rate law,

$$[CH_3CH_2Cl]_{10\ h} = [CH_3CH_2Cl]_0\, e^{-kt}$$

$$= 0.0200\ M\ exp\left[\left(-1.6 \times 10^{-6}\ s^{-1}\right)(10\ h)\,(60\ min/h)\,(60\ s/min)\right]$$

\(= 0.0189\;M

We could also have used the logarithmic form of the integrated rate law (Equation 13.3.7):

$$ln\,[CH_3CH_2Cl]_{10\ h} = ln\,[CH_3CH_2Cl]_0 - kt$$

$$= ln 0.0200\ M - \left(-1.6 \times 10^{-6}\ s^{-1}\right)(10\ h)\,(60\ min/h)\,(60\ s/min)$$

$$= -3.912 - -0.0576 = -3.970$$

$$[CH_3CH_2Cl]_{10\ h} = e^{-3.970}\ M$$

=0.0189\;M

B To calculate the amount of time required to reach a given concentration, we must solve the integrated rate law for t. Equation 13.3.7 gives the following:

$$ln\,[CH_3CH_2Cl]_t = ln\,[CH_3CH_2Cl]_0 - kt$$

$$kt = ln\,[CH_3CH_2Cl]_0 - ln\,[CH_3CH_2Cl]_t = ln\,\frac{[CH_3CH_2Cl]_0}{[CH_3CH_2Cl]_t}$$

$$t = \frac{1}{k}\,ln\frac{[CH_3CH_2Cl]_0}{[CH_3CH_2Cl]_t} = \frac{1}{1.6 \times 10^{-6}\ s^{-1}}\,ln\frac{0.0200\ M}{0.0050\ M}$$

$$t = \frac{ln\ 4.0}{k} = 8.7 \times 10^5\ s = 240\ h = 2.4 \times 10^2\ h$$

Exercise

In the exercise in Example 4, you found that the decomposition of sulfuryl chloride (SO_2Cl_2) is first order, and you calculated the rate constant at 320°C. Use the form(s) of the integrated rate law to find the amount of SO_2Cl_2 that remains after 20 h if a sample with an original concentration of 0.123 M is heated at 320°C. How long would it take for 90% of the SO_2Cl_2 to decompose?

Answer: 0.0252 M; 29 h

Second-Order Reactions

The simplest kind of second-order reactionA reaction whose rate is proportional to the square of the concentration of the reactant (for a reaction with the general form 2A → products) or is proportional to the product of the concentrations of two reactants (for a

reaction with the general form A + B → products). is one whose rate is proportional to the square of the concentration of one reactant. These generally have the form 2A → products. A second kind of second-order reaction has a reaction rate that is proportional to the *product* of the concentrations of two reactants. Such reactions generally have the form A + B → products. An example of the former is a *dimerization reaction*, in which two smaller molecules, each called a *monomer*, combine to form a larger molecule (a *dimer*).

The differential rate law for the simplest second-order reaction in which 2A → products is as follows:

$$rate = -\frac{d[A]}{2dt} = k[reactant]^2$$

Consequently, doubling the concentration of A quadruples the reaction rate. For the units of the reaction rate to be moles per liter per second (M/s), the units of a second-order rate constant must be the inverse ($M^{-1}{\cdot}s^{-1}$). Because the units of molarity are expressed as mol/L, the unit of the rate constant can also be written as L(mol·s).

Integrating Equation 13.3.13

$$\int d[A] = -\int k[A]^2 dt \tag{13.3.14}$$

$$\int_{A_o}^{A} \frac{d[A]}{[A]^2} = -\int_0^t kdt \tag{13.3.15}$$

yields

$$\frac{1}{[A]} - \frac{1}{[A_0]} = kt$$

Rearranging this by moving the second term $1/[A]_o$ moves to the right hand side of the equation leads to the integrated rate law for the reaction 2A → products,

$$\frac{1}{[A]} = \frac{1}{[A_0]} + kt$$

Because Equation 13.3.17 has the form of an algebraic equation for a straight line, $y = mx + b$, with $y = 1/[A]$ and $b = 1/[A]_0$, a plot of $1/[A]$ versus t for a simple second-order reaction is a straight line with a slope of k and an intercept of $1/[A]_0$.

Note the Pattern

Second-order reactions generally have the form 2A → products or A + B → products.

Simple second-order reactions are common. In addition to dimerization reactions, two other examples are the decomposition of NO_2 to NO and O_2 and the decomposition of HI to I_2 and H_2. Most examples involve simple inorganic molecules, but there are organic examples as well. We can follow the progress of the reaction described in the following paragraph by monitoring the decrease in the intensity of the red color of the reaction mixture.

Many cyclic organic compounds that contain two carbon–carbon double bonds undergo a dimerization reaction to give complex structures. One example is as follows:

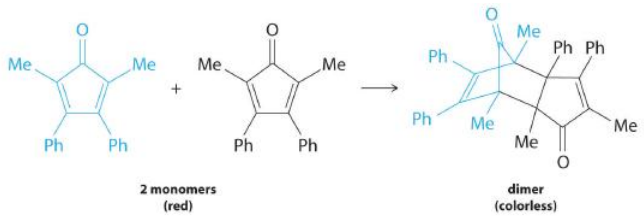


Figure 13.3.7. Dimerization of monomeric 2,5-dimethyl-3,4-diphenylcyclopentadienone

For simplicity, we will refer to this reactant and product as “monomer” and “dimer,” respectively.The systematic name of the monomer is 2,5-dimethyl-3,4-diphenylcyclopentadienone. The systematic name of the dimer is the name of the monomer followed by “dimer.” Because the monomers are the same, the general equation for this reaction is 2A → product. This reaction represents an important class of organic reactions used in the pharmaceutical industry to prepare complex carbon skeletons for the synthesis of

drugs. Like the first-order reactions studied previously, it can be analyzed using either the differential rate law (Equation 13.3.13) or the integrated rate law (Equation 13.3.17).

To determine the differential rate law for the reaction, we need data on how the reaction rate varies as a function of monomer concentrations, which are provided in Table 13.3.2 . From the data, we see that the reaction rate is not independent of the monomer concentration, so this is not a zeroth-order reaction. We also see that the reaction rate is not proportional to the monomer concentration, so the reaction is not first order. Comparing the data in the second and fourth rows shows that the reaction rate decreases by a factor of 2.8 when the monomer concentration decreases by a factor of 1.7:

$$\frac{5.0 \times 10^{-5}\ M/min}{1.8 \times 10^{-5}\ M/mi} = 2.8 \quad and \quad \frac{3.4 \times 10^{-3}\ M/min}{2.0 \times 10^{-3}\ M/mi} = 1.7$$

Table 13.3.2 Rates of Reaction as a Function of Monomer Concentration for an Initial Monomer Concentration of 0.0054 M

Time (min)	[Monomer] (M)	Instantaneous Rate (M/min)
10	0.0044	8.0×10^{-5}
26	0.0034	5.0×10^{-5}
44	0.0027	3.1×10^{-5}
70	0.0020	1.8×10^{-5}
120	0.0014	8.0×10^{-6}

Because $(1.7)^2 = 2.9 \approx 2.8$, the reaction rate is approximately proportional to the square of the monomer concentration.

$$rate\ \alpha\ [monomer]^2$$

This means that the reaction is second order in the monomer. Using Equation 13.3.13 and the data from any row in Table 13.3.2, we can calculate the rate constant. Substituting values at time 10 min, for example, gives the following:

$$rate = k\,[A^2]$$

$$8.0 \times 10^{-5}\ M/min = k\left(4.4 \times 10^{-3}\ M\right)$$

$$4.1\ min^{-1} = k$$

We can also determine the reaction order using the integrated rate law. To do so, we use the decrease in the concentration of the monomer as a function of time for a single reaction, plotted in part (a) in Figure 13.3.8. The measurements show that the concentration of the monomer (initially 5.4×10^{-3} M) decreases with increasing time. This graph also shows that the reaction *rate* decreases smoothly with increasing time. According to the integrated rate law for a second-order reaction, a plot of 1/[monomer] versus *t* should be a straight line, as shown in part (b) in Figure 13.3.8. Any pair of points on the line can be used to calculate the slope, which is the second-order rate constant. In this example, k = 4.1 $M^{-1}{\cdot}min^{-1}$, which is consistent with the result obtained using the differential rate equation. Although in this example the stoichiometric coefficient is the same as the reaction order, this is not always the case. *The reaction order must always be determined experimentally.*

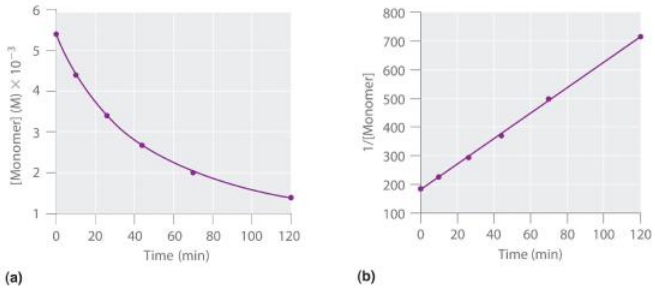


Figure 13.3.8 Dimerization of a Monomeric Compound, a Second-Order Reaction *These plots correspond to dimerization of the monomer in Figure 13.3.7 as (a) the experimentally determined concentration of monomer versus time and (b) 1/[monomer]*

versus time. The straight line in (b) is expected for a simple second-order reaction.

For two or more reactions of the *same order*, the reaction with the largest rate constant is the fastest. Because the units of the rate constants for zeroth-, first-, and second-order reactions are different, however, we cannot compare the magnitudes of rate constants for reactions that have different orders. The differential and integrated rate laws for zeroth-, first-, and second-order reactions and their corresponding graphs are shown in Figure 13.4.2.

Example 13.3.3

At high temperatures, nitrogen dioxide decomposes to nitric oxide and oxygen.

$$2NO_2\,(g) \xrightarrow{\Delta} 2NO\,(g) + O_2\,(g)$$

Experimental data for the reaction at 300°C and four initial concentrations of NO_2 are listed in the following table:

Experiment	$[NO_2]_0$ (M)	Initial Rate (M/s)
1	0.015	1.22×10^{-4}
2	0.010	5.40×10^{-5}
3	0.0080	3.46×10^{-5}
4	0.0050	1.35×10^{-5}

Determine the reaction order and the rate constant.

Given: balanced chemical equation, initial concentrations, and initial rates

Asked for: reaction order and rate constant

Strategy:

A From the experiments, compare the changes in the initial reaction rates with the corresponding changes in the initial concentrations. Determine whether the changes are characteristic of zeroth-, first-, or second-order reactions.

B Determine the appropriate rate law. Using this rate law and data from any experiment, solve for the rate constant (k).

Solution:

A We can determine the reaction order with respect to nitrogen dioxide by comparing the changes in NO_2 concentrations with the corresponding reaction rates. Comparing Experiments 2 and 4, for example, shows that doubling the concentration quadruples the reaction rate [$(5.40 \times 10^{-5}) \div (1.35 \times 10^{-5}) = 4.0$], which means that the reaction rate is proportional to $[NO_2]^2$. Similarly, comparing Experiments 1 and 4 shows that tripling the concentration increases the reaction rate by a factor of 9, again indicating that the reaction rate is proportional to $[NO_2]^2$. This behavior is characteristic of a second-order reaction.

B We have rate = $k[NO_2]^2$. We can calculate the rate constant (k) using data from any experiment in the table. Selecting Experiment 2, for example, gives the following:

$$rate = k\,[NO_2]^2$$

$$5.40 \times 10^{-5}\ M/s = k\,(0.010\ M)^2$$

$$0.540\ M^{-1}s^{-1} = k$$

Exercise

When the highly reactive species HO_2 forms in the atmosphere, one important reaction that then removes it from the atmosphere is as follows:

$2HO_2(g) \rightarrow H_2O_2(g) + O_2(g)$

The kinetics of this reaction have been studied in the laboratory, and some initial rate data at 25°C are listed in the following table:

Experiment	$[HO_2]_0$ (M)	Initial Rate (M/s)
1	1.1×10^{-8}	1.7×10^{-7}
2	2.5×10^{-8}	8.8×10^{-7}
3	3.4×10^{-8}	1.6×10^{-6}
4	5.0×10^{-8}	3.5×10^{-6}

Determine the reaction order and the rate constant.

Answer: second order in HO_2; $k = 1.4 \times 10^9\ M^{-1}{\cdot}s^{-1}$

Note the Pattern

If a plot of reactant concentration versus time is not linear but a plot of 1/reaction concentration versus time is linear, then the reaction is second order.

Example 13.3.4

If a flask that initially contains 0.056 M NO_2 is heated at 300°C, what will be the concentration of NO_2 after 1.0 h? How long will it take for the concentration of NO_2 to decrease to 10% of the initial concentration? Use the integrated rate law for a second-order reaction (Equation 13.3.17) and the rate constant calculated in Example 6.

Given: balanced chemical equation, rate constant, time interval, and initial concentration

Asked for: final concentration and time required to reach specified concentration

Strategy:

A Given k, t, and $[A]_0$, use the integrated rate law for a second-order reaction to calculate [A].

B Setting [A] equal to 1/10 of $[A]_0$, use the same equation to solve for t.

Solution:

A We know k and $[NO_2]_0$, and we are asked to determine $[NO_2]$ at t = 1 h (3600 s). Substituting the appropriate values into Equation 13.3.17,

$$\frac{1}{[NO_2]_{3600}} = \frac{1}{[NO_2]_0} + kt = \frac{1}{0.056\ M} + (0.54\ M^{-1}s^{-1})\,(3600\ s)$$
$$= 2.0 \times 10^{-3}\ M^{-1}$$

Thus $[NO_2]_{3600} = 5.1 \times 10^{-4}$ M.

B In this case, we know k and $[NO_2]_0$, and we are asked to calculate at what time $[NO_2] = 0.1[NO_2]_0 = 0.1(0.056\ M) = 0.0056$ M. To do this, we solve Equation 13.3.17 for t, using the concentrations given.

$$\frac{\frac{1}{[NO_2]_{3600}} - \frac{1}{[NO_2]_0}}{k} = \frac{(1/0.0056\ M) - (1/0.056\ M)}{0.54\ M^{-1}s^{-1}} = 3.0 \times 10^2\ s = 5\ min$$

NO_2 decomposes very rapidly; under these conditions, the reaction is 90% complete in only 5.0 min.

Exercise

In the exercise in Example 6, you calculated the rate constant for the decomposition of HO_2 as $k = 1.4 \times 10^9\ M^{-1}{\cdot}s^{-1}$. This high rate constant means that HO_2 decomposes rapidly under the reaction conditions given in the problem. In fact, the HO_2 molecule is so reactive that it is virtually impossible to obtain in high concentrations. Given a 0.0010 M sample of HO_2, calculate the concentration of HO_2 that remains after 1.0 h at 25°C. How long will it take for 90% of the HO_2 to decompose? Use the integrated rate law for a second-order reaction (Equation 13.3.17) and the rate constant calculated in the exercise in Example 6.

Answer: 2.0×10^{-13} M; 6.4×10^{-6} s

In addition to the simple second-order reaction and rate law we have just described, another very common second-order reaction has the general form A + B → products, in which the reaction is first order in A and first order in B. The differential rate law for this reaction is as follows:

$$rate = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B]$$

Because the reaction is first order both in A and in B, it has an overall reaction order of 2. (The integrated rate law for this reaction is rather complex, so we will not describe it.) We can recognize second-order reactions of this sort because the reaction rate is proportional to the concentrations of each reactant. We presented one example at the end of Section 13.2, the reaction of CH_3Br with OH^- to produce CH_3OH.

Determining the Rate Law of a Reaction

The number of fundamentally different mechanisms (sets of steps in a reaction) is actually rather small compared to the large number of chemical reactions that can occur. Thus understanding reaction mechanismsThe sequence of events that occur at the molecular level during a reaction. can simplify what might seem to be a confusing variety of chemical reactions. The first step in discovering the reaction mechanism is to determine the reaction's rate law. This can be done by designing experiments that measure the concentration(s) of one or more reactants or products as a function of time. For the reaction A + B → products, for example, we need to determine *k* and the exponents *m* and *n* in the following equation:

$$rate = k[A]^m[B]^n$$

To do this, we might keep the initial concentration of B constant while varying the initial concentration of A and calculating the initial reaction rate. This information would permit us to deduce the reaction order with respect to A. Similarly, we could determine the reaction order with respect to B by studying the initial reaction rate when the initial concentration of A is kept constant while the initial concentration of B is varied. In earlier examples, we determined the reaction order with respect to a given reactant by comparing the different rates obtained when only the concentration of the reactant in question was changed. An alternative way of determining reaction orders is to set up a proportion using the rate laws for two different experiments.

Rate data for a hypothetical reaction of the type A + B → products are given in Table 13.3.3. The general rate law for the reaction is given in Equation 13.3.19. We can obtain *m* or *n* directly by using a proportion of the rate laws for two experiments in which the concentration of one reactant is the same, such as Experiments 1 and 3 in Table 13.3.3.

Table 13.3.3 Rate Data for a Hypothetical Reaction of the Form A + B → Products

Experiment	[A] (M)	[B] (M)	Initial Rate (M/min)
1	0.50	0.50	8.5×10^{-3}
2	0.75	0.50	19×10^{-3}
3	1.00	0.50	34×10^{-3}
4	0.50	0.75	8.5×10^{-3}
5	0.50	1.00	8.5×10^{-3}

$$\frac{rate^1}{rate^3} = \frac{k[A^1]^m[B^1]^n}{k[A^3]^m[B^3]^n}$$

Inserting the appropriate values from Table 13.3.3,

$$\frac{8.5 \times 10^{-3}\ \cancel{M/min}}{34. \times 10^{-3}\ \cancel{M/min}} = \frac{k\left[0.50\ \cancel{M}\right]^m\ \cancel{[0.50\ M]^n}}{k\left[1.00\ \cancel{M}\right]^m\ \cancel{[0.50\ M]^n}}$$

Because 1.00 to any power is 1, $[1.00\ M]^m = 1.00\ M$. We can cancel like terms to give $0.25 = [0.50]^m$, which can also be written as $1/4 = [1/2]^m$. Thus we can conclude that $m = 2$ and that the reaction is second order in A. By selecting two experiments in which the concentration of B is the same, we were able to solve for *m*.

Conversely, by selecting two experiments in which the concentration of A is the same (e.g., Experiments 5 and 1), we can solve for *n*.

$$\frac{rate^1}{rate^3} = \frac{k\,[A^1]^m\,[B^1]^n}{k\,[A^5]^m\,[B^5]^n}$$

Substituting the appropriate values from Table 13.3.3,

$$\frac{8.5 \times 10^{-3}\ \cancel{M/min}}{8.5 \times 10^{-3}\ \cancel{M/min}} = \frac{k\,[0.50\ \cancel{M}]^m\,[05.0\ \cancel{M}]^n}{k\,[0.50\ \cancel{M}]^m\,[1.00\ \cancel{M}]^n}$$

Canceling leaves 1.0 = $[0.50]^n$, which gives $n = 0$; that is, the reaction is zeroth order in B. The experimentally determined rate law is therefore

$$rate = k\,[A]^2\,[B]^0$$

We can now calculate the rate constant by inserting the data from any row of Table 13.3.3into the experimentally determined rate law and solving for *k*. Using Experiment 2, we obtain

$$19. \times 10^{-3}\ M/min = k\,(0.75\ M)^2$$

$$3.4 \times 10^{-2}\ M^{-1}min^{-1} = k$$

You should verify that using data from any other row of Table 13.3.3 gives the same rate constant. This must be true as long as the experimental conditions, such as temperature and solvent, are the same.

Example 13.3.5

Nitric oxide is produced in the body by several different enzymes and acts as a signal that controls blood pressure, long-term memory, and other critical functions. The major route for removing NO from biological fluids is via reaction with O_2 to give NO_2, which then reacts rapidly with water to give nitrous acid and nitric acid:

$$2NO + O_2 \longrightarrow 2NO_2 \xrightarrow{H_2O} HNO_2 + HNO_3$$

These reactions are important in maintaining steady levels of NO. The following table lists kinetics data for the reaction of NO with O_2 at 25°C:

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

Determine the rate law for the reaction and calculate the rate constant.

Experiment	$[NO]_0$ (M)	$[O_2]_0$ (M)	Initial Rate (M/s)
1	0.0235	0.0125	7.98×10^{-3}
2	0.0235	0.0250	15.9×10^{-3}
3	0.0470	0.0125	32.0×10^{-3}
4	0.0470	0.0250	63.5×10^{-3}

Given: balanced chemical equation, initial concentrations, and initial rates

Asked for: rate law and rate constant

Strategy:

A Compare the changes in initial concentrations with the corresponding changes in rates of reaction to determine the reaction order for each species. Write the rate law for the reaction.

B Using data from any experiment, substitute appropriate values into the rate law. Solve the rate equation for *k*.

Solution:

A Comparing Experiments 1 and 2 shows that as $[O_2]$ is doubled at a constant value of $[NO_2]$, the reaction rate approximately doubles. Thus the reaction rate is proportional to $[O_2]^1$, so the reaction is first order in O_2. Comparing Experiments 1 and 3 shows that the reaction rate essentially quadruples when [NO] is doubled and $[O_2]$ is held constant. That is, the reaction rate is proportional to $[NO]^2$, which indicates that the reaction is second order in NO. Using these relationships, we can write the rate law for the reaction:

$$rate = k[NO]^2[O_2]$$

B The data in any row can be used to calculate the rate constant. Using Experiment 1, for example, gives

$$k = \frac{k}{[NO]^2[O_2]} = \frac{7.98 \times 10{-}3\ M/s}{(0.0235\ M)^2(0.0125\ M)} = 1.16 \times 103\ M^{-2}s^{-1}$$

The overall reaction order ($m + n$) is 3, so this is a third-order reaction, a reaction whose rate is determined by three reactants. The units of the rate constant become more complex as the overall reaction order increases.

Exercise

The peroxydisulfate ion ($S_2O_8^{2-}$) is a potent oxidizing agent that reacts rapidly with iodide ion in water:

$$S_2O_8^{2-}(aq) + 3I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_3^-(aq)$$

The following table lists kinetics data for this reaction at 25°C. Determine the rate law and calculate the rate constant.

Experiment	$[S_2O_8^{2-}]_0$ (M)	$[I^-]_0$ (M)	Initial Rate (M/s)
1	0.27	0.38	2.05
2	0.40	0.38	3.06
3	0.40	0.22	1.76

Answer: rate = $k[S_2O_8^{2-}][I^-]$; $k = 20\ M^{-1}{\cdot}s^{-1}$

Summary

The reaction rate of a **zeroth-order reaction** is independent of the concentration of the reactants. The reaction rate of a **first-order reaction** is directly proportional to the concentration of one reactant. The reaction rate of a simple **second-order reaction** is proportional to the square of the concentration of one reactant. Knowing the **rate law** of a reaction gives clues to the **reaction mechanism**.

Key Takeaway

- Either the differential rate law or the integrated rate law can be used to determine the reaction order from experimental data.

Key Equations

zeroth-order reaction

Equation 13.3.1 $rate = -\frac{d[A]}{dt} = k$

Equation 13.3.4: $[A] = [A_0] - kt$

first-order reaction

Equation 13.3.7: $rate = -\frac{d[A]}{dt} = k[A]$

Equation 13.3.12: $[A] = [A_0]e^{-kt}$

Equation 13.3/10: $ln[A] = ln[A_0] - kt$

second-order reaction

Equation 13.3.13: $rate = -\frac{d[A]}{dt} = k[reactant]^2$

Equation 13.3.17: $\frac{1}{[A]} = \frac{1}{[A_0]} + kt$

Conceptual Problems

1. What are the characteristics of a zeroth-order reaction? Experimentally, how would you determine whether a reaction is zeroth order?
2. Predict whether the following reactions are zeroth order and explain your reasoning.
    1. a substitution reaction of an alcohol with HCl to form an alkyl halide and water
    2. catalytic hydrogenation of an alkene
    3. hydrolysis of an alkyl halide to an alcohol
    4. enzymatic conversion of nitrate to nitrite in a soil bacterium
3. In a first-order reaction, what is the advantage of using the integrated rate law expressed in natural logarithms over the rate law expressed in exponential form?
4. If the reaction rate is directly proportional to the concentration of a reactant, what does this tell you about (a) the reaction order with respect to the reactant and (b) the overall reaction order?
5. The reaction of NO with O_2 is found to be second order with respect to NO and first order with respect to O_2. What is the overall reaction order? What is the effect of doubling the concentration of each reagent on the reaction rate?

Numerical Problems

1. Iodide reduces Fe(III) according to the following reaction:

    $2Fe^{3+}(soln) + 2I^{-}(soln) \rightarrow 2Fe^{2+}(soln) + I_2(soln)$

    Experimentally, it was found that doubling the concentration of Fe(III) doubled the reaction rate, and doubling the iodide concentration increased the reaction rate by a factor of 4. What is the reaction order with respect to each species? What is the overall rate law? What is the overall reaction order?

2. Benzoyl peroxide is a medication used to treat acne. Its rate of thermal decomposition at several concentrations was determined experimentally, and the data were tabulated as follows:

Experiment	$[\text{Benzoyl Peroxide}]_0$ (M)	Initial Rate (M/s)
1	1.00	2.22×10^{-4}
2	0.70	1.64×10^{-4}
3	0.50	1.12×10^{-4}
4	0.25	0.59×10^{-4}

    What is the reaction order with respect to benzoyl peroxide? What is the rate law for this reaction?

3. 1-Bromopropane is a colorless liquid that reacts with $S_2O_3^{2-}$ according to the following reaction:

    $C_3H_7Br + S_2O_3^{2-} \rightarrow C_3H_7S_2O_3^{-} + Br^{-}$

    The reaction is first order in 1-bromopropane and first order in $S_2O_3^{2-}$, with a rate constant of $8.05 \times 10^{-4}\ M^{-1}{\cdot}s^{-1}$. If you began a reaction with 40 mmol/100 mL of C_3H_7Br and an equivalent concentration of $S_2O_3^{2-}$, what would the initial reaction rate be? If you were to decrease the concentration of each reactant to 20 mmol/100 mL, what would the initial reaction rate be?

4. The experimental rate law for the reaction 3A + 2B → C + D was found to be $\Delta[C]/\Delta t = k[A]^2[B]$ for an overall reaction that is third order. Because graphical analysis is difficult beyond second-order reactions, explain the procedure for determining the rate law experimentally.

Answers

1. First order in Fe^{3+}; second order in I^-; third order overall; rate = $k[Fe^{3+}][I^-]^2$.
2.
3. 1.29×10^{-4} M/s; 3.22×10^{-5} M/s
4.

Contributors

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Chapter 13.4: Using Graphs to Determine Rate Laws, Rate Constants and Reaction Orders

Learning Objective

- To use graphs to analyze the kinetics of a reaction.

In Section 13.3, you learned that the integrated rate law for each common type of reaction (zeroth, first, or second order in a single reactant) can be plotted as a straight line. Using these plots offers an alternative to the methods described for showing how reactant concentration changes with time and determining reaction order.

We will illustrate the use of these graphs by considering the thermal decomposition of NO_2 gas at elevated temperatures, which occurs according to the following reaction:

$$2NO_2\,(g) \xrightarrow{\Delta} 2NO\,(g) + O_2\,(g)$$

Experimental data for this reaction at 330°C are listed in Table 13.4.1; they are provided as $[NO_2]$, $\ln[NO_2]$, and $1/[NO_2]$ versus time to correspond to the integrated rate laws for zeroth-, first-, and second-order reactions, respectively. The actual concentrations of NO_2 are plotted versus time in part (a) in Figure 13.4.1. Because the plot of $[NO_2]$ versus t is not a straight line, we know the reaction is not zeroth order in NO_2. A plot of $\ln[NO_2]$ versus t (part (b) in Figure 13.4.1) shows us that the reaction is not first order in NO_2 because a first-order reaction would give a straight line. Having eliminated zeroth-order and first-order behavior, we construct a plot of $1/[NO_2]$ versus t (part (c) in Figure 13.4.1). This plot is a straight line, indicating that the reaction is second order in NO_2.

Table 13.4.1 Concentration of NO_2 as a Function of Time at 330°C

Time (s)	$[NO_2]$ (M)	$\ln[NO_2]$	$1/[NO_2]$ (M^{-1})
0	1.00×10^{-2}	−4.605	100
60	6.83×10^{-3}	−4.986	146
120	5.18×10^{-3}	−5.263	193
180	4.18×10^{-3}	−5.477	239
240	3.50×10^{-3}	−5.655	286
300	3.01×10^{-3}	−5.806	332
360	2.64×10^{-3}	−5.937	379

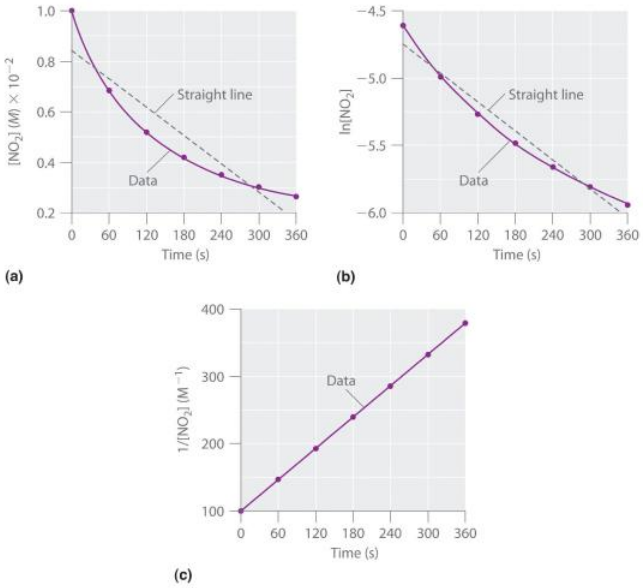


Figure 13.4.1 The Decomposition of NO_2 These plots show the decomposition of a sample of NO_2 at 330°C as (a) the concentration of NO_2 versus t, (b) the natural logarithm of $[NO_2]$ versus t, and (c) $1/[NO_2]$ versus t.

We have just determined the reaction order using data from a single experiment by plotting the concentration of the reactant as a function of time. Because of the characteristic shapes of the lines shown in Figure 13.4.2, the graphs can be used to determine the reaction order of an unknown reaction. In contrast, the method described in Section 13.3 required multiple experiments at different NO_2 concentrations as well as accurate initial rates of reaction, which can be difficult to obtain for rapid reactions.

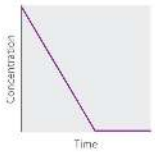
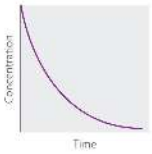
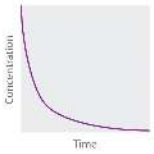
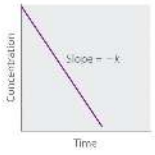
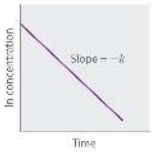
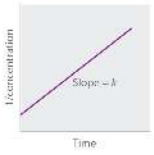
	Zeroth Order	First Order	Second Order
Differential rate law	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$
Concentration vs. time			
Integrated rate law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$ or $\ln[A] = \ln[A]_0 - kt$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$
Straight-line plot to determine rate constant			
Relative rate vs. concentration	[A], M | Rate, M/s 1 | 1 2 | 1 3 | 1	[A], M | Rate, M/s 1 | 1 2 | 2 3 | 3	[A], M | Rate, M/s 1 | 1 2 | 4 3 | 9
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$
Units of k, rate constant	M/s	1/s	$M^{-1}\cdot s^{-1}$

Figure 13.4.2 Properties of Reactions That Obey Zeroth-, First-, and Second-Order Rate Laws

Example 13.4.1

Dinitrogen pentoxide (N_2O_5) decomposes to NO_2 and O_2 at relatively low temperatures in the following reaction:

$$2N_2O_5\,(soln) \rightarrow 4NO_2\,(soln) + O_2\,(g)$$

This reaction is carried out in a CCl_4 solution at 45°C. The concentrations of N_2O_5 as a function of time are listed in the following table, together with the natural logarithms and reciprocal N_2O_5 concentrations. Plot a graph of the concentration versus *t*, ln concentration versus *t*, and 1/concentration versus *t* and then determine the rate law and calculate the rate constant.

Time (s)	$[N_2O_5]$ (M)	$\ln[N_2O_5]$	$1/[N_2O_5]$ (M^{-1})
0	0.0365	−3.310	27.4
600	0.0274	−3.597	36.5
1200	0.0206	−3.882	48.5
1800	0.0157	−4.154	63.7
2400	0.0117	−4.448	85.5
3000	0.00860	−4.756	116
3600	0.00640	−5.051	156

Given: balanced chemical equation, reaction times, and concentrations

Asked for: graph of data, rate law, and rate constant

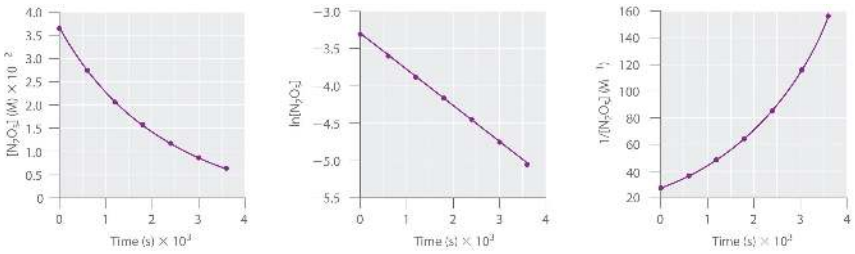
Strategy:

A Use the data in the table to separately plot concentration, the natural logarithm of the concentration, and the reciprocal of the concentration (the vertical axis) versus time (the horizontal axis). Compare the graphs with those in Figure 13.4.2 to determine the reaction order.

B Write the rate law for the reaction. Using the appropriate data from the table and the linear graph corresponding to the rate law for the reaction, calculate the slope of the plotted line to obtain the rate constant for the reaction.

Solution:

A Here are plots of $[N_2O_5]$ versus *t*, $\ln[N_2O_5]$ versus *t*, and $1/[N_2O_5]$ versus *t*:



The plot of $\ln[N_2O_5]$ versus *t* gives a straight line, whereas the plots of $[N_2O_5]$ versus *t* and $1/[N_2O_5]$ versus *t* do not. This means that the decomposition of N_2O_5 is first order in $[N_2O_5]$.

B The rate law for the reaction is therefore

$$rate = k\,[N_2O_5]$$

Calculating the rate constant is straightforward because we know that the slope of the plot of ln[A] versus *t* for a first-order reaction is $-k$. We can calculate the slope using any two points that lie on the line in the plot of $\ln[N_2O_5]$ versus *t*. Using the points for $t = 0$ and 3000 s,

$$slope = \frac{ln\,[N_2O_5]_{3000} - ln\,[N_2O_5]_0}{3000\ s - 0\ s} = \frac{[-4.756] - [-3.310]}{3000\ s} = 4.820 \times 10^{-4}\ s^{-1}$$

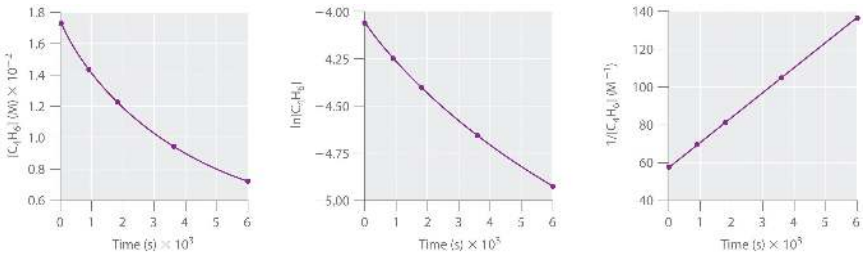
Thus $k = 4.820 \times 10^{-4}\ s^{-1}$.

Exercise

1,3-Butadiene (CH_2=CH—CH=CH_2; C_4H_6) is a volatile and reactive organic molecule used in the production of rubber. Above room temperature, it reacts slowly to form products. Concentrations of C_4H_6 as a function of time at 326°C are listed in the following table along with ln[C_4H_6] and the reciprocal concentrations. Graph the data as concentration versus *t*, ln concentration versus *t*, and 1/concentration versus *t*. Then determine the reaction order in C_4H_6, the rate law, and the rate constant for the reaction.

Time (s)	[C_4H_6] (M)	ln[C_4H_6]	1/[C_4H_6] (M^{-1})
0	1.72×10^{-2}	−4.063	58.1
900	1.43×10^{-2}	−4.247	69.9
1800	1.23×10^{-2}	−4.398	81.3
3600	9.52×10^{-3}	−4.654	105
6000	7.30×10^{-3}	−4.920	137

Answer:



second order in C_4H_6; rate = $k[C_4H_6]^2$; $k = 1.3 \times 10^{-2}\ M^{-1}{\cdot}s^{-1}$

Summary

For a zeroth-order reaction, a plot of the concentration of any reactant versus time is a straight line with a slope of −*k*. For a first-order reaction, a plot of the natural logarithm of the concentration of a reactant versus time is a straight line with a slope of −*k*. For a second-order reaction, a plot of the inverse of the concentration of a reactant versus time is a straight line with a slope of *k*.

Key Takeaway

- Plotting the concentration of a reactant as a function of time produces a graph with a characteristic shape that can be used to identify the reaction order in that reactant.

Conceptual Problems

1. Compare first-order differential and integrated rate laws with respect to the following. Is there any information that can be obtained from the integrated rate law that cannot be obtained from the differential rate law?
    1. the magnitude of the rate constant
    2. the information needed to determine the order
    3. the shape of the graphs
2. In the single-step, second-order reaction 2A → products, how would a graph of [A] versus time compare to a plot of 1/[A] versus time? Which of these would be the most similar to the same set of graphs for A during the single-step, second-order reaction A + B → products? Explain.

3. For reactions of the same order, what is the relationship between the magnitude of the rate constant and the reaction rate? If you were comparing reactions with different orders, could the same arguments be made? Why?

Answers

1. 1. For a given reaction under particular conditions, the magnitude of the first-order rate constant does not depend on whether a differential rate law or an integrated rate law is used.
   2. The differential rate law requires multiple experiments to determine reactant order; the integrated rate law needs only one experiment.
   3. Using the differential rate law, a graph of concentration versus time is a curve with a slope that becomes less negative with time, whereas for the integrated rate law, a graph of ln[reactant] versus time gives a straight line with slope = $-k$. The integrated rate law allows you to calculate the concentration of a reactant at any time during the reaction; the differential rate law does not.
2.
3. The reaction rate increases as the rate constant increases. We cannot directly compare reaction rates and rate constants for reactions of different orders because they are not mathematically equivalent.

Numerical Problems

1. One method of using graphs to determine reaction order is to use relative rate information. Plotting the log of the relative rate versus log of relative concentration provides information about the reaction. Here is an example of data from a zeroth-order reaction:

Relative [A] (M)	Relative Rate (M/s)
1	1
2	1
3	1

   Varying [A] does not alter the reaction rate. Using the relative rates in the table, generate plots of log(rate) versus log(concentration) for zeroth-, first- and second-order reactions. What does the slope of each line represent?

2. The table below follows the decomposition of N_2O_5 gas by examining the partial pressure of the gas as a function of time at 45°C. What is the reaction order? What is the rate constant? How long would it take for the pressure to reach 105 mmHg at 45°C?

Time (s)	Pressure (mmHg)
0	348
400	276
1600	156
3200	69
4800	33

Contributors

- Anonymous

Modified by Joshua Halpern (Howard University), Scott Sinex, and Scott Johnson (PGCC)

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Chapter 13.5: Half Lives and Radioactive Decay Kinetics

Learning Objective

- To know how to use half-lives to describe the rates of first-order reactions.

Half-Lives

Another approach to describing reaction rates is based on the time required for the concentration of a reactant to decrease to one-half its initial value. This period of time is called the half-lifeThe period of time it takes for the concentration of a reactant to decrease to one-half its initial value. of the reaction, written as $t_{1/2}$. Thus the half-life of a reaction is the time required for the reactant concentration to decrease from $[A]_0$ to $[A]_0/2$. If two reactions have the same order, the faster reaction will have a shorter half-life, and the slower reaction will have a longer half-life.

The half-life of a first-order reaction under a given set of reaction conditions is a constant. This is not true for zeroth- and second-order reactions. The half-life of a first-order reaction is *independent of the concentration of the reactants*. This becomes evident when we rearrange the integrated rate law for a first-order reaction (Equation 13.5.1) to produce the following equation:

$$ln\frac{[A]_0}{[A]} = kt$$

Substituting $[A]_0/2$ for [A] and $t_{1/2}$ for t (to indicate a half-life) into Equation 13.5.1 gives

$$ln\frac{[A]_0}{[A]_0/2} = ln2 = kt_{1/2}$$

The natural logarithm of 2 (to three decimal places) is 0.693. Substituting this value into the equation, we obtain the expression for the half-life of a first-order reaction:

$$t_{1/2} = \frac{0.693}{k}$$

Thus, for a first-order reaction, each successive half-life is the same length of time, as shown in Figure 13.5.1 , and is independent of [A].

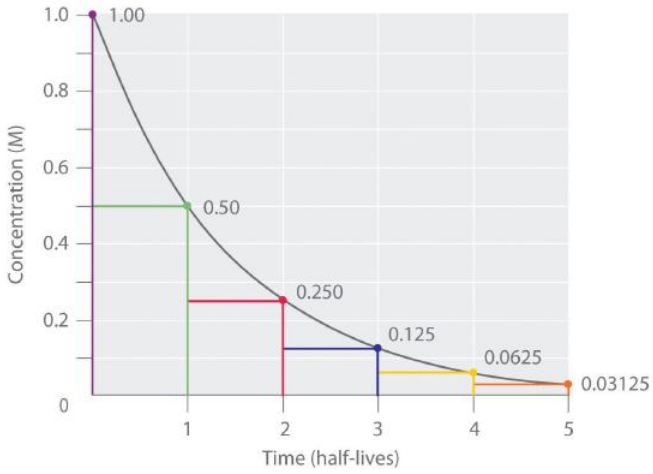


Figure 13.5.1 The Half-Life of a First-Order Reaction *This plot shows the concentration of the reactant in a first-order reaction as a function of time and identifies a series of half-lives, intervals in which the reactant concentration decreases by a factor of 2. In a first-order reaction, every half-life is the same length of time.*

If we know the rate constant for a first-order reaction, then we can use half-lives to predict how much time is needed for the reaction to reach a certain percent completion.

Number of Half-Lives	Percentage of Reactant Remaining	
1	$\frac{100\%}{2} = 50\%$	$\frac{1}{2}(100\%) = 50\%$
2	$\frac{50\%}{2} = 25\%$	$\frac{1}{2}\left(\frac{1}{2}\right)(100\%) = 25\%$
3	$\frac{25\%}{2} = 12.5\%$	$\frac{1}{2}\left(\frac{1}{2}\right)\left(\frac{1}{2}\right)(100\%) = 12.5\%$
n	$\frac{100\%}{2^n}$	$\left(\frac{1}{2}\right)^n(100\%) = \left(\frac{1}{2}\right)^n\%$

As you can see from this table, the amount of reactant left after n half-lives of a first-order reaction is $(1/2)^n$ times the initial concentration.

Note the Pattern

For a first-order reaction, the concentration of the reactant decreases by a constant with each half-life and is independent of [A].

Example 13.5.1

The anticancer drug cisplatin hydrolyzes in water with a rate constant of 1.5×10^{-3} min^{-1} at pH 7.0 and 25°C. Calculate the half-life for the hydrolysis reaction under these conditions. If a freshly prepared solution of cisplatin has a concentration of 0.053 M, what will be the concentration of cisplatin after 5 half-lives? after 10 half-lives? What is the percent completion of the reaction after 5 half-lives? after 10 half-lives?

Given: rate constant, initial concentration, and number of half-lives

Asked for: half-life, final concentrations, and percent completion

Strategy:

A Use Equation 13.5.3 to calculate the half-life of the reaction.

B Multiply the initial concentration by 1/2 to the power corresponding to the number of half-lives to obtain the remaining concentrations after those half-lives.

C Subtract the remaining concentration from the initial concentration. Then divide by the initial concentration, multiplying the fraction by 100 to obtain the percent completion.

Solution:

A We can calculate the half-life of the reaction using Equation 13.5.3:

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.5 \times 10^{-3}\ min^{-1}} = 4.6 \times 10^{2}\ min$$

Thus it takes almost 8 h for half of the cisplatin to hydrolyze.

B After 5 half-lives (about 38 h), the remaining concentration of cisplatin will be as follows:

$$\frac{0.053\ M}{2^5} = \frac{0.053\ M}{32} = 0.0017\ M$$

After 10 half-lives (77 h), the remaining concentration of cisplatin will be as follows:

$$\frac{0.053\ M}{2^{10}} = \frac{0.053\ M}{1024} = 5.2 \times 10^{-5}\ M$$

C The percent completion after 5 half-lives will be as follows:

$$percent\ completion = \frac{(0.053\ M - 0.0017\ M)\,100}{0.53\ M} = 97\%$$

The percent completion after 10 half-lives will be as follows:

$$percent\ completion = \frac{(0.053\ M - 5.2 \times 10^{-5}\ M)\,100}{0.53\ M} = 100\%$$

Thus a first-order chemical reaction is 97% complete after 5 half-lives and 100% complete after 10 half-lives.

Exercise

In Example 4 you found that ethyl chloride decomposes to ethylene and HCl in a first-order reaction that has a rate constant of 1.6×10^{-6} s^{-1} at 650°C. What is the half-life for the reaction under these conditions? If a flask that originally contains 0.077 M ethyl chloride is heated at 650°C, what is the concentration of ethyl chloride after 4 half-lives?

Answer: 4.3×10^{5} s = 120 h = 5.0 days; 4.8×10^{-3} M

Radioactive Decay Rates

As you learned in Chapter 1 radioactivity, or radioactive decay, is the emission of a particle or a photon that results from the spontaneous decomposition of the unstable nucleus of an atom. The rate of radioactive decay is an intrinsic property of each radioactive isotope that is independent of the chemical and physical form of the radioactive isotope. The rate is also independent of temperature. In this section, we will describe radioactive decay rates and how half-lives can be used to monitor radioactive decay processes.

In any sample of a given radioactive substance, the number of atoms of the radioactive isotope must decrease with time as their nuclei decay to nuclei of a more stable isotope. Using *N* to represent the number of atoms of the radioactive isotope, we can define the rate of decayThe decrease in the number of a radioisotope's nuclei per unit time. of the sample, which is also called its activity (*A*)The decrease in the number of a radioisotope's nuclei per unit time: A=−dN/dt as the decrease in the number of the radioisotope's nuclei per unit time:

$$A = -\frac{dN}{dt}$$

Activity is usually measured in *disintegrations per second (dps) or disintegrations per minute (dpm)*.

The activity of a sample is directly proportional to the number of atoms of the radioactive isotope in the sample:

$$A = kN$$

Here, the symbol *k* is the *radioactive decay constant*, which has units of inverse time (e.g., s^{-1}, yr^{-1}) and a characteristic value for each radioactive isotope. If we combine Equation 13.5.4 and Equation 13.5.5, we obtain the relationship between the number of decays per unit time and the number of atoms of the isotope in a sample:

$$-\frac{dN}{dt} = kN$$

Equation 13.5.6 is the same as the equation for the reaction rate of a first-order reaction (Equation 13.3.2), except that it uses numbers of atoms instead of concentrations. In fact, radioactive decay *is* a first-order process and can be described in terms of either the differential rate law (Equation 13.5.7) or the integrated rate law:

$$N = N_0 e^{-kt}$$

$$ln\frac{N}{N_0} = -kt$$

Because radioactive decay is a first-order process, the time required for half of the nuclei in any sample of a radioactive isotope to decay is a constant, called the *half-life of the isotope*. The half-life tells us how radioactive an isotope is (the number of decays per unit time); thus it is the most commonly cited property of any radioisotope. For a given number of atoms, isotopes with shorter half-lives decay more rapidly, undergoing a greater number of radioactive decays per unit time than do isotopes with longer half-lives. The half-lives of several isotopes are listed in Table 13.5.1, along with some of their applications.

Table 13.5.1 Half-Lives and Applications of Some Radioactive Isotopes

Radioactive Isotope	Half-Life	Typical Uses
hydrogen-3 (tritium)	12.32 yr	biochemical tracer
carbon-11	20.33 min	positron emission tomography (biomedical imaging)
carbon-14	5.70×10^3 yr	dating of artifacts
sodium-24	14.951 h	cardiovascular system tracer
phosphorus-32	14.26 days	biochemical tracer
potassium-40	1.248×10^9 yr	dating of rocks
iron-59	44.495 days	red blood cell lifetime tracer
cobalt-60	5.2712 yr	radiation therapy for cancer
technetium-99*m**	6.006 h	biomedical imaging
iodine-131	8.0207 days	thyroid studies tracer
radium-226	1.600×10^3 yr	radiation therapy for cancer
uranium-238	4.468×10^9 yr	dating of rocks and Earth's crust
americium-241	432.2 yr	smoke detectors

*The *m* denotes metastable, where an excited state nucleus decays to the ground state of the same isotope.

Note the Pattern

Radioactive decay is a first-order process.

Radioisotope Dating Techniques

In our earlier discussion, we used the half-life of a first-order reaction to calculate how long the reaction had been occurring. Because nuclear decay reactions follow first-order kinetics and have a rate constant that is independent of temperature and the chemical or physical environment, we can perform similar calculations using the half-lives of isotopes to estimate the ages of geological and archaeological artifacts. The techniques that have been developed for this application are known as *radioisotope dating* techniques.

The most common method for measuring the age of ancient objects is *carbon-14 dating*. The carbon-14 isotope, created continuously in the upper regions of Earth's atmosphere by nuclear reactions initiated by energetic cosmic rays, reacts with atmospheric oxygen or ozone to form $^{14}CO_2$. As a result, the CO_2 that plants use as a carbon source for synthesizing organic compounds always includes a certain proportion of $^{14}CO_2$ molecules as well as nonradioactive $^{12}CO_2$ and $^{13}CO_2$. Any animal that eats a plant ingests a mixture of organic compounds that contains approximately the same proportions of carbon isotopes as those in the atmosphere. When the animal or plant dies, the carbon-14 nuclei in its tissues decay to nitrogen-14 nuclei by a radioactive process known as *beta decay*, which releases low-energy electrons (β particles) that can be detected and measured:

$$^{14}C \rightarrow ^{14}N + \beta^-$$

The half-life for this reaction is 5700 ± 30 yr.

The $^{14}C/^{12}C$ ratio in living organisms is 1.3×10^{-12}, with a decay rate of 15 dpm/g of carbon (Figure 13.5.2). Comparing the disintegrations per minute per gram of carbon from an archaeological sample with those from a recently living sample enables scientists to estimate the age of the artifact, as illustrated in Example 11. Using this method implicitly assumes that the $^{14}CO_2/^{12}CO_2$ ratio in the atmosphere is constant, which is not strictly correct because the intensity of the cosmic ray flux varies somewhat. Moreover the method is not useful for samples that were alive after 1945 because of the relatively large amount of ^{14}C created by nuclear bomb explosions in the atmosphere. Other methods, such as dating by counting tree-rings and comparing the

tree-ring dates to the $^{14}C/^{12}C$ ratio in a ring, have been used to calibrate the dates obtained by radiocarbon dating. All radiocarbon dates reported are now corrected for minor changes in the $^{14}CO_2/^{12}CO_2$ ratio over time.

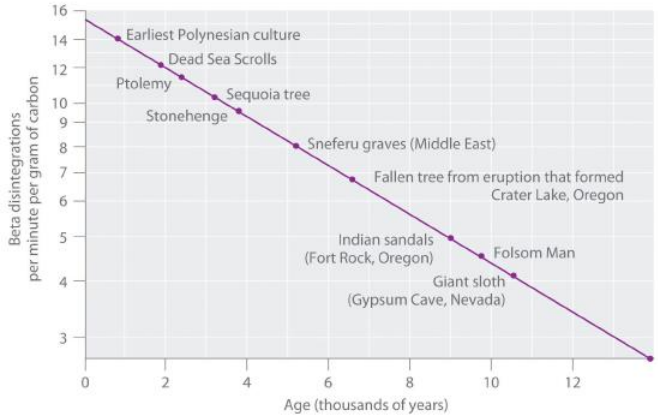


Figure 13.5.2 Radiocarbon Dating *A plot of the specific activity of ^{14}C versus age for a number of archaeological samples shows an inverse linear relationship between ^{14}C content (a log scale) and age (a linear scale).*

Example 13.5.2

In 1990, the remains of an apparently prehistoric man were found in a melting glacier in the Italian Alps. Analysis of the ^{14}C content of samples of wood from his tools gave a decay rate of 8.0 dpm/g carbon. How long ago did the man die?

Given: isotope and final activity

Asked for: elapsed time

Strategy:

A Use Equation 13.5.5 to calculate N_0/N. Then substitute the value for the half-life of ^{14}C into Equation 13.5.3 to find the rate constant for the reaction.

B Using the values obtained for N_0/N and the rate constant, solve Equation 13.5.7 to obtain the elapsed time.

Solution:

We know the initial activity from the isotope's identity (15 dpm/g), the final activity (8.0 dpm/g), and the half-life, so we can use the integrated rate law for a first-order nuclear reaction (Equation 13.5.7) to calculate the elapsed time (the amount of time elapsed since the wood for the tools was cut and began to decay).

$$ln\frac{N}{N_0} = -kt$$

$$\frac{ln\,(N_0/N)}{k} = t$$

A From Equation 13.5.5, we know that $A = kN$. We can therefore use the initial and final activities (A_0 = 15 dpm and A = 8.0 dpm) to calculate N_0/N:

$$\frac{A_0}{A} = \frac{\cancel{k}N_0}{\cancel{k}N} = \frac{N_0}{N} = \frac{15.}{8.0}$$

Now we need only calculate the rate constant for the reaction from its half-life (5730 yr) using Equation 13.5.3:

$$t_{1/2} = \frac{0.693}{k}$$

This equation can be rearranged as follows:

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730\ yr} = 1.22 \times 10^{-4}\ yr^{-1}$$

B Substituting into the equation for t,

$$t = \frac{ln\,(N_0/N)}{k} = \frac{ln\,(15./8.0)}{1.22 \times 10^{-4}\ yr^{-1}} = 5.2 \times 10^3\ yr$$

From our calculations, the man died 5200 yr ago.

Exercise

It is believed that humans first arrived in the Western Hemisphere during the last Ice Age, presumably by traveling over an exposed land bridge between Siberia and Alaska. Archaeologists have estimated that this occurred about 11,000 yr ago, but some argue that recent discoveries in several sites in North and South America suggest a much earlier arrival. Analysis of a sample of charcoal from a fire in one such site gave a ^{14}C decay rate of 0.4 dpm/g of carbon. What is the approximate age of the sample?

Answer: 30,000 yr

Summary

The **half-life** of a reaction is the time required for the reactant concentration to decrease to one-half its initial value. The half-life of a first-order reaction is a constant that is related to the rate constant for the reaction: $t_{1/2} = 0.693/k$.

Radioactive decay reactions are first-order reactions. The **rate of decay**, or **activity**, of a sample of a radioactive substance is the decrease in the number of radioactive nuclei per unit time.

Key Takeaways

- The half-life of a first-order reaction is independent of the concentration of the reactants.
- The half-lives of radioactive isotopes can be used to date objects.

Key Equations

half-life of first-order reaction

Equation 13.5.3 $t_{1/2} = \frac{0.693}{k}$

radioactive decay

Equation 13.5.5: $A = kN$

Conceptual Problems

1. What do chemists mean by the *half-life* of a reaction?
2. If a sample of one isotope undergoes more disintegrations per second than the same number of atoms of another isotope, how do their half-lives compare?

Numerical Problems

1. Half-lives for the reaction A + B → C were calculated at three values of $[A]_0$, and [B] was the same in all cases. The data are listed in the following table:

$[A]_0$ (M)	$t_{½}$ (s)
0.50	420
0.75	280
1.0	210

   Does this reaction follow first-order kinetics? On what do you base your answer?

2. Ethyl-2-nitrobenzoate ($NO_2C_6H_4CO_2C_2H_5$) hydrolyzes under basic conditions. A plot of $[NO_2C_6H_4CO_2C_2H_5]$ versus t was used to calculate $t_{½}$, with the following results:

$[NO_2C_6H_4CO_2C_2H_5]$ (M/cm^3)	$t_{½}$ (s)
0.050	240
0.040	300
0.030	400

Is this a first-order reaction? Explain your reasoning.

3. Azomethane ($CH_3N_2CH_3$) decomposes at 600 K to C_2H_6 and N_2. The decomposition is first order in azomethane. Calculate $t_{½}$ from the data in the following table:

Time (s)	$P_{Azomethane}$ (atm)
0	8.2×10^{-2}
2000	3.99×10^{-2}
4000	1.94×10^{-2}

How long will it take for the decomposition to be 99.9% complete?

4. The first-order decomposition of hydrogen peroxide has a half-life of 10.7 h at 20°C. What is the rate constant (expressed in s^{-1}) for this reaction? If you started with a solution that was 7.5×10^{-3} M H_2O_2, what would be the initial rate of decomposition (M/s)? What would be the concentration of H_2O_2 after 3.3 h?

Answers

1. No; the reaction is second order in A because the half-life decreases with increasing reactant concentration according to $t_{1/2} = 1/k[A_0]$.
2.
3. $t_{1/2} = 1.92 \times 10^3$ s or 1920 s; 19100 s or 5.32 hrs.
4.

Contributors

- Anonymous

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Chapter 13.6: Reaction Rates - A Microscopic View

Learning Objective

- To determine the individual steps of a simple reaction.

One of the major reasons for studying chemical kinetics is to use measurements of the macroscopic properties of a system, such as the rate of change in the concentration of reactants or products with time, to discover the sequence of events that occur at the molecular level during a reaction. This molecular description is the *mechanism* of the reaction; it describes how individual atoms, ions, or molecules interact to form particular products. The stepwise changes are collectively called the **reaction mechanism**.

In an internal combustion engine, for example, isooctane reacts with oxygen to give carbon dioxide and water:

$$2C_8H_{18}\,(l) + 25O_2\,(g) \rightarrow 16CO_2\,(g) + 18H_2O\,(g)$$

For this reaction to occur in a single step, 25 dioxygen molecules and 2 isooctane molecules would have to collide simultaneously and be converted to 34 molecules of product, which is very unlikely. It is more likely that a complex series of reactions takes place in a stepwise fashion. Each individual reaction, which is called an elementary reactionEach of the complex series of reactions that take place in a stepwise fashion to convert reactants to products., involves one, two, or (rarely) three atoms, molecules, or ions. The overall sequence of elementary reactions is the mechanism of the reaction. *The sum of the individual steps, or elementary reactions, in the mechanism must give the balanced chemical equation for the overall reaction.*

Molecularity and the Rate-Determining Step

To demonstrate how the analysis of elementary reactions helps us determine the overall reaction mechanism, we will examine the much simpler reaction of carbon monoxide with nitrogen dioxide.

$$NO_2\,(g) + CO\,(g) \rightarrow NO\,(g) + CO_2\,(g)$$

From the balanced chemical equation, one might expect the reaction to occur via a collision of one molecule of NO_2 with a molecule of CO that results in the transfer of an oxygen atom from nitrogen to carbon. The experimentally determined rate law for the reaction, however, is as follows:

$$rate = k\,[NO_2]^2$$

The fact that the reaction is second order in [NO_2] and independent of [CO] tells us that it does not occur by the simple collision model outlined previously. If it did, its predicted rate law would be rate = k[NO_2][CO].

The following two-step mechanism is consistent with the rate law if step 1 is much slower than step 2:

$$\begin{array}{lll} step\ 1 & NO_2 + NO_2 \overset{slow}{\rightarrow} NO_3 + NO & elementary\ reaction \\ step\ 2 & \underline{NO_3 + CO \rightarrow NO_2 + CO_2} & elementary\ reaction \\ sum & NO_2 + CO \rightarrow NO + CO_2 & overall\ reaction \end{array}$$

According to this mechanism, the overall reaction occurs in two steps, or elementary reactions. Summing steps 1 and 2 and canceling on both sides of the equation gives the overall balanced chemical equation for the reaction. The NO_3 molecule is an intermediateA species in a reaction mechanism that does not appear in the balanced chemical equation for the overall reaction. in the reaction, a species that does not appear in the balanced chemical equation for the overall reaction. It is formed as a product of the first step but is consumed in the second step.

Note the Pattern

The sum of the elementary reactions in a reaction mechanism must give the overall balanced chemical equation of the reaction.

Using Molecularity to Describe a Rate Law

The molecularityThe number of molecules that collide during any step in a reaction mechanism. of an elementary reaction is the number of molecules that collide during that step in the mechanism. If there is only a single reactant molecule in an elementary reaction, that step is designated as *unimolecular*; if there are two reactant molecules, it is *bimolecular*; and if there are three reactant molecules (a relatively rare situation), it is *termolecular*. Elementary reactions that involve the simultaneous collision of

more than three molecules are highly improbable and have never been observed experimentally. (To understand why, try to make three or more marbles or pool balls collide with one another simultaneously!)

Writing the rate law for an elementary reaction is straightforward because we know how many molecules must collide simultaneously for the elementary reaction to occur; hence the order *of the elementary reaction* is the same as its molecularity (Table 13.6.1). In contrast, the rate law for the reaction cannot be determined from the balanced chemical equation for the overall reaction. The general rate law for a unimolecular elementary reaction (A → products) is rate = k[A]. For bimolecular reactions, the reaction rate depends on the number of collisions per unit time, which is proportional to the product of the concentrations of the reactants, as shown in Figure 13.6.1 For a bimolecular elementary reaction of the form A + B → products, the general rate law is rate = k[A][B].

Table 13.6.1 Common Types of Elementary Reactions and Their Rate Laws

Elementary Reaction	Molecularity	Rate Law	Reaction Order
A → products	unimolecular	rate = k[A]	first
2A → products	bimolecular	rate = k[A]^2	second
A + B → products	bimolecular	rate = k[A][B]	second
2A + B → products	termolecular	rate = k[A]^2[B]	third
A + B + C → products	termolecular	rate = k[A][B][C]	third

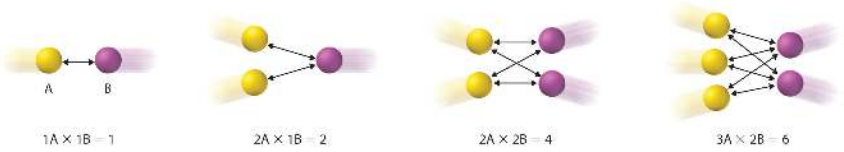


Figure 13.6.1 The Basis for Writing Rate Laws of Elementary Reactions *This diagram illustrates how the number of possible collisions per unit time between two reactant species, A and B, depends on the number of A and B particles present. The number of collisions between A and B particles increases as the product of the number of particles, not as the sum. This is why the rate law for an elementary reaction depends on the product of the concentrations of the species that collide in that step.*

Identifying the Rate-Determining Step

Note the important difference between writing rate laws for elementary reactions and the balanced chemical equation of the overall reaction. Because the balanced chemical equation does not necessarily reveal the individual elementary reactions by which the reaction occurs, we *cannot* obtain the rate law for a reaction from the overall balanced chemical equation alone. In fact, it is the rate law for the *slowest* overall reaction, which is the same as the rate law for the slowest step in the reaction mechanism, the rate-determining stepThe slowest step in a reaction mechanism., that must give the experimentally determined rate law for the overall reaction.This statement is true if one step is substantially slower than all the others, typically by a factor of 10 or more. If two or more slow steps have comparable rates, the experimentally determined rate laws can become complex. Our discussion is limited to reactions in which one step can be identified as being substantially slower than any other. The reason for this is that any process that occurs through a sequence of steps can take place no faster than the slowest step in the sequence. In an automotive assembly line, for example, a component cannot be used faster than it is produced. Similarly, blood pressure is regulated by the flow of blood through the smallest passages, the capillaries. Because movement through capillaries constitutes the rate-determining step in blood flow, blood pressure can be regulated by medications that cause the capillaries to contract or dilate. A chemical reaction that occurs via a series of elementary reactions can take place no faster than the slowest step in the series of reactions.



Rate-determining step. *The phenomenon of a rate-determining step can be compared to a succession of funnels. The smallest-diameter funnel controls the rate at which the bottle is filled, whether it is the first or the last in the series. Pouring liquid into the first funnel faster than it can drain through the smallest results in an overflow.*

Look at the rate laws for each elementary reaction in our example as well as for the overall reaction.

$$\textit{step 1} \quad NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO \qquad rate = k_1[NO_2]^2 \quad \textit{predicted}$$

$$\textit{step 2} \quad \underline{NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2} \qquad rate = k_2[NO_3][CO_2] \quad \textit{predicted}$$

$$\textit{sum} \quad NO_2 + CO \xrightarrow{k} NO + CO_2 \qquad rate = k[NO_2]^2 \quad \textit{observed}$$

The experimentally determined rate law for the reaction of NO_2 with CO is the same as the predicted rate law for step 1. This tells us that the first elementary reaction is the rate-determining step, so k for the overall reaction must equal k_1. That is, NO_3 is formed slowly in step 1, but once it is formed, it reacts very rapidly with CO in step 2.

Sometimes chemists are able to propose two or more mechanisms that are consistent with the available data. If a proposed mechanism predicts the wrong experimental rate law, however, the mechanism must be incorrect.

Example 13.6.1

In an alternative mechanism for the reaction of NO_2 with CO, N_2O_4 appears as an intermediate.

$$\textit{step 1} \qquad NO_2 + NO_2 \xrightarrow{k_1} N_2O_4$$

$$\textit{step 2} \quad \underline{N_2O_4 + CO \xrightarrow{k_2} NO + NO_2 + CO_2}$$

$$\textit{sum} \qquad NO_2 + CO \rightarrow NO + CO_2$$

Write the rate law for each elementary reaction. Is this mechanism consistent with the experimentally determined rate law (rate = $k[NO_2]^2$)?

Given: elementary reactions

Asked for: rate law for each elementary reaction and overall rate law

Strategy:

A Determine the rate law for each elementary reaction in the reaction.

B Determine which rate law corresponds to the experimentally determined rate law for the reaction. This rate law is the one for the rate-determining step.

Solution:

A The rate law for step 1 is rate = $k_1[NO_2]^2$; for step 2, it is rate = $k_2[N_2O_4][CO]$.

B If step 1 is slow (and therefore the rate-determining step), then the overall rate law for the reaction will be the same: rate = $k_1[NO_2]^2$. This is the same as the experimentally determined rate law. Hence this mechanism, with N_2O_4 as an intermediate, and the one described previously, with NO_3 as an intermediate, are kinetically indistinguishable. In this case, further experiments are

needed to distinguish between them. For example, the researcher could try to detect the proposed intermediates, NO_3 and N_2O_4, directly.

Exercise A

Iodine monochloride (ICl) reacts with H_2 as follows:

$$2ICl\,(g) + H_2\,(g) \rightarrow HCl\,(g) + I_2\,(s)$$

The experimentally determined rate law is rate = k[ICl][H_2]. Write a two-step mechanism for this reaction using only bimolecular elementary reactions and show that it is consistent with the experimental rate law. (Hint: HI is an intermediate.)

Answer:

$$\textit{step 1} \quad ICl + H_2 \xrightarrow{k_1} HCl + HI \quad rate = k_1\,[ICl]\,[H_2]\ slow$$

$$\textit{step 2} \quad \underline{HI + ICl \xrightarrow{k_2} HCl + I_2} \quad rate = k_2\,[HI]\,[ICl]\ fast$$

$$\textit{sum} \quad 2ICl + H_2 \rightarrow 2HCl + I_2$$

This mechanism is consistent with the experimental rate law *if* the first step is the rate-determining step.

Exercise B

The reaction between NO and H_2 occurs via a three-step process:

$$\textit{step 1} \quad NO + NO \xrightarrow{k_1} N_2O_2 + NO \quad fast$$

$$\textit{step 2} \quad N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O \quad slow$$

$$\textit{step3} \quad N_2O + H_2 \xrightarrow{k_3} N_2 + H_2O \quad fast$$

Write the rate law for each elementary reaction, write the balanced chemical equation for the overall reaction, and identify the rate-determining step. Is the rate law for the rate-determining step consistent with the experimentally derived rate law for the overall reaction: rate = k[NO]^2[H_2]^2?

Answer:

- rate = k_1[NO]^2;
- rate = k_2[N_2O_2][H_2];
- rate = k_3[N_2O][H_2];
- 2NO(g) + 2H_2(g) → N_2(g) + 2H_2O(g)
- step 2
- Yes, because the rate of formation of [N_2O_2] = k_1[NO]^2. Substituting k_1[NO]^2 for [N_2O_2] in the rate law for step 2 gives the experimentally derived rate law for the overall chemical reaction, where $k = k_1k_2$.

Chain Reactions

Many reaction mechanisms, like those discussed so far, consist of only two or three elementary reactions. Many others consist of long series of elementary reactions. The most common mechanisms are chain reactionsA reaction mechanism in which one or more elementary reactions that contain a highly reactive species repeat again and again during the reaction process., in which one or more elementary reactions that contain a highly reactive species repeat again and again during the reaction process. Chain reactions occur in fuel combustion, explosions, the formation of many polymers, and the tissue changes associated with aging. They are also important in the chemistry of the atmosphere.

Chain reactions are described as having three stages. The first is *initiation*, a step that produces one or more reactive intermediates. Often these intermediates are radicalsSpecies that have one or more unpaired valence electrons., species that have an unpaired valence electron. In the second stage, *propagation*, reactive intermediates are continuously consumed and regenerated while products are formed. Intermediates are also consumed but not regenerated in the final stage of a chain reaction, *termination*, usually by forming stable products.

Let us look at the reaction of methane with chlorine at elevated temperatures (400°C–450°C), a chain reaction used in industry to manufacture methyl chloride (CH_3Cl), dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4):

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$$

$$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$$

$$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$$

Direct chlorination generally produces a mixture of all four carbon-containing products, which must then be separated by distillation. In our discussion, we will examine only the chain reactions that lead to the preparation of CH_3Cl.

In the initiation stage of this reaction, the relatively weak Cl–Cl bond cleaves at temperatures of about 400°C to produce chlorine atoms (Cl·):

$$Cl_2 \rightarrow 2Cl\cdot$$

During propagation, a chlorine atom removes a hydrogen atom from a methane molecule to give HCl and CH_3·, the methyl radical:

$$Cl\cdot + CH_4 \rightarrow CH_3\cdot + HCl$$

The methyl radical then reacts with a chlorine molecule to form methyl chloride and another chlorine atom, Cl·:

$$CH_3\cdot + Cl_2 \rightarrow CH_3Cl + Cl\cdot$$

The sum of the propagation reactions is the same as the overall balanced chemical equation for the reaction:

$$\begin{array}{l} \cancel{Cl\cdot} + CH_4 \rightarrow \cancel{CH_3\cdot} + HCl \\ \cancel{CH_3\cdot} + Cl_2 \rightarrow CH_3Cl + \cancel{Cl\cdot} \\ \hline Cl_2 + CH_4 \rightarrow CH_3Cl + HCl \end{array}$$

Without a chain-terminating reaction, propagation reactions would continue until either the methane or the chlorine was consumed. Because radical species react rapidly with almost anything, however, including each other, they eventually form neutral compounds, thus terminating the chain reaction in any of three ways:

$$\begin{array}{r} CH_3\cdot + Cl\cdot \rightarrow CH_3Cl \\ CH_3\cdot + CH_3\cdot \rightarrow H_3CCH_3 \\ Cl\cdot + Cl\cdot \rightarrow Cl_2 \end{array}$$

Here is the overall chain reaction, with the desired product (CH_3Cl) in bold:

Initiation:	$Cl_2 \rightarrow 2Cl\cdot$
Propagation:	$Cl\cdot + CH_4 \rightarrow CH_3\cdot + HCl$
	$CH_3\cdot + Cl_2 \rightarrow \mathbf{CH_3Cl} + Cl\cdot$
Termination:	$CH_3\cdot + Cl\cdot \rightarrow \mathbf{CH_3Cl}$
	$CH_3\cdot + CH_3\cdot \rightarrow H_3CCH_3$
	$Cl\cdot + Cl\cdot \rightarrow Cl_2$

The chain reactions responsible for explosions generally have an additional feature: the existence of one or more *chain branching steps*, in which one radical reacts to produce two or more radicals, each of which can then go on to start a new chain reaction. Repetition of the branching step has a cascade effect such that a single initiation step generates large numbers of chain reactions. The result is a very rapid reaction or an explosion.

The reaction of H_2 and O_2, used to propel rockets, is an example of a chain branching reaction:

Initiation:	$H_2 + O_2 \rightarrow HO_2\cdot + H\cdot$
Propagation:	$HO_2\cdot + H_2 \rightarrow H_2O + OH\cdot$
	$OH\cdot + H_2 \rightarrow H_2O + H\cdot$
Termination:	$H\cdot + O_2 \rightarrow OH\cdot + \cdot O\cdot$
	$\cdot O\cdot + H_2 \rightarrow OH\cdot + H\cdot$

Termination reactions occur when the extraordinarily reactive H· or OH· radicals react with a third species. The complexity of a chain reaction makes it unfeasible to write a rate law for the overall reaction.

Summary

A **reaction mechanism** is the microscopic path by which reactants are transformed into products. Each step is an **elementary reaction**. Species that are formed in one step and consumed in another are **intermediates**. Each elementary reaction can be described in terms of its **molecularity**, the number of molecules that collide in that step. The slowest step in a reaction mechanism is the **rate-determining step**. **Chain reactions** consist of three kinds of reactions: initiation, propagation, and termination. Intermediates in chain reactions are often **radicals**, species that have an unpaired valence electron.

Key Takeaway

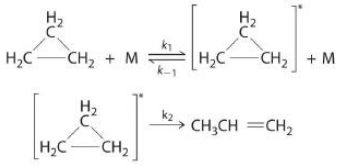
- A balanced chemical reaction does not necessarily reveal either the individual elementary reactions by which a reaction occurs or its rate law.

Conceptual Problems

1. How does the term *molecularity* relate to elementary reactions? How does it relate to the overall balanced chemical equation?
2. What is the relationship between the reaction order and the molecularity of a reaction? What is the relationship between the reaction order and the balanced chemical equation?
3. When you determine the rate law for a given reaction, why is it valid to assume that the concentration of an intermediate does not change with time during the course of the reaction?
4. If you know the rate law for an overall reaction, how would you determine which elementary reaction is rate determining? If an intermediate is contained in the rate-determining step, how can the experimentally determined rate law for the reaction be derived from this step?
5. Give the rate-determining step for each case.
    1. Traffic is backed up on a highway because two lanes merge into one.
    2. Gas flows from a pressurized cylinder fitted with a gas regulator and then is bubbled through a solution.
    3. A document containing text and graphics is downloaded from the Internet.
6. Before being sent on an assignment, an aging James Bond was sent off to a health farm where part of the program's focus was to purge his body of radicals. Why was this goal considered important to his health?

Numerical Problems

1. Cyclopropane, a mild anesthetic, rearranges to propylene via a collision that produces and destroys an energized species. The important steps in this rearrangement are as follows:



where M is any molecule, including cyclopropane. Only those cyclopropane molecules with sufficient energy (denoted with an asterisk) can rearrange to propylene. Which step determines the rate constant of the overall reaction?

2. Above approximately 500 K, the reaction between NO_2 and CO to produce CO_2 and NO follows the second-order rate law $\Delta[CO_2]/\Delta t = k[NO_2][CO]$. At lower temperatures, however, the rate law is $\Delta[CO_2]/\Delta t = k'[NO_2]^2$, for which it is known that NO_3 is an intermediate in the mechanism. Propose a complete low-temperature mechanism for the reaction based on this rate law. Which step is the slowest?

3. Nitramide (O_2NNH_2) decomposes in aqueous solution to N_2O and H_2O. What is the experimental rate law ($\Delta[N_2O]/\Delta t$) for the decomposition of nitramide if the mechanism for the decomposition is as follows?

$$O_2NNH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2NNH^- + H^+ \quad fast$$

$$O_2NNH^- \overset{k_2}{\rightarrow} N_2O + OH^- \quad slow$$

$$H^+ + OH^- \overset{k_3}{\rightarrow} H_2O \quad fast$$

Assume that the rates of the forward and reverse reactions in the first equation are equal.

4. The following reactions are given:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D$$

$$D + E \overset{k_2}{\rightarrow} F$$

What is the relationship between the relative magnitudes of k_{-1} and k_2 if these reactions have the rate law $\Delta[F]/\Delta t = k[A][B][E]/[C]$? How does the magnitude of k_1 compare to that of k_2? Under what conditions would you expect the rate law to be $\Delta[F]/\Delta t = k'[A][B]$? Assume that the rates of the forward and reverse reactions in the first equation are equal.

Answers

1. The k_2 step is likely to be rate limiting; the rate cannot proceed any faster than the second step.
2.
3. $$rate = k_2 \frac{k_1 [O_2NNH_2]}{k_{-1}[H^+]} = k\frac{[O_2NNH_2]}{[H^+]}$$
4.

Contributors

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Modified by Joshua Halpern (Howard University), Scott Sinex, and Scott Johnson (PGCC)

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Chapter 13.7: The Collision Model of Chemical Kinetics

Learning Objective

- To understand why and how chemical reactions occur.

In Section 13.6 , you saw that it is possible to use kinetics studies of a chemical system, such as the effect of changes in reactant concentrations, to deduce events that occur on a microscopic scale, such as collisions between individual particles. Such studies have led to the *collision model of chemical kinetics*, which is a useful tool for understanding the behavior of reacting chemical species. According to the collision model, a chemical reaction can occur only when the reactant molecules, atoms, or ions collide with more than a certain amount of kinetic energy and in the proper orientation. The collision model explains why, for example, most collisions between molecules do *not* result in a chemical reaction. Nitrogen and oxygen molecules in a single liter of air at room temperature and 1 atm of pressure collide about 10^{30} times per second. If every collision produced two molecules of NO, the atmosphere would have been converted to NO and then NO_2 a long time ago. Instead, in most collisions, the molecules simply bounce off one another without reacting, much as marbles bounce off each other when they collide. The collision model also explains why such chemical reactions occur more rapidly at higher temperatures. For example, the reaction rates of many reactions that occur at room temperature approximately double with a temperature increase of only 10°C. In this section, we will use the collision model to analyze this relationship between temperature and reaction rates.

Activation Energy

In Chapter 6.6 we discussed the kinetic molecular theory of gases, which showed that the average kinetic energy of the particles of a gas increases with increasing temperature. Because the speed of a particle is proportional to the square root of its kinetic energy, increasing the temperature will also increase the number of collisions between molecules per unit time. What the kinetic molecular theory of gases does not explain is why the reaction rate of most reactions approximately doubles with a 10°C temperature increase. This result is surprisingly large considering that a 10°C increase in the temperature of a gas from 300 K to 310 K increases the kinetic energy of the particles by only about 4%, leading to an increase in molecular speed of only about 2% and a correspondingly small increase in the number of bimolecular collisions per unit time.

The collision model of chemical kinetics explains this behavior by introducing the concept of activation energy (E_a)The energy barrier or threshold that corresponds to the minimum amount of energy the particles in a reaction must have to react when they colllide.. We will define this concept using the reaction of NO with ozone, which plays an important role in the depletion of ozone in the ozone layer:

$$NO\,(g) + O_3\,(g) \rightarrow NO_2\,(g) + O_2\,(g)$$

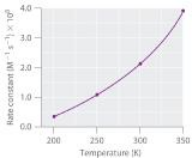


Figure 13.7.1 Rate Constant versus Temperature for the Reaction of NO with O_3 The nonlinear shape of the curve is caused by a distribution of kinetic energy over a population of molecules. Only a fraction of the particles have enough energy to overcome an energy barrier, but as the temperature is increased, the size of that fraction increases.

Increasing the temperature from 200 K to 350 K causes the rate constant for this particular reaction to increase by a factor of more than 10, whereas the increase in the frequency of bimolecular collisions over this temperature range is only 30%. Thus something other than an increase in the collision rate must be affecting the reaction rate.

The reaction rate, not the rate constant, will vary with concentration. The rate constant, however, does vary with temperature. Figure 13..7.1 shows a plot of the rate constant of the reaction of NO with O_3 at various temperatures. The relationship is not linear but instead resembles the relationships seen in graphs of vapor pressure versus temperature (Section 7.4) and of conductivity versus temperature (Chapter 8). In all three cases, the shape of the plots results from a distribution of kinetic energy over a population of particles (electrons in the case of conductivity; molecules in the case of vapor pressure; and molecules, atoms, or ions in the case of reaction rates). Only a fraction of the particles have sufficient energy to overcome an energy barrier.

In the case of vapor pressure, particles must overcome an energy barrier to escape from the liquid phase to the gas phase. This barrier corresponds to the energy of the intermolecular forces that hold the molecules together in the liquid. In conductivity, the barrier is the energy gap between the filled and empty bands. In chemical reactions, the energy barrier corresponds to the amount of energy the particles must have to react when they collide. This energy threshold, called the activation energy, was first postulated in 1888 by the Swedish chemist Svante Arrhenius (1859–1927; Nobel Prize in Chemistry 1903). It is the minimum amount of energy needed for a reaction to occur. Reacting molecules must have enough energy to overcome electrostatic repulsion, and a minimum amount of energy is required to break chemical bonds so that new ones may be formed. Molecules that collide with less than the threshold energy bounce off one another chemically unchanged, with only their direction of travel and their speed altered by the collision. Molecules that are able to overcome the energy barrier are able to react and form an arrangement of atoms called the activated complexAlso called the transition state, the arrangement of atoms that first forms when molecules are able to overcome the activation energy and react. or the transition stateAlso called the activated complex, the arrangement of atoms that first forms when molecules are able to overcome the activation energy and react. of the reaction. The activated complex is *not* a reaction intermediate; it does not last long enough to be detected readily.

Note the Pattern

Any phenomenon that depends on the distribution of thermal energy in a population of particles has a nonlinear temperature dependence.

Graphing Energy Changes during a Reaction

We can graph the energy of a reaction by plotting the potential energy of the system as the reaction progresses. Figure 13.7.2 shows a plot for the NO–O_3 system, in which the vertical axis is potential energy and the horizontal axis is the *reaction coordinate*, which indicates the progress of the reaction with time. The activated complex is shown in brackets with an asterisk. The overall change in potential energy for the reaction (ΔE) is negative, which means that the reaction releases energy. (In this case, ΔE is −200.8 kJ/mol.) To react, however, the molecules must overcome the energy barrier to reaction (E_a is 9.6 kJ/mol). That is, 9.6 kJ/mol must be put into the system as the activation energy. Below this threshold, the particles do not have enough energy for the reaction to occur.

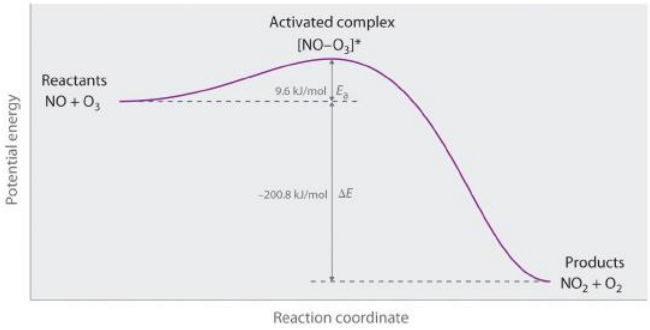


Figure 13.7.2 Energy of the Activated Complex for the NO–O_3 System The diagram shows how the energy of this system varies as the reaction proceeds from reactants to products. Note the initial increase in energy required to form the activated complex.

Part (a) in Figure 13.7.3 illustrates the general situation in which the products have a lower potential energy than the reactants. In contrast, part (b) in Figure 13.7.3 illustrates the case in which the products have a higher potential energy than the reactants, so the overall reaction requires an input of energy; that is, it is energetically uphill, and $\Delta E > 0$. Although the energy changes that result from a reaction can be positive, negative, or even zero, in all cases an energy barrier must be overcome before a reaction can occur. This means that the activation energy is always positive.

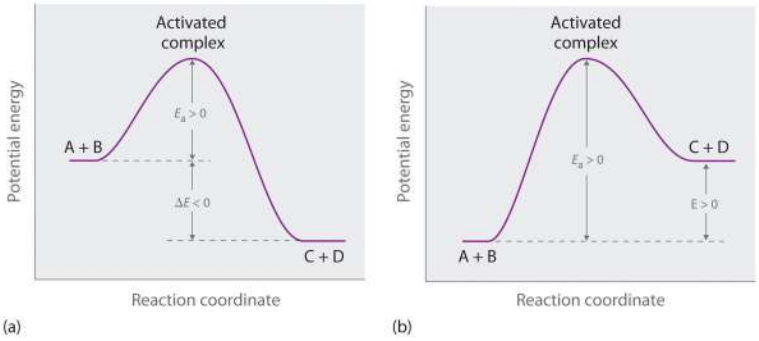


Figure 13.7.3 Differentiating between E_a and ΔE The potential energy diagrams for a reaction with (a) $\Delta E < 0$ and (b) $\Delta E > 0$ illustrate the change in the potential energy of the system as reactants are converted to products. E_a is always positive. For a reaction such as the one shown in (b), E_a must be *greater* than ΔE.

Note the Pattern

For similar reactions under comparable conditions, the one with the smallest E_a will occur most rapidly.

Whereas ΔE is related to the tendency of a reaction to occur spontaneously, E_a gives us information about the reaction rate and how rapidly the reaction rate changes with temperature. (For more information on spontaneous reactions, see Chapter 17.) *For two similar reactions under comparable conditions, the reaction with the smallest E_a will occur more rapidly.*

Even when the energy of collisions between two reactant species is greater than E_a, however, most collisions do not produce a reaction. The probability of a reaction occurring depends not only on the collision energy but also on the spatial orientation of the molecules when they collide. For NO and O_3 to produce NO_2 and O_2, a terminal oxygen atom of O_3 must collide with the nitrogen atom of NO at an angle that allows O_3 to transfer an oxygen atom to NO to produce NO_2 (Figure 13.7.4. All other collisions produce no reaction. Because fewer than 1% of all possible orientations of NO and O_3 result in a reaction at kinetic energies greater than E_a, most collisions of NO and O_3 are unproductive. The fraction of orientations that result in a reaction is called the steric factor (p)The fraction of orientations of particles that result in a chemical reaction., and, in general, its value can range from 0 (no orientations of molecules result in reaction) to 1 (all orientations result in reaction).

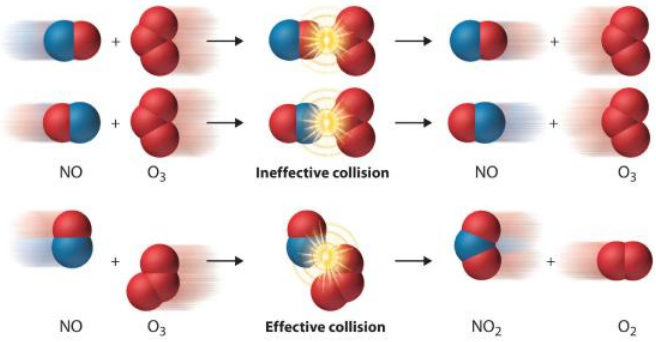


Figure 13.7.4 The Effect of Molecular Orientation on the Reaction of NO and O_3 Most collisions of NO and O_3 molecules occur with an incorrect orientation for a reaction to occur. Only those collisions in which the N atom of NO collides with one of the terminal O atoms of O_3 are likely to produce NO_2 and O_2, even if the molecules collide with $E > E_a$.

The Arrhenius Equation

Figure 13.7.5 shows both the kinetic energy distributions and a potential energy diagram for a reaction. The shaded areas show that at the lower temperature (300 K), only a small fraction of molecules collide with kinetic energy greater than E_a; however, at the higher temperature (500 K) a much larger fraction of molecules collide with kinetic energy greater than E_a. Consequently, the reaction rate is much slower at the lower temperature because only a relatively few molecules collide with enough energy to overcome the potential energy barrier.

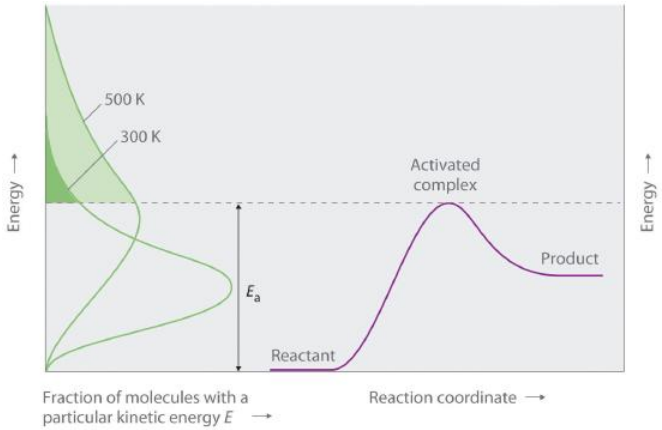


Figure 13.7.5 Surmounting the Energy Barrier to a Reaction This chart juxtaposes the energy distributions of lower-temperature (300 K) and higher-temperature (500 K) samples of a gas against the potential energy diagram for a reaction. Only those molecules in the shaded region of the energy distribution curve have $E > E_a$ and are therefore able to cross the energy barrier separating reactants and products. The fraction of molecules with $E > E_a$ is much greater at 500 K than at 300 K, so the reaction will occur much more rapidly at 500 K.

For an A + B elementary reaction, all the factors that affect the reaction rate can be summarized in a single series of relationships:

rate = (collision frequency)(steric factor)(fraction of collisions with $E > E_a$)

where

$$rate = k\,[A]\,[B]$$

Arrhenius used these relationships to arrive at an equation that relates the magnitude of the rate constant for a reaction to the temperature, the activation energy, and the constant, *A*, called the frequency factorA constant in the Arrhenius equation, it converts concentrations to collisions per second.:

$$k = Ae^{-E_a/RT}$$

The frequency factor is used to convert concentrations to collisions per second.Because the frequency of collisions depends on the temperature, *A* is actually *not* constant. Instead, *A* increases slightly with temperature as the increased kinetic energy of molecules at higher temperatures causes them to move slightly faster and thus undergo more collisions per unit time. Equation 13.7.3 is known as the Arrhenius equationAn expression that summarizes the collision model of chemical kinetics: k= Aexp(E_a/RT) and summarizes the collision model of chemical kinetics, where *T* is the absolute temperature (in K) and *R* is the ideal gas constant [8.314 J/(K·mol)]. E_a indicates the sensitivity of the reaction to changes in temperature. The reaction rate with a large E_a increases rapidly with increasing temperature, whereas the reaction rate with a smaller E_a increases much more slowly with increasing temperature.

If we know the reaction rate at various temperatures, we can use the Arrhenius equation to calculate the activation energy. Taking the natural logarithm of both sides of Equation 13.7.3,

$$\ln k = \ln A - \frac{E_a}{RT} = \ln A + \left[\left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right)\right]$$

Equation 13.7.4 is the equation of a straight line, $y = mx + b$, where $y = \ln k$ and $x = 1/T$. This means that a plot of ln *k* versus $1/T$ is a straight line with a slope of $-E_a/R$ and an intercept of ln *A*. In fact, we need to measure the reaction rate at only two temperatures to estimate E_a.

Knowing the E_a at one temperature allows us to predict the reaction rate at other temperatures. This is important in cooking and food preservation, for example, as well as in controlling industrial reactions to prevent potential disasters. The procedure for determining E_a from reaction rates measured at several temperatures is illustrated in Example 13.

Example 13.7.1

Many people believe that the rate of a tree cricket's chirping is related to temperature. To see whether this is true, biologists have carried out accurate measurements of the rate of tree cricket chirping (f) as a function of temperature (T). Use the data in the following table, along with the graph of ln[chirping rate] versus $1/T$ in Figure 13.7.6 to calculate E_a for the biochemical reaction that controls cricket chirping. Then predict the chirping rate on a very hot evening, when the temperature is 308 K (35°C, or 95°F).

Frequency (f; chirps/min)	ln f	T (K)	$1/T$ (K)
200	5.30	299	3.34×10^{-3}
179	5.19	298	3.36×10^{-3}
158	5.06	296	3.38×10^{-3}
141	4.95	294	3.40×10^{-3}
126	4.84	293	3.41×10^{-3}
112	4.72	292	3.42×10^{-3}
100	4.61	290	3.45×10^{-3}
89	4.49	289	3.46×10^{-3}
79	4.37	287	3.48×10^{-3}

Given: chirping rate at various temperatures

Asked for: activation energy and chirping rate at specified temperature

Strategy:

A From the plot of ln f versus $1/T$ in Figure 13.7.6, calculate the slope of the line ($-E_a/R$) and then solve for the activation energy.

B Express Equation 13.7.4 in terms of k_1 and T_1 and then in terms of k_2 and T_2.

C Subtract the two equations; rearrange the result to describe k_2/k_1 in terms of T_2 and T_1.

D Using measured data from the table, solve the equation to obtain the ratio k_2/k_1. Using the value listed in the table for k_1, solve for k_2.

Solution:

A If cricket chirping is controlled by a reaction that obeys the Arrhenius equation, then a plot of ln f versus $1/T$ should give a straight line (Figure 13.7.6). Also, the slope of the plot of ln f versus $1/T$ should be equal to $-E_a/R$. We can use the two endpoints in Figure 13.7.6 to estimate the slope:

$$slope = \frac{\Delta\, ln\, f}{\Delta\,(1/T)} = \frac{5.30 - 4.37}{3.34 \times 10^{-3}\ K^{-1} - 3.48 \times 10^{-3}\ K^{-1}}$$

A computer best-fit line through all the points has a slope of -6.67×10^3 K, so our estimate is very close. We now use it to solve for the activation energy:

$$E_a = \frac{0.93}{-0.041 \times 10^{-3}\ K^{-1}} = 6.6 \times 10^3\ K$$

B If the activation energy of a reaction and the rate constant at one temperature are known, then we can calculate the reaction rate at any other temperature. We can use Equation 13.7.4 to express the known rate constant (k_1) at the first temperature (T_1) as follows:

$$ln\ k_1 = ln\ A - \frac{E_a}{RT_1}$$

Similarly, we can express the unknown rate constant (k_2) at the second temperature (T_2) as follows:

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$

C These two equations contain four known quantities (E_a, T_1, T_2, and k_1) and two unknowns (A and k_2). We can eliminate A by subtracting the first equation from the second:

$$\ln k_2 - \ln k_1 = \left(\ln A - \frac{E_a}{RT_2}\right) - \left(\ln A - \frac{E_a}{RT_1}\right) = -\frac{E_a}{RT_2} + \frac{E_a}{RT_1}$$

Then

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

D To obtain the best prediction of chirping rate at 308 K (T_2), we try to choose for T_1 and k_1 the measured rate constant and corresponding temperature in the data table that is closest to the best-fit line in the graph. Choosing data for T_1 = 296 K, where f = 158, and using the E_a calculated previously,

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \frac{55\ kJ/mol}{8.314\ J/(K \cdot mol)}\left(\frac{1000\ J}{1\ kJ}\right)\left(\frac{1}{296\ K} - \frac{1}{308\ K}\right) = 0.87$$

Thus k_{308}/k_{296} = 2.4 and k_{308} = (2.4)(158) = 380, and the chirping rate on a night when the temperature is 308 K is predicted to be 380 chirps per minute.

Exercise

The equation for the decomposition of NO_2 to NO and O_2 is second order in NO_2:

$$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$$

Data for the reaction rate as a function of temperature are listed in the following table. Calculate E_a for the reaction and the rate constant at 700 K.

T (K)	k ($M^{-1}{\cdot}s^{-1}$)
592	522
603	755
627	1700
652	4020
656	5030

Answer: E_a = 114 kJ/mol; k_{700} = 18,600 $M^{-1}{\cdot}s^{-1}$ = 1.86 × 10^4 $M^{-1}{\cdot}s^{-1}$.

What E_a results in a doubling of the reaction rate with a 10°C increase in temperature from 20° to 30°C?

Answer: about 51 kJ/mol

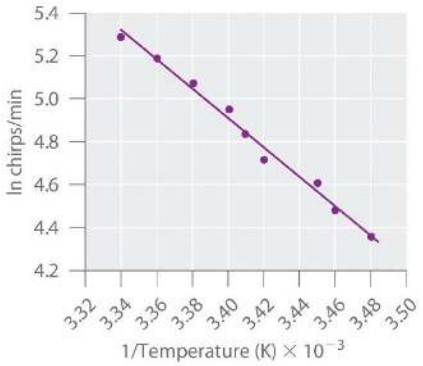


Figure 13.7.6 Graphical Determination of E_a for Tree Cricket Chirping When the natural logarithm of the rate of tree cricket chirping is plotted versus 1/T, a straight line results. The slope of the line suggests that the chirping rate is controlled by a single

reaction with an E_a of 55 kJ/mol.

Summary

A minimum energy (**activation energy, E_a**) is required for a collision between molecules to result in a chemical reaction. Plots of potential energy for a system versus the reaction coordinate show an energy barrier that must be overcome for the reaction to occur. The arrangement of atoms at the highest point of this barrier is the **activated complex**, or **transition state**, of the reaction. At a given temperature, the higher the E_a, the slower the reaction. The fraction of orientations that result in a reaction is the **steric factor**. The **frequency factor**, steric factor, and activation energy are related to the rate constant in the **Arrhenius equation**: k = Aexp(-E_a/RT). A plot of the natural logarithm of k versus $1/T$ is a straight line with a slope of $-E_a/R$.

Key Takeaway

- For a chemical reaction to occur, an energy threshold must be overcome, and the reacting species must also have the correct spatial orientation.

Key Equation

Arrhenius equation

$$k = Ae^{-E_a/RT}$$

Conceptual Problems

1. Although an increase in temperature results in an increase in kinetic energy, this increase in kinetic energy is not sufficient to explain the relationship between temperature and reaction rates. How does the activation energy relate to the chemical kinetics of a reaction? Why does an increase in temperature increase the reaction rate despite the fact that the average kinetic energy is still less than the activation energy?
2. For any given reaction, what is the relationship between the activation energy and each of the following?
    1. electrostatic repulsions
    2. bond formation in the activated complex
    3. the nature of the activated complex
3. If you are concerned with whether a reaction will occur rapidly, why would you be more interested in knowing the magnitude of the activation energy than the change in potential energy for the reaction?
4. The product C in the reaction A + B → C + D can be separated easily from the reaction mixture. You have been given pure A and pure B and are told to determine the activation energy for this reaction to determine whether the reaction is suitable for the industrial synthesis of C. How would you do this? Why do you need to know the magnitude of the activation energy to make a decision about feasibility?
5. Above E_a, molecules collide with enough energy to overcome the energy barrier for a reaction. Is it possible for a reaction to occur at a temperature less than that needed to reach E_a? Explain your answer.
6. What is the relationship between A, E_a, and T? How does an increase in A affect the reaction rate?
7. Of two highly exothermic reactions with different values of E_a, which would need to be monitored more carefully: the one with the smaller value or the one with the higher value? Why?

Numerical Problems

1. What happens to the approximate rate of a reaction when the temperature of the reaction is increased from 20°C to 30°C? What happens to the reaction rate when the temperature is raised to 70°C? For a given reaction at room temperature (20°C), what is the shape of a plot of reaction rate versus temperature as the temperature is increased to 70°C?
2. Acetaldehyde, used in silvering mirrors and some perfumes, undergoes a second-order decomposition between 700 and 840 K. From the data in the following table, would you say that acetaldehyde follows the general rule that each 10 K increase in temperature doubles the reaction rate?

T (K)	k ($M^{-1}·s^{-1}$)
720	0.024
740	0.051
760	0.105
800	0.519

3. Bromoethane reacts with hydroxide ion in water to produce ethanol. The activation energy for this reaction is 90 kJ/mol. If the reaction rate is 3.6×10^{-5} M/s at 25°C, what would the reaction rate be at the following temperatures?
    1. 15°C
    2. 30°C
    3. 45°C
4. An enzyme-catalyzed reaction has an activation energy of 15 kcal/mol. How would the value of the rate constant differ between 20°C and 30°C? If the enzyme reduced the E_a from 25 kcal/mol to 15 kcal/mol, by what factor has the enzyme increased the reaction rate at each temperature?
5. The data in the following table are the rate constants as a function of temperature for the dimerization of 1,3-butadiene. What is the activation energy for this reaction?

T (K)	k ($M^{-1}·min^{-1}$)
529	1.4
560	3.7
600	25
645	82

6. The reaction rate at 25°C is 1.0×10^{-4} M/s. Increasing the temperature to 75°C causes the reaction rate to increase to 7.0×10^{-2} M/s. Estimate E_a for this process. If E_a were 25 kJ/mol and the reaction rate at 25°C is 1.0×10^{-4} M/s, what would be the reaction rate at 75°C?

Answers

1. The reaction rate will approximately double: 20°C to 30°C, the reaction rate increases by about $2^1 = 2$; 20°C to 70°C, the reaction rate increases by about $2^5 = 32$-fold. A plot of reaction rate versus temperature will give an exponential increase: rate $\propto 2^{\Delta T/10}$.
2.
3.
    1. 1.0×10^{-5} M/s
    2. 6.6×10^{-5} M/s
    3. 3.5×10^{-4} M/s
4.
5. 100 kJ/mol
6.

Contributors

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Chapter 13.8: Catalysis

Learning Objective

- To understand how catalysts increase the reaction rate and the selectivity of chemical reactions.

Chapter 11.6 described catalystsA substance that participates in a reaction and causes it to occur more rapidly but that can be recovered unchanged at the end of the reaction and reused. Catalysts may also control which products are formed in a reaction. as substances that increase the reaction rate of a chemical reaction without being consumed in the process. A catalyst, therefore, does not appear in the overall stoichiometry of the reaction it catalyzes, but it *must* appear in at least one of the elementary reactions in the mechanism for the catalyzed reaction. The catalyzed pathway has a lower E_a, but the *net* change in energy that results from the reaction (the difference between the energy of the reactants and the energy of the products) is *not* affected by the presence of a catalyst (Figure 13.8.1). Nevertheless, because of its lower E_a, the reaction rate of a catalyzed reaction is faster than the reaction rate of the uncatalyzed reaction at the same temperature. Because a catalyst decreases the height of the energy barrier, its presence increases the reaction rates of *both* the forward *and* the reverse reactions by the same amount. In this section, we will examine the three major classes of catalysts: heterogeneous catalysts, **homogeneous catalysts**, and **enzymes**.

Note the Pattern

A catalyst affects E_a, not ΔE.

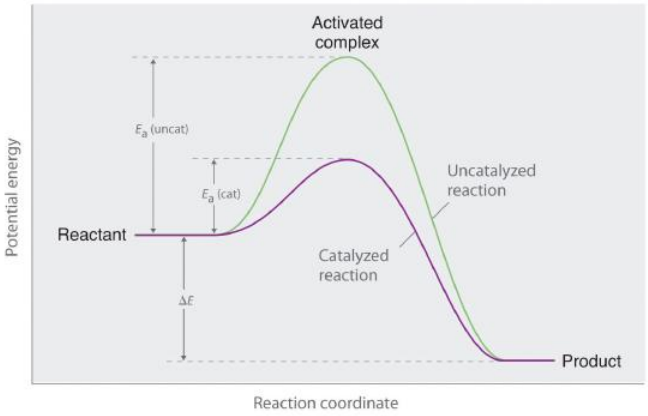
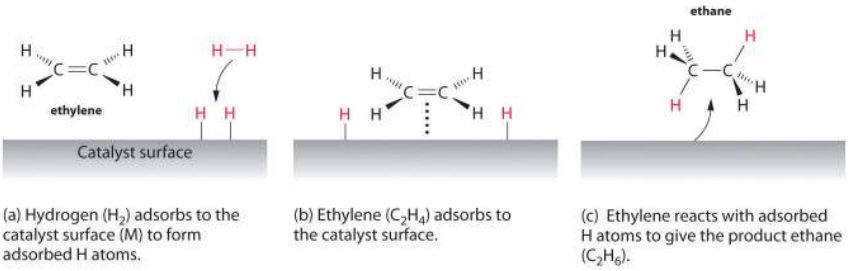


Figure 13.8.1 Lowering the Activation Energy of a Reaction by a Catalyst *This graph compares potential energy diagrams for a single-step reaction in the presence and absence of a catalyst. The only effect of the catalyst is to lower the activation energy of the reaction. The catalyst does not affect the energy of the reactants or products (and thus does not affect ΔE).*

Heterogeneous Catalysis

In heterogeneous catalysisA catalytic reaction in which the catalyst is in a different phase from the reactants., the catalyst is in a different phase from the reactants. At least one of the reactants interacts with the solid surface in a physical process called *adsorption* in such a way that a chemical bond in the reactant becomes weak and then breaks. *Poisons* are substances that bind irreversibly to catalysts, preventing reactants from adsorbing and thus reducing or destroying the catalyst's efficiency.

An example of heterogeneous catalysis is the interaction of hydrogen gas with the surface of a metal, such as Ni, Pd, or Pt. As shown in part (a) in Figure 13.8.2, the hydrogen–hydrogen bonds break and produce individual adsorbed hydrogen atoms on the surface of the metal. Because the adsorbed atoms can move around on the surface, two hydrogen atoms can collide and form a molecule of hydrogen gas that can then leave the surface in the reverse process, called *desorption*. Adsorbed H atoms on a metal surface are substantially more reactive than a hydrogen molecule. Because the relatively strong H–H bond (dissociation energy = 432 kJ/mol) has already been broken, the energy barrier for most reactions of H_2 is substantially lower on the catalyst surface.



(a) Hydrogen (H_2) adsorbs to the catalyst surface (M) to form adsorbed H atoms.

(b) Ethylene (C_2H_4) adsorbs to the catalyst surface.

(c) Ethylene reacts with adsorbed H atoms to give the product ethane (C_2H_6).

Figure 13.8.2 Hydrogenation of Ethylene on a Heterogeneous Catalyst *When a molecule of hydrogen adsorbs to the catalyst surface, the H–H bond breaks, and new M–H bonds are formed. The individual H atoms are more reactive than gaseous H_2. When a molecule of ethylene interacts with the catalyst surface, it reacts with the H atoms in a stepwise process to eventually produce ethane, which is released.*

Figure 13.8.2 shows a process called *hydrogenation*, in which hydrogen atoms are added to the double bond of an alkene, such as ethylene, to give a product that contains C–C single bonds, in this case ethane. Hydrogenation is used in the food industry to convert vegetable oils, which consist of long chains of alkenes, to more commercially valuable solid derivatives that contain alkyl chains. Hydrogenation of some of the double bonds in polyunsaturated vegetable oils, for example, produces margarine, a product with a melting point, texture, and other physical properties similar to those of butter.

Several important examples of industrial heterogeneous catalytic reactions are in Table 13.8.1. Although the mechanisms of these reactions are considerably more complex than the simple hydrogenation reaction described here, they all involve adsorption of the reactants onto a solid catalytic surface, chemical reaction of the adsorbed species (sometimes via a number of intermediate species), and finally desorption of the products from the surface.

Table 13.8.1 Some Commercially Important Reactions that Employ Heterogeneous Catalysts

Commercial Process	Catalyst	Initial Reaction	Final Commercial Product
contact process	V_2O_5 or Pt	$2SO_2 + O_2 \rightarrow 2SO_3$	H_2SO_4
Haber process	Fe, K_2O, Al_2O_3	$N_2 + 3H_2 \rightarrow 2NH_3$	NH_3
Ostwald process	Pt and Rh	$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$	HNO_3
water–gas shift reaction	Fe, Cr_2O_3, or Cu	$CO + H_2O \rightarrow CO_2 + H_2$	H_2 for NH_3, CH_3OH, and other fuels
steam reforming	Ni	$CH_4 + H_2O \rightarrow CO + 3H_2$	H_2
methanol synthesis	ZnO and Cr_2O_3	$CO + 2H_2 \rightarrow CH_3OH$	CH_3OH
Sohio process	bismuth phosphomolybdate	$CH_2{=}CHCH_3 + NH_3 + 3/2O_2 \rightarrow CH_2{=}CHCN + 3H_2O$	$CH_2{=}CHCN$
catalytic hydrogenation	Ni, Pd, or Pt	$RCH{=}CHR' + H_2 \rightarrow RCH_2{-}CH_2R'$	partially hydrogenated oils for margarine, and so forth

Homogeneous Catalysis

In homogeneous catalysisA catalytic reaction in which the catalyst is uniformly dispersed throughout the reactant mixture to form a solution., the catalyst is in the same phase as the reactant(s). The number of collisions between reactants and catalyst is at a maximum because the catalyst is uniformly dispersed throughout the reaction mixture. Many homogeneous catalysts in industry are transition metal compounds (Table 13.8.2), but recovering these expensive catalysts from solution has been a major challenge. As an added barrier to their widespread commercial use, many homogeneous catalysts can be used only at relatively low temperatures, and even then they tend to decompose slowly in solution. Despite these problems, a number of commercially viable processes have been developed in recent years. High-density polyethylene and polypropylene are produced by homogeneous catalysis.

Table 13.8.2 Some Commercially Important Reactions that Employ Homogeneous Catalysts

Commercial Process	Catalyst	Reactants	Final Product
Union Carbide	$[Rh(CO)_2I_2]^-$	$CO + CH_3OH$	CH_3CO_2H
hydroperoxide process	Mo(VI) complexes	$CH_3CH{=}CH_2 + R{-}O{-}O{-}H$	
hydroformylation	Rh/PR_3 complexes	$RCH{=}CH_2 + CO + H_2$	RCH_2CH_2CHO
adiponitrile process	Ni/PR_3 complexes	$2HCN + CH_2{=}CHCH{=}CH_2$	$NCCH_2CH_2CH_2CH_2CN$ used to synthesize nylon
olefin polymerization	$(RC_5H_5)_2ZrCl_2$	$CH_2{=}CH_2$	$-(CH_2CH_2-)_n$: high-density polyethylene

Enzymes



Figure 13.8.3 A Catalytic Defense Mechanism *The scalding, foul-smelling spray emitted by this bombardier beetle is produced by the catalytic decomposition of H_2O_2.*

Enzymes, catalysts that occur naturally in living organisms, are almost all protein molecules with typical molecular masses of 20,000–100,000 amu. Some are homogeneous catalysts that react in aqueous solution within a cellular compartment of an organism. Others are heterogeneous catalysts embedded within the membranes that separate cells and cellular compartments from their surroundings. The reactant in an enzyme-catalyzed reaction is called a substrateThe reactant in an enzyme-catalyzed reaction..

Because enzymes can increase reaction rates by enormous factors (up to 10^{17} times the uncatalyzed rate) and tend to be very specific, typically producing only a single product in quantitative yield, they are the focus of active research. At the same time, enzymes are usually expensive to obtain, they often cease functioning at temperatures greater than 37°C, have limited stability in solution, and have such high specificity that they are confined to turning one particular set of reactants into one particular product. This means that separate processes using different enzymes must be developed for chemically similar reactions, which is time-consuming and expensive. Thus far, enzymes have found only limited industrial applications, although they are used as ingredients in laundry detergents, contact lens cleaners, and meat tenderizers. The enzymes in these applications tend to be *proteases*, which are able to cleave the amide bonds that hold amino acids together in proteins. Meat tenderizers, for example, contain a protease called papain, which is isolated from papaya juice. It cleaves some of the long, fibrous protein molecules that make inexpensive cuts of beef tough, producing a piece of meat that is more tender. Some insects, like the bombadier beetle, carry an enzyme capable of catalyzing the decomposition of hydrogen peroxide to water (Figure 13.8.3).

Enzyme inhibitorsSubstances that decrease the reaction rate of an enzyme-catalyzed reaction by binding to a specific portion of the enzyme, thus slowing or preventing a reaction from occurring. cause a decrease in the reaction rate of an enzyme-catalyzed reaction by binding to a specific portion of an enzyme and thus slowing or preventing a reaction from occurring. Irreversible inhibitors are therefore the equivalent of poisons in heterogeneous catalysis. One of the oldest and most widely used commercial enzyme inhibitors is aspirin, which selectively inhibits one of the enzymes involved in the synthesis of molecules that trigger inflammation. The design and synthesis of related molecules that are more effective, more selective, and less toxic than aspirin are important objectives of biomedical research.

Summary

Catalysts participate in a chemical reaction and increase its rate. They do not appear in the reaction's net equation and are not consumed during the reaction. Catalysts allow a reaction to proceed via a pathway that has a lower activation energy than the uncatalyzed reaction. In **heterogeneous catalysis**, catalysts provide a surface to which reactants bind in a process of adsorption. In **homogeneous catalysis**, catalysts are in the same phase as the reactants. **Enzymes** are biological catalysts that produce large increases in reaction rates and tend to be specific for certain reactants and products. The reactant in an enzyme-catalyzed reaction is called a **substrate**. **Enzyme inhibitors** cause a decrease in the reaction rate of an enzyme-catalyzed reaction.

Key Takeaway

- Catalysts allow a reaction to proceed via a pathway that has a lower activation energy.

Conceptual Problems

1. What effect does a catalyst have on the activation energy of a reaction? What effect does it have on the frequency factor (*A*)? What effect does it have on the change in potential energy for the reaction?
2. How is it possible to affect the product distribution of a reaction by using a catalyst?
3. A heterogeneous catalyst works by interacting with a reactant in a process called *adsorption*. What occurs during this process? Explain how this can lower the activation energy.
4. What effect does increasing the surface area of a heterogeneous catalyst have on a reaction? Does increasing the surface area affect the activation energy? Explain your answer.
5. Identify the differences between a heterogeneous catalyst and a homogeneous catalyst in terms of the following.
    1. ease of recovery
    2. collision frequency
    3. temperature sensitivity
    4. cost
6. An area of intensive chemical research involves the development of homogeneous catalysts, even though homogeneous catalysts generally have a number of operational difficulties. Propose one or two reasons why a homogenous catalyst may be preferred.
7. Consider the following reaction between cerium(IV) and thallium(I) ions:

    $2Ce^{4+} + Tl^{+} \rightarrow 2Ce^{3+} + Tl^{3+}$

    This reaction is slow, but Mn^{2+} catalyzes it, as shown in the following mechanism:

    $Ce^{4+} + Mn^{2+} \rightarrow Ce^{3+} + Mn^{3+}$

    $Ce^{4+} + Mn^{3+} \rightarrow Ce^{3+} + Mn^{4+}$

    $Mn^{4+} + Tl^{+} \rightarrow Tl^{3+} + Mn^{2+}$

    In what way does Mn^{2+} increase the reaction rate?
8. The text identifies several factors that limit the industrial applications of enzymes. Still, there is keen interest in understanding how enzymes work for designing catalysts for industrial applications. Why?
9. Most enzymes have an optimal pH range; however, care must be taken when determining pH effects on enzyme activity. A decrease in activity could be due to the effects of changes in pH on groups at the catalytic center or to the effects on groups located elsewhere in the enzyme. Both examples are observed in chymotrypsin, a digestive enzyme that is a protease that hydrolyzes polypeptide chains. Explain how a change in pH could affect the catalytic activity due to (a) effects at the catalytic center and (b) effects elsewhere in the enzyme. (*Hint*: remember that enzymes are composed of functional amino acids.)

Answers

1. A catalyst lowers the activation energy of a reaction. Some catalysts can also orient the reactants and thereby increase the frequency factor. Catalysts have no effect on the change in potential energy for a reaction.

2.

3. In adsorption, a reactant binds tightly to a surface. Because intermolecular interactions between the surface and the reactant weaken or break bonds in the reactant, its reactivity is increased, and the activation energy for a reaction is often decreased.

4.

5. 1. Heterogeneous catalysts are easier to recover.
   2. Collision frequency is greater for homogeneous catalysts.
   3. Homogeneous catalysts are often more sensitive to temperature.
   4. Homogeneous catalysts are often more expensive.

6.

7. The Mn^{2+} ion donates two electrons to Ce^{4+}, one at a time, and then accepts two electrons from Tl^{+}. Because Mn can exist in three oxidation states separated by one electron, it is able to couple one-electron and two-electron transfer reactions.

8.

9.

Numerical Problems

1. At some point during an enzymatic reaction, the concentration of the activated complex, called an enzyme–substrate complex (ES), and other intermediates involved in the reaction is nearly constant. When a single substrate is involved, the reaction can be represented by the following sequence of equations:

$$\begin{gathered} enzyme\ (E) + substrate\ (S) \rightleftharpoons \\ enzyme - substrate\ complex\ (ES) \rightleftharpoons \\ enzyme\ (E) + product\ (P) \end{gathered}$$

   This can also be shown as follows:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightarrow}} ES \underset{k_{-2}}{\overset{k_2}{\leftarrow}} E + P$$

   Using molar concentrations and rate constants, write an expression for the rate of disappearance of the enzyme–substrate complex. Typically, enzyme concentrations are small, and substrate concentrations are high. If you were determining the rate law by varying the substrate concentrations under these conditions, what would be your apparent reaction order?

2. A particular reaction was found to proceed via the following mechanism:

   A + B → C + D

   2C → E

   E + A → 3B + F

   What is the overall reaction? Is this reaction catalytic, and if so, what species is the catalyst? Identify the intermediates.

3. A particular reaction has two accessible pathways (A and B), each of which favors conversion of *X* to a different product (*Y* and *Z*, respectively). Under uncatalyzed conditions pathway A is favored, but in the presence of a catalyst pathway B is favored. Pathway B is reversible, whereas pathway A is not. Which product is favored in the presence of a catalyst? without a catalyst? Draw a diagram illustrating what is occurring with and without the catalyst.

4. The kinetics of an enzyme-catalyzed reaction can be analyzed by plotting the reaction rate versus the substrate concentration. This type of analysis is referred to as a Michaelis–Menten treatment. At low substrate concentrations, the plot shows behavior characteristic of first-order kinetics, but at very high substrate concentrations, the behavior shows zeroth-order kinetics. Explain this phenomenon.

Answers

1. $\frac{\Delta(ES)}{\Delta t} = -(k_2 + k_{-1})[ES] + k_1[E][S] + k_{-2}[E][P] \approx 0$; zeroth order in substrate.

2.

3. In both cases, the product of pathway A is favored. All of the *Z* produced in the catalyzed reversible pathway B will eventually be converted to *X* as *X* is converted irreversibly to *Y* by pathway A.

$$Z \underset{B}{\rightleftharpoons} X \xrightarrow{A} Y$$

4.

Contributors

- Anonymous

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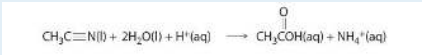
Chapter 13.9: End of Chapter Materials

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PROBLEMS

Problems marked with a ♦ involve multiple concepts.

1. Atmospheric chemistry in the region below the clouds of Venus appears to be dominated by reactions of sulfur and carbon-containing compounds. Included in representative elementary reactions are the following:
   $SO_2 + CO \rightarrow SO + CO_2$
   $SO + CO \rightarrow S + CO_2$
   $SO + SO_2 \rightarrow S + SO_3$
   For each elementary reaction, write an expression for the net rate of reaction in terms of the concentrations of reactants and products.
2. In acid, nitriles hydrolyze to produce a carboxylic acid and ammonium ion. For example, acetonitrile, a substance used to extract fatty acids from fish liver oils, is hydrolyzed to acetic acid via the following reaction:

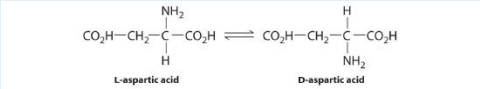


   Express the reaction rate in terms of changes in the concentrations of each reactant and each product with time.
3. ♦ Ozone production occurs at lower altitudes according to the elementary reaction $O + O_2 \rightarrow O_3$, with an estimated rate of ozone production of 4.86×10^{31} molecules·s^{-1} worldwide. What is the overall reaction order? If the reaction rate of loss of O_3 due to absorption of UV light is 0.89×10^{31} molecules·s^{-1}, and 0.06×10^{31} molecules·s^{-1} of ozone is transported to other atmospheric regions, is ozone being produced faster than it is being destroyed? Measurements show that ozone concentrations are not increasing rapidly. What conclusion can you draw from these data?
4. ♦ The water in a fishery became polluted when toxic waste was dumped into its pond, causing the fish population to substantially decline. The percentage of fish that survived is recorded in the following table.

Day	1	2	3	4	5
% survival	79	55	38	31	19

   What is the reaction order of live fish → dead fish? What is the rate constant? If the fish continue to die at this rate, how many fish will be alive after 10 days?
5. Until 200 yr ago, manufactured iron contained charcoal produced from freshly cut wood that was added during the smelting process. As a result of this practice, older samples of iron can be dated accurately using the carbon-14 method. An archaeologist found a cast iron specimen that she believed dated to the period between 480 and 221 BC in Hunan, China. Radiocarbon dating of the sample indicated a 24% reduction in carbon-14 content. Was the archaeologist correct?
6. ♦ Because of its short half-life, ^{32}P-labeled compounds must be shipped as quickly as possible so that they can be used as radioactive tags in biological studies. A 50 g sample that contained 0.60% ^{32}P by mass was shipped at 11 a.m. on Monday morning. The package was delivered to a chemist via an overnight delivery service such that it arrived the next day.
   a. What would be the mass of ^{32}P remaining in the sample if he received the package on Tuesday afternoon but was unable to use it until 9 a.m. on Wednesday?
   b. What would be the mass of ^{32}P present in the sample if the shipper had not delivered the sample until Friday afternoon and then it sat on a loading dock until 9 a.m. on Monday morning?
   c. The late shipment was used immediately on Monday morning, but the biological samples were not analyzed until Thursday at 5 p.m. What percentage of the sample still consists of ^{32}P?
7. ♦ Tritium (^3H) is a radioactive isotope that is commonly used to follow biochemical reactions.
   a. Using the data in Table 14.6, calculate the radioactive decay constant (k) for tritium.
   b. Use the value of k to determine the mass of tritium that is still present in a 5.00 g sample of NaB_3H_4 that is 17.57 yr old.
8. ♦ L-Aspartic acid is an amino acid found in fossil bone. It can convert to a geometrically different form (D-aspartic acid) at 20°C, with a half-life corresponding to the conversion of L → D of 14,000–20,000 yr. If the temperature of an archaeological

site is constant, then the extent of the conversion can be used to date fossils. In one such case, archaeologists dated the arrival of humans on the North American continent to be 20,000 yr ago, but the conversion of L-aspartic acid to D-aspartic acid in human fossils indicated that Paleo-Indians were living in California at least 48,000 yr ago. What would be the relative concentrations of the L- and D-forms that produced this result? Carbon-14 has a half-life of approximately 5730 yr. What percentage of the carbon-14 originally present would have been found in the bones?



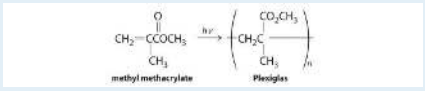
The technique described is frequently used in conjunction with radiocarbon dating. In cases where the results from the two techniques are in gross disagreement, what information can you get by comparing the two results?

9. ♦ Peroxides are able to initiate the radical polymerization of alkenes. Polyethylene, for example, is a high-molecular-weight polymer used as a film in packaging, as kitchenware, and as tubing. It is produced by heating ethylene at high pressure in the presence of oxygen or peroxide. It is formed by the following radical process:

$$RO:OR \xrightarrow{\Delta} 2RO$$
$$RO\cdot + CH_2=CH_2 \rightarrow RO-CH_2-CH_2\cdot$$
$$RO-CH_2-CH_2\cdot + CH_2=CH_2 \rightarrow RO-CH_2-CH_2-CH_2-CH_2\cdot$$

   a. Label the steps that correspond to initiation and propagation.
   b. Show all available chain-terminating steps.
   c. The polymerization of styrene ($C_6H_5CH{=}CH_2$) occurs by a similar process to produce polystyrene, which is used as a packaging material. Draw the structure of the polymer that results from five propagation cycles.

10. Lucite and Plexiglas are transparent polymers used as a glass substitute when a plastic material is preferred for safety. The compound used to synthesize Lucite and Plexiglas is methyl methacrylate, which is shown here. During the polymerization reaction, light produces a radical initiator from hydrogen peroxide ($H_2O_2 \rightarrow 2HO\cdot$). Show the mechanism for the polymerization, being sure to include the initiation and propagation steps.



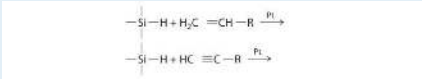
11. ♦ At higher altitudes ozone is converted to O_2 by the reaction $O + O_3 \rightarrow 2O_2$, with a rate constant at 220 K of 6.8×10^{-16} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$.
   a. What is the overall reaction order?
   b. What is E_a for this reaction if $A = 8 \times 10^{-12}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$? If Cl is present, the rate constant at 220 K becomes 3.7×10^{-11} $cm^3 \cdot molecule^{-1} \cdot s^{-1}$, with $A = 4.7 \times 10^{-11}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$.
   c. Calculate E_a for the depletion of ozone in the presence of Cl.
   d. Show an energy-level diagram for these two processes, clearly labeling reactants, products, and activation energies.
   e. If you were an environmental scientist using these data to explain the effects of Cl on ozone concentration, what would be your conclusions?

12. ♦ Nitric acid is produced commercially by the catalytic oxidation of ammonia by air over platinum gauze at approximately 900°C. The following reactions occur:

$$NH_3(g) + dfrac54O_3(g) \rightarrow NO(g) + \frac{3}{2}H_2O(g) \quad \Delta H^o = -226.3\ kJ/mol$$
$$NO(g) + \frac{1}{2}O_2(g) \rightarrow \qquad \Delta H^o = -57.1\ kJ/mol$$
$$NO_2(g) + H_2O(g) \rightarrow 2HNO_3(l)\,NO(g) \qquad \Delta H^o = -71.17\ kJ/mol$$

Why is platinum gauze rather than platinum wire used for the initial reaction? The reaction $4NH_3(g) + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(g)$ has $\Delta H° = -316.6$ kJ/mol. What would occur if the catalyst were not present? If the gas leaving the catalyst is not free of NH_3, the following reaction takes place: $6NO(g) + 4NH_3(g) \rightarrow 5N_2(g) + 6H_2O(g)$. If this occurs, what will be the overall reaction?

13. Figure 13.8.2 illustrates the mechanism for the reduction of ethylene on a platinum surface to produce ethane. Industrially important silanes are synthesized using a related mechanism and are used to increase adhesion between layers of glass fiber and between layers of silicone rubber. Predict the products of the following reactions:



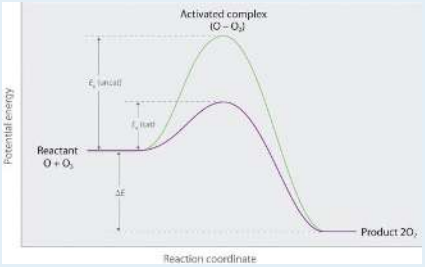
14. ♦ In catalysis, if a molecule forms strong bonds to the catalyst, then the catalyst may become poisoned. Experiments on various catalysts showed the following results:
    a. Fe, Ru, and Os form weak bonds with N_2; however, O_2, alkynes, alkenes, CO, H_2, and CO_2 interact more strongly.
    b. CO_2 and H_2 form weak bonds with a Co or Ni surface.
    c. Rh, Pd, Ir, and Pt form weak bonds with H_2 but do not bond with CO_2.
    d. Cu, Ag, and Au form weak bonds with CO and ethylene.
    a. Explain why Fe was chosen as a catalyst to convert nitrogen and hydrogen to ammonia. Why is Fe more suitable than Ru or Os?
    b. Because alkenes generally interact more strongly with metal surfaces than does H_2, what catalyst would you choose for hydrogenation of an alkene such as ethylene?
    c. Although platinum is used in catalytic converters for automobile exhaust, it was not found to be a particularly effective catalyst for the reaction of H_2 with a mixture of carbon monoxide and carbon dioxide to produce methane. Why?
    d. If you were interested in developing a catalyst to reversibly bind ethylene, which of the catalysts listed here would you choose?
15. Nonstoichiometric metal oxides can be effective catalysts for oxidation–reduction reactions. One such catalyst is $Ni_{1-x}O$, found to be effective for converting CO to CO_2 when oxygen is present. Why is it so effective?
16. The chemical reactions in an organism can be controlled by regulating the activity of certain enzymes. Efficient regulation results in an enzyme being active only when it is needed. For example, if a cell needed histidine, the nine enzymes needed to synthesize histidine would all be active. If the cell had adequate histidine, however, those enzymes would be inactive. The following diagram illustrates a situation in which three amino acids (D, F, H) are all synthesized from a common species, A. The numbers above the arrows refer to the enzymes that catalyze each step. Which enzymes would need to be regulated to produce D? F? H?

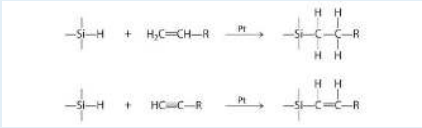


17. ♦ Because phosphorus-32 is incorporated into deoxyribonucleic acid (DNA), it can be used to detect DNA fragments. Consequently, it is used extensively in biological research, including the Human Genome Project, whose goal was to determine the complete sequence of human DNA. If you were to start with a 20 g sample of phosphorus that contained 10% ^{32}P by mass, converted it into DNA via several chemical steps that had an overall yield of 75% and took 25 days, and then incorporated it into bacteria and allowed them to grow for 5 more days, what mass of ^{32}P would be available for analysis at the end of this time?
18. The enzyme urease contains two atoms of nickel and catalyzes the hydrolysis of urea by the following reaction:
    $H_2NC(O)NH_2 + H_2O \rightarrow 2NH_3 + CO_2$
    Urease is one of the most powerful catalysts known. It lowers the activation energy for the hydrolysis of urea from 137 kJ/mol to only 37 kJ/mol. Calculate the ratio of the reaction rate of the catalyzed reaction to the reaction rate of the uncatalyzed reaction at 37°C. Assume that the frequency factor is the same for both reactions.
19. As noted in Section 13.8, the reaction rate for the hydrogenation of ethylene to give ethane can be increased by heterogeneous catalysts such as Pt or Ni:
    $$H_2(g) + H_2C{=}CH_2(g) \xrightarrow{Pt,Ni} H_3C{-}CH_3(g)$$
    The activation energy for the uncatalyzed reaction is large (188 kJ/mol), so the reaction is very slow at room temperature. In the presence of finely divided metallic Ni, the activation energy is only 84 kJ/mol. Calculate the ratio of the reaction rate of the catalyzed reaction to the reaction rate of the uncatalyzed reaction at 75°C.

ANSWERS

1. rate = $k_f[SO_2][CO] - k_r[SO][CO_2]$; rate = $k_f[SO][CO] - k_r[S][CO_2]$; rate = $k_f[SO][SO_2] - k_r[S][SO_3]$
2.

3. The reaction is second order: first order in O and first order in O_3. Ozone is being produced faster than it is being destroyed. If ozone concentrations are not increasing, then either some other reaction must be consuming some of the ozone produced in this reaction or the ozone-producing reaction does not operate at this rate continuously.
4.
5. Yes; the object is about 2300 yr old.
6.
7. a. $k = 0.05626\ \text{yr}^{-1}$
   b. 0.487 g of ^{3}H
8.
9.
10.
11. a. second order, first order in O and first order in O_3;
    b. 17 kJ/mol;
    c. 0.44 kJ/mol;
    d.
    

    e. Cl is a potent catalyst for ozone destruction because there is a large decrease in E_a when Cl is present.
12.
13.
    
14.
15. $Ni_{1-x}O$ is a nonstoichiometric oxide that contains a fraction of Ni(I) sites. These can react with oxygen to form a Ni(III)-oxide site, which is reduced by CO to give Ni(I) and CO_2.
16.
17. 0.35 g of ^{32}P
18.
19. 4.1×10^{15}

Contributors

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CHAPTER OVERVIEW

Chapter 14: Chemical Equilibrium

- Chapter 14.1: The Concept of Chemical Equilibrium
- Chapter 14.2: The Equilibrium Constant
- Chapter 14.3: Solving Equilibrium Problems
- Chapter 14.4: Non-equilibrium Conditions
- Chapter 14.5: Factors That Affect Equilibrium
- Chapter 14.6: Controlling the Products of Reactions
- Chapter 14.7: End of Chapter Materials

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Chapter 14.1: The Concept of Chemical Equilibrium

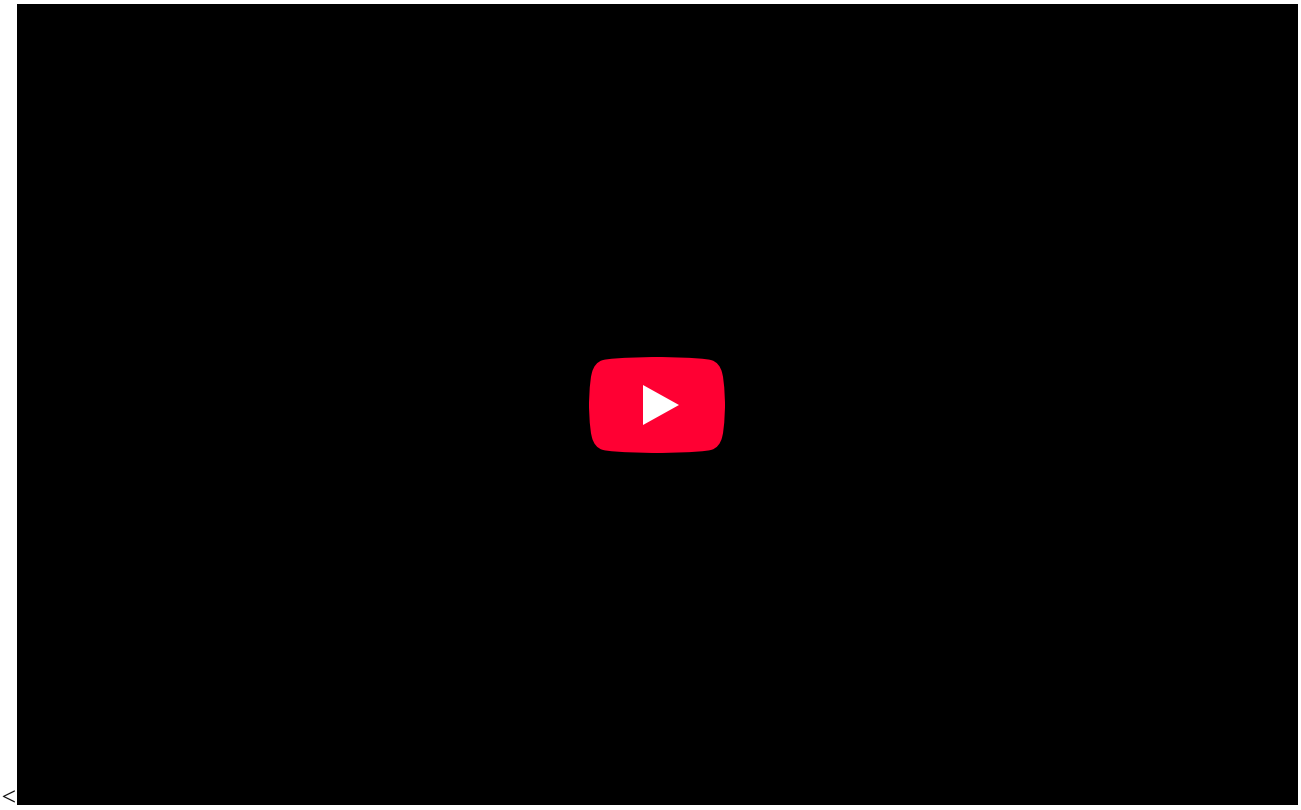
Learning Objective

- To understand what is meant by chemical equilibrium.

Chemical equilibrium is a dynamic process that consists of a forward reaction, in which reactants are converted to products, and a reverse reaction, in which products are converted to reactants. At equilibrium, the forward and reverse reactions proceed at equal rates. Consider, for example, a simple system that contains only one reactant and one product, the reversible dissociation of dinitrogen tetroxide (N_2O_4) to nitrogen dioxide (NO_2). NO_2 is responsible for the brown color we associate with smog. When a sealed tube containing solid N_2O_4 (mp = −9.3°C; bp = 21.2°C) is heated from −78.4°C to 25°C, the red-brown color of NO_2 appears (Figure 14.1.1). The reaction can be followed visually because the product (NO_2) is colored, whereas the reactant (N_2O_4) is colorless:

$$N_2O_4\ (g)\ colorless \rightleftharpoons 2NO_2\ (g)\ red-brown \tag{14.1.1}$$

The double arrow indicates that both the forward and reverse reactions are occurring simultaneously; it is read “is in equilibrium with.”





>

Figure 14.1.1 The $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ System at Different Temperatures *At room temperature a mixture of gaseous N_2O_4 and NO_2 is present. If the sample is placed in a warm bath, the equilibrium shifts to the right and NO_2 predominates as shown by the redder color. If it is placed in an ice bath the equilibrium shifts to the left and colorless N_2O_4 predominates . The composition of the mixture and hence the color do not change further with time once the system reaches equilibrium at the new temperature. At dry ice temperature (−78.4°C), the system would contain essentially pure solid N_2O_4, which is colorless. The video is from NuclearRabbit on YouTube*

Figure 14.1.2 shows how the composition of this system would vary as a function of time at a constant temperature. If the initial concentration of NO_2 were zero, then it increases as the concentration of N_2O_4 decreases. Eventually the composition of the system stops changing with time, and chemical equilibrium is achieved. Conversely, if we start with a sample that contains no N_2O_4 but an initial NO_2 concentration twice the initial concentration of N_2O_4 in part (a) in Figure 14.1.2, in accordance with the stoichiometry of the reaction, we reach exactly the same equilibrium composition, as shown in part (b) in Figure 14.1.2. Thus equilibrium can be approached from *either direction* in a chemical reaction.

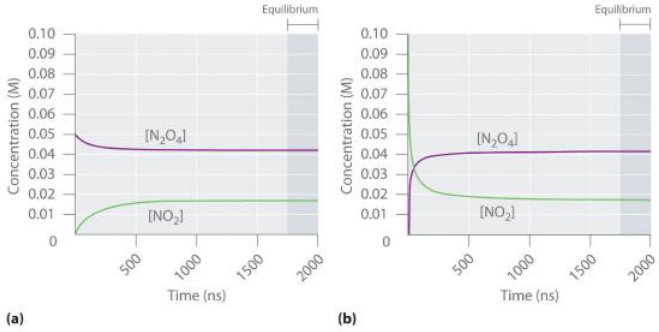


Figure 14.1.2 The Composition of N_2O_4/NO_2 Mixtures as a Function of Time at Room Temperature *(a) Initially, this idealized system contains 0.0500 M gaseous N_2O_4 and no gaseous NO_2. The concentration of N_2O_4 decreases with time as the concentration of NO_2 increases. (b) Initially, this system contains 0.1000 M NO_2 and no N_2O_4. The concentration of NO_2 decreases with time as the concentration of N_2O_4 increases. In both cases, the final concentrations of the substances are the same: $[N_2O_4]$ = 0.0422 M and $[NO_2]$ = 0.0156 M at equilibrium.*

Figure 14.1.3 shows the forward and reverse reaction rates for a sample that initially contains pure NO_2. Because the initial concentration of N_2O_4 is zero, the forward reaction rate (dissociation of N_2O_4) is initially zero as well. In contrast, the reverse reaction rate (dimerization of NO_2) is initially very high (2.0×10^6 M/s), but it decreases rapidly as the concentration of NO_2 decreases. (Recall from Chapter 13 that the reaction rate of the dimerization reaction is expected to decrease rapidly because the reaction is second order in NO_2: rate = $k_r[NO_2]^2$, where k_r is the rate constant for the reverse reaction shown in Equation 14.1.1.) As the concentration of N_2O_4 increases, the rate of dissociation of N_2O_4 increases—but more slowly than the dimerization of NO_2—because the reaction is only first order in N_2O_4 (rate = $k_f[N_2O_4]$, where k_f is the rate constant for the forward reaction in Equation

14.1.1). Eventually, the forward and reverse reaction rates become identical, $k_F = k_r$, and the system has reached chemical equilibrium. If the forward and reverse reactions occur at *different* rates, then the system is *not* at equilibrium.

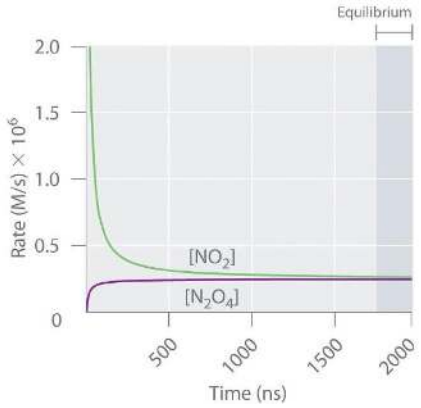


Figure 14.1.3 The Forward and Reverse Reaction Rates as a Function of Time for the $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ System *Shown in Part (b) in Figure 14.1.2*

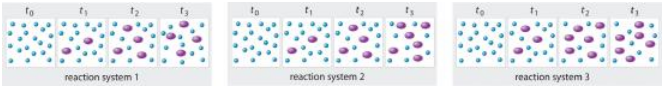
The rate of dimerization of NO_2 (reverse reaction) decreases rapidly with time, as expected for a second-order reaction. Because the initial concentration of N_2O_4 is zero, the rate of the dissociation reaction (forward reaction) at $t = 0$ is also zero. As the dimerization reaction proceeds, the N_2O_4 concentration increases, and its rate of dissociation also increases. Eventually the rates of the two reactions are equal: chemical equilibrium has been reached, and the concentrations of N_2O_4 and NO_2 no longer change.

Note the Pattern

At equilibrium, the forward reaction rate is equal to the reverse reaction rate.

Example 14.1.1

The three reaction systems (1, 2, and 3) depicted in the accompanying illustration can all be described by the equation $2\ A \rightleftharpoons B$, where the blue circles are A and the purple ovals are B. Each set of panels shows the changing composition of one of the three reaction mixtures as a function of time. Which system took the longest to reach chemical equilibrium?



Given: three reaction systems

Asked for: relative time to reach chemical equilibrium

Strategy:

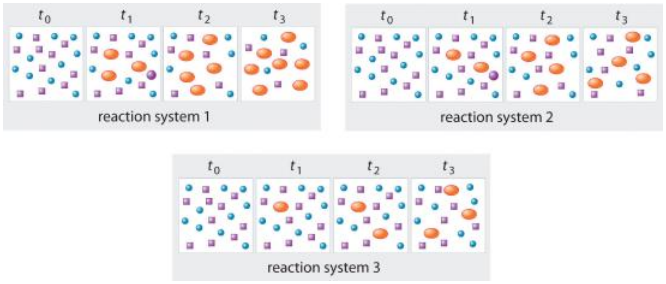
Compare the concentrations of A and B at different times. The system whose composition takes the longest to stabilize took the longest to reach chemical equilibrium.

Solution:

In systems 1 and 3, the concentration of A decreases from t_0 through t_2 but is the same at both t_2 and t_3. Thus systems 1 and 3 are at equilibrium by t_3. In system 2, the concentrations of A and B are still changing between t_2 and t_3, so system 2 may not yet have reached equilibrium by t_3. Thus system 2 took the longest to reach chemical equilibrium.

Exercise

In the following illustration, A is represented by blue circles, B by purple squares, and C by orange ovals; the equation for the reaction is $A + B \rightleftharpoons C$. The sets of panels represent the compositions of three reaction mixtures as a function of time. Which, if any, of the systems shown has reached equilibrium?



Answer: system 2

Summary

Chemical equilibrium is a dynamic process consisting of forward and reverse reactions that proceed at equal rates. At equilibrium, the composition of the system no longer changes with time. The composition of an equilibrium mixture is independent of the direction from which equilibrium is approached.

Key Takeaway

- At equilibrium, the forward and reverse reactions of a system proceed at equal rates.

Conceptual Problems

1. What is meant when a reaction is described as “having reached equilibrium”? What does this statement mean regarding the forward and reverse reaction rates? What does this statement mean regarding the concentrations or amounts of the reactants and the products?
2. Is it correct to say that the reaction has “stopped” when it has reached equilibrium? Explain your answer and support it with a specific example.
3. Why is chemical equilibrium described as a dynamic process? Describe this process in the context of a saturated solution of NaCl in water. What is occurring on a microscopic level? What is happening on a macroscopic level?
4. Which of these systems exists in a state of chemical equilibrium?
    1. oxygen and hemoglobin in the human circulatory system
    2. iodine crystals in an open beaker
    3. the combustion of wood
    4. the amount of ^{14}C in a decomposing organism

Answer

3. Both forward and reverse reactions occur but at the same rate. Na^+ and Cl^- ions continuously leave the surface of an NaCl crystal to enter solution, while at the same time Na^+ and Cl^- ions in solution precipitate on the surface of the crystal.

1.
4.

Contributors

- Anonymous

Modified by Joshua Halpern (Howard University), Scott Sinex, and Scott Johnson (PGCC)

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- Anonymous

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Chapter 14.2: The Equilibrium Constant

Learning Objectives

- To know the relationship between the equilibrium constant and the rate constants for the forward and reverse reactions.
- To write an equilibrium constant expression for any reaction.

To know the relationship between the equilibrium constant and the rate constants for the forward and reverse reactions.

To write an equilibrium constant expression for any reaction.

Because an equilibrium state is achieved when the forward reaction rate equals the reverse reaction rate, under a given set of conditions there must be a relationship between the composition of the system at equilibrium and the kinetics of a reaction (represented by rate constants). We can show this relationship using the system described in Equation 14.1.1, the decomposition of N_2O_4 to NO_2. Both the forward and reverse reactions for this system consist of a single elementary reaction, so the reaction rates are as follows:

$$\text{forward rate} = k_f[N_2O_4] \tag{14.2.1}$$

and

$$\text{reverse rate} = k_r[NO_2]^2 \tag{14.2.2}$$

At equilibrium, the forward rate equals the reverse rate:

$$k_f[N_2O_4] = k_r[NO_2]^2 \tag{14.2.3}$$

so

$$\frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]} \tag{14.2.4}$$

The ratio of the rate constants gives us a new constant, the equilibrium constant (K)which is defined as follows:

$$K = \frac{k_f}{k_r} \tag{14.2.5}$$

Hence there is a fundamental relationship between chemical kinetics and chemical equilibrium: *under a given set of conditions, the composition of the equilibrium mixture is determined by the magnitudes of the rate constants for the forward and the reverse reactions.*

Note the Pattern

The equilibrium constant is equal to the rate constant for the *forward* reaction divided by the rate constant for the *reverse* reaction.

Table 14.2.1 lists the initial and equilibrium concentrations from five different experiments using the reaction system described by Equation 14.1.1. At equilibrium the magnitude of the quantity $[NO_2]^2/[N_2O_4]$ is essentially the same for all five experiments. In fact, no matter what the initial concentrations of NO_2 and N_2O_4 are, at equilibrium the quantity $[NO_2]^2/[N_2O_4]$ will *always* be $6.53 \pm 0.03 \times 10^{-3}$ at 25°C, which corresponds to the ratio of the rate constants for the forward and reverse reactions. That is, at a given temperature, the equilibrium constant for a reaction always has the same value, even though the specific concentrations of the reactants and products vary depending on their initial concentrations.

Table 14.2.1 Initial and Equilibrium Concentrations for $NO_2 : N_2O_4$ Mixtures at 25°C

	Initial Concentrations		Concentrations at Equilibrium		
Experiment	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$K = [NO_2]^2/[N_2O_4]$
1	0.0500	0.0000	0.0417	0.0165	6.54×10^{-3}
2	0.0000	0.1000	0.0417	0.0165	6.54×10^{-3}
3	0.0750	0.0000	0.0647	0.0206	6.56×10^{-3}
4	0.0000	0.0750	0.0304	0.0141	6.54×10^{-3}
5	0.0250	0.0750	0.0532	0.0186	6.50×10^{-3}

Developing an Equilibrium Constant Expression

In 1864, the Norwegian chemists Cato Guldberg (1836–1902) and Peter Waage (1833–1900) carefully measured the compositions of many reaction systems at equilibrium. They discovered that for *any* reversible reaction of the general form

$$aA + bB \rightleftharpoons cC + dD \tag{14.2.6}$$

where A and B are reactants, C and D are products, and *a*, *b*, *c*, and *d* are the stoichiometric coefficients in the balanced chemical equation for the reaction, the ratio of the product of the equilibrium concentrations of the products (raised to their coefficients in the balanced chemical equation) to the product of the equilibrium concentrations of the reactants (raised to their coefficients in the balanced chemical equation) is always a constant under a given set of conditions. This relationship is known as the law of mass action and can be stated as follows:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{14.2.7}$$

where K is the equilibrium constant for the reaction. Equation 14.2.7 is called the equilibrium equation, and the right side of Equation 14.2.7 is called the equilibrium constant expression. The relationship shown in Equation 14.2.7 is true for *any* pair of opposing reactions regardless of the mechanism of the reaction or the number of steps in the mechanism.

The equilibrium constant can vary over a wide range of values. The values of K shown in Table 14.2.2 , for example, vary by 60 orders of magnitude. Because products are in the numerator of the equilibrium constant expression and reactants are in the denominator, values of K greater than 10^3 indicate a strong tendency for reactants to form products. In this case, chemists say that equilibrium lies to the right as written, favoring the formation of products. An example is the reaction between H_2 and Cl_2 to produce HCl, which has an equilibrium constant of 1.6×10^{33} at 300 K. Because H_2 is a good reductant and Cl_2 is a good oxidant, the reaction proceeds essentially to completion. In contrast, values of K less than 10^{-3} indicate that the ratio of products to reactants at equilibrium is very small. That is, reactants do not tend to form products readily, and the equilibrium lies to the left as written, favoring the formation of reactants.

Table 14.2.2 Equilibrium Constants for Selected Reactions*

Reaction	Temperature (K)	Equilibrium Constant (K)
$S_{(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)}$	300	4.4×10^{53}
$2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H2O_{(g)}$	500	2.4×10^{47}
$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$	300	1.6×10^{33}
$H_{2(g)} + Br_{2(g)} \rightleftharpoons 2HBr_{(g)}$	300	4.1×10^{18}
$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$	300	4.2×10^{13}
$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$	300	2.7×10^{8}
$H_{2(g)} + D_{2(g)} \rightleftharpoons 2HD_{(g)}$	100	1.92
$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$	300	2.9×10^{-1}
$I_{2(g)} \rightleftharpoons 2I_{(g)}$	800	4.6×10^{-7}
$Br_{2(g)} \rightleftharpoons 2Br_{(g)}$	1000	4.0×10^{-7}
$Cl_{2(g)} \rightleftharpoons 2Cl_{(g)}$	1000	1.8×10^{-9}
$F_{2(g)} \rightleftharpoons 2F_{(g)}$	500	7.4×10^{-13}

***Equilibrium constants vary with temperature. The *K* values shown are for systems at the indicated temperatures.**

You will also notice in Table 14.2.2 that equilibrium constants have no units, even though Equation 14.2.7 suggests that the units of concentration might not always cancel because the exponents may vary. In fact, equilibrium constants are calculated using "effective concentrations," or *activities*, of reactants and products, which are the ratios of the measured concentrations to a standard state of 1 M. As shown in Equation 14.2.8, the units of concentration cancel, which makes *K* unitless as well:

$$\frac{[A]_{measured}}{[A]_{standard\ state}} = \frac{\cancel{M}}{\cancel{M}} = \frac{\frac{\cancel{mol}}{\cancel{L}}}{\frac{\cancel{mol}}{\cancel{L}}} \tag{14.2.8}$$

Many reactions have equilibrium constants between 1000 and 0.001 ($10^{3} \geq K \geq 10^{-3}$), neither very large nor very small. At equilibrium, these systems tend to contain significant amounts of both products and reactants, indicating that there is not a strong tendency to form either products from reactants or reactants from products. An example of this type of system is the reaction of gaseous hydrogen and deuterium, a component of high-stability fiber-optic light sources used in ocean studies, to form HD:

$$H_{2(g)} + D_{2(g)} \rightleftharpoons 2HD_{(g)} \tag{14.2.9}$$

The equilibrium constant expression for this reaction is

$$K = \frac{[HD]^2}{[H_2][D_2]} \tag{Chapter 14.2.1}$$

with *K* varying between 1.9 and 4 over a wide temperature range (100–1000 K). Thus an equilibrium mixture of H_2, D_2, and HD contains significant concentrations of both product and reactants.

Figure 14.2.1 summarizes the relationship between the magnitude of *K* and the relative concentrations of reactants and products at equilibrium for a general reaction, written as reactants ⇌ products Because there is a direct relationship between the kinetics of a reaction and the equilibrium concentrations of products and reactants (Equation 14.2.8 and Equation 14.2.7), when $k_f >> k_r$, *K* is a large number, and the concentration of products at equilibrium predominate. This corresponds to an essentially irreversible reaction. Conversely, when $k_f << k_r$, *K* is a very small number, and the reaction produces almost no products as written. Systems for which $k_f \approx k_r$ have significant concentrations of both reactants and products at equilibrium.

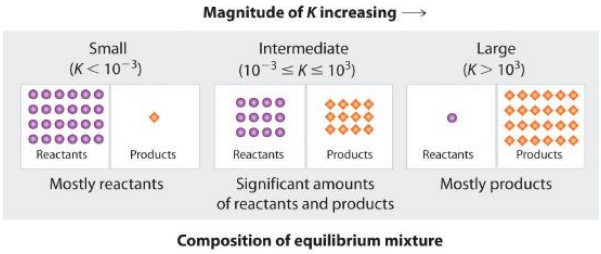


Figure 14.2.1 The Relationship between the Composition of the Mixture at Equilibrium and the Magnitude of the Equilibrium Constant*The larger the K, the farther the reaction proceeds to the right before equilibrium is reached, and the greater the ratio of products to reactants at equilibrium.*

Note the Pattern

A large value of the equilibrium constant *K* means that products predominate at equilibrium; a small value means that reactants predominate at equilibrium.

Example 14.2.1

Write the equilibrium constant expression for each reaction.

1. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
2. $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons CO_{2(g)}$
3. $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)}$

Given: balanced chemical equations

Asked for: equilibrium constant expressions

Strategy:

Refer to Equation 14.2.7. Place the arithmetic product of the concentrations of the products (raised to their stoichiometric coefficients) in the numerator and the product of the concentrations of the reactants (raised to their stoichiometric coefficients) in the denominator.

Solution:

1. The only product is ammonia, which has a coefficient of 2. For the reactants, N_2 has a coefficient of 1 and H_2 has a coefficient of 3. The equilibrium constant expression is as follows:

$$\frac{[NH_3]^2}{[N_2][H_2]^3} \tag{Chapter 14.2.2}$$

2. The only product is carbon dioxide, which has a coefficient of 1. The reactants are CO, with a coefficient of 1, and O_2, with a coefficient of 1/2 Thus the equilibrium constant expression is as follows:

$$\frac{[CO_2]}{[CO][O_2]^{1/2}} \tag{Chapter 14.2.3}$$

3. This reaction is the reverse of the reaction in part b, with all coefficients multiplied by 2 to remove the fractional coefficient for O_2. The equilibrium constant expression is therefore the inverse of the expression in part b, with all exponents multiplied by 2:

$$\frac{[CO]^2[O_2]}{[CO_2]^2} \quad \text{(Chapter 14.2.4)}$$

Exercise

Write the equilibrium constant expression for each reaction.

1. $N_2O_{(g)} \rightleftharpoons N_{2(g)} + \frac{1}{2}O_{2(g)}$
2. $2C_8H_{18(g)} + 25O_{2(g)} \rightleftharpoons 16CO_{2(g)} + 18H_2O_{(g)}$
3. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

Answer:

1. $K = \frac{[N_2][O_2]^{1/2}}{[N_2O]}$
2. $K = \frac{[CO_2]^{16}[H_2O]^{18}}{[C_8H_{18}]^2[O_2]^{25}}$
3. $K = \frac{[HI]^2}{[H_2][I_2]}$

Example 14.2.2

Predict which systems at equilibrium will (a) contain essentially only products, (b) contain essentially only reactants, and (c) contain appreciable amounts of both products and reactants.

1. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad K_{(700K)} = 54$
2. $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)} \qquad K_{(1200K)} = 3.1 \times 10^{-18}$
3. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad K_{(613K)} = 97$
4. $2O_{3(g)} \rightleftharpoons 3O_{2(g)} \qquad K_{(298K)} = 5.9 \times 10^{55}$

Given: systems and values of *K*

Asked for: composition of systems at equilibrium

Strategy:

Use the value of the equilibrium constant to determine whether the equilibrium mixture will contain essentially only products, essentially only reactants, or significant amounts of both.

Solution:

1. Only system 4 has $K >> 10^3$, so at equilibrium it will consist of essentially only products.
2. System 2 has $K << 10^{-3}$, so the reactants have little tendency to form products under the conditions specified; thus, at equilibrium the system will contain essentially only reactants.
3. Both systems 1 and 3 have equilibrium constants in the range $10^3 \geq K \geq 10^{-3}$, indicating that the equilibrium mixtures will contain appreciable amounts of both products and reactants.

Exercise

Hydrogen and nitrogen react to form ammonia according to the following balanced chemical equation:

$$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad \text{(Chapter 14.2.5)}$$

Values of the equilibrium constant at various temperatures were reported as $K_{25°C} = 3.3 \times 10^8$, $K_{177°C} = 2.6 \times 10^3$, and $K_{327°C} = 4.1$.

1. At which temperature would you expect to find the highest proportion of H_2 and N_2 in the equilibrium mixture?

2. Assuming that the reaction rates are fast enough so that equilibrium is reached quickly, at what temperature would you design a commercial reactor to operate to maximize the yield of ammonia?

Answer:

1. 327°C, where K is smallest
2. 25°C

Variations in the Form of the Equilibrium Constant Expression

Because equilibrium can be approached from either direction in a chemical reaction, the equilibrium constant expression and thus the magnitude of the equilibrium constant depend on the form in which the chemical reaction is written. For example, if we write the reaction described in Equation 14.2.6 in reverse, we obtain the following:

$$cC + dD \rightleftharpoons aA + bB \tag{14.2.10}$$

The corresponding equilibrium constant K' is as follows:

$$K' = \frac{[A]^a[B]^b}{[C]^c[D]^d} \tag{14.2.11}$$

This expression is the inverse of the expression for the original equilibrium constant, so $K' = 1/K$. That is, when we write a reaction in the reverse direction, the equilibrium constant expression is inverted. For instance, the equilibrium constant for the reaction $N_2O_4 \rightleftharpoons 2NO_2$ is as follows:

$$K = \frac{[NO_2]^2}{[N_2O_4]} \tag{14.2.12}$$

but for the opposite reaction, $2NO_2 \rightleftharpoons N_2O_4$ the equilibrium constant K' is given by the inverse expression:

$$K' = \frac{[N_2O_4]}{[NO_2]^2} \tag{14.2.13}$$

Consider another example, the formation of water: $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$ Because H_2 is a good reductant and O_2 is a good oxidant, this reaction has a very large equilibrium constant ($K = 2.4 \times 10^{47}$ at 500 K). Consequently, the equilibrium constant for the reverse reaction, the decomposition of water to form O_2 and H_2, is very small: $K' = 1/K = 1/(2.4 \times 10^{47}) = 4.2 \times 10^{-48}$. As suggested by the very small equilibrium constant, and fortunately for life as we know it, a substantial amount of energy is indeed needed to dissociate water into H_2 and O_2.

Note the Pattern

The equilibrium constant for a reaction written in reverse is the *inverse* of the equilibrium constant for the reaction as written originally.

Writing an equation in different but chemically equivalent forms also causes both the equilibrium constant expression and the magnitude of the equilibrium constant to be different. For example, we could write the equation for the reaction

$$2NO_2 \rightleftharpoons N_2O_4 \tag{Chapter 14.2.6}$$

as

$$NO_2 \rightleftharpoons \frac{1}{2}N_2O_4 \tag{Chapter 14.2.7}$$

with the equilibrium constant K'' is as follows:

$$K'' = \frac{[N_2O_4]^{1/2}}{[NO_2]} \tag{14.2.14}$$

The values for K' (Equation 14.2.13) and K'' are related as follows:

$$K'' = (K')^{1/2} = \sqrt{K'} \tag{14.2.15}$$

In general, if all the coefficients in a balanced chemical equation are subsequently multiplied by n, then the new equilibrium constant is the original equilibrium constant raised to the nth power.

Example 14.2.3

At 745 K, K is 0.118 for the following reaction:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \tag{Chapter 14.2.8}$$

What is the equilibrium constant for each related reaction at 745 K?

1. $2NH_{3(g)} \rightleftharpoons N2(g) + 3H_{2(g)}$
2. $\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \rightleftharpoons NH_{3(g)}$

Given: balanced equilibrium equation, K at a given temperature, and equations of related reactions

Asked for: values of K for related reactions

Strategy:

Write the equilibrium constant expression for the given reaction and for each related reaction. From these expressions, calculate K for each reaction.

Solution:

The equilibrium constant expression for the given reaction of $N_2(g)$ with $H_2(g)$ to produce $NH_3(g)$ at 745 K is as follows:

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.118 \tag{Chapter 14.2.9}$$

1. This reaction is the reverse of the one given, so its equilibrium constant expression is as follows:

$$K' = \frac{1}{K} = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{0.118} = 8.47 \tag{Chapter 14.2.10}$$

2. In this reaction, the stoichiometric coefficients of the given reaction are divided by 2, so the equilibrium constant is calculated as follows:

$$K'' = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = K^{1/2} = \sqrt{K} = \sqrt{0.118} = 0.344 \tag{Chapter 14.2.11}$$

Exercise

At 527°C, the equilibrium constant for the reaction

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \tag{Chapter 14.2.12}$$

is 7.9×10^4. Calculate the equilibrium constant for the following reaction at the same temperature:

$$SO_{3(g)} \rightleftharpoons SO_{2(g)} + \frac{1}{2}O_{2(g)} \tag{Chapter 14.2.13}$$

Answer: 3.6×10^{-3}

Equilibrium Constant Expressions for Systems that Contain Gases

For reactions that involve species in solution, the concentrations used in equilibrium calculations are usually expressed in moles/liter. For gases, however, the concentrations are usually expressed in terms of partial pressures rather than molarity, where the standard state is 1 atm of pressure. The symbol K_p is used to denote equilibrium constants calculated from partial pressures. For the general reaction aA + bB ⇌ cC + dD in which all the components are gases, we can write the equilibrium constant expression as the ratio of the partial pressures of the products and reactants (each raised to its coefficient in the chemical equation):

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} \tag{14.2.16}$$

Thus K_p for the decomposition of N_2O_4 (Equation 14.1.1) is as follows:

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} \tag{14.2.17}$$

Like K, K_p is a unitless quantity because the quantity that is actually used to calculate it is an “effective pressure,” the ratio of the measured pressure to a standard state of 1 bar (approximately 1 atm), which produces a unitless quantity.The “effective pressure” is called the *fugacity*, just as activity is the effective concentration.

Because partial pressures are usually expressed in atmospheres or Torr, the molar concentration of a gas and its partial pressure do not have the same numerical value. Consequently, the numerical values of K and K_p are usually different. They are, however, related by the ideal gas constant (R) and the temperature (T):

$$K_p = K(RT)^{\Delta n} \tag{14.2.18}$$

where K is the equilibrium constant expressed in units of concentration and Δn is the difference between the numbers of moles of gaseous products and gaseous reactants ($n_p - n_r$). The temperature is expressed as the absolute temperature in kelvins. You can prove this by starting from the ideal gas law for the partial pressure of each gas $p_iV = n_iRT$ and the concentration of each gas is given by n_i/V.

According to Equation 14.2.18, $K_p = K$ only if the moles of gaseous products and gaseous reactants are the same (i.e., $\Delta n = 0$). For the decomposition of N_2O_4, there are 2 mol of gaseous product and 1 mol of gaseous reactant, so $\Delta n = 1$. Thus, for this reaction, $K_p = K(RT)^1 = KRT$.

Example 14.2.4

The equilibrium constant for the reaction of nitrogen and hydrogen to give ammonia is 0.118 at 745 K. The balanced equilibrium equation is as follows:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \tag{Chapter 14.2.14}$$

What is K_p for this reaction at the same temperature?

Given: equilibrium equation, equilibrium constant, and temperature

Asked for: K_p

Strategy:

Use the coefficients in the balanced chemical equation to calculate Δn. Then use Equation 14.2.18 to calculate K from K_p.

Solution:

This reaction has 2 mol of gaseous product and 4 mol of gaseous reactants, so $\Delta n = (2 - 4) = -2$. We know K, and $T = 745$ K. Thus, from Equation 14.2.15, we have the following:

$$K_p = K(RT)^{-2} = \frac{K}{(RT)^2} \tag{Chapter 14.2.15}$$

$$= \frac{0.118}{\{[0.08206(L \cdot atm)/(mol \cdot K)][745\ K]\}^2} = 3.16 \times 10^{-5}$$

Because K_p is a unitless quantity, the answer is $K_p = 3.16 \times 10^{-5}$.

Exercise

Calculate K_p for the reaction

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \tag{Chapter 14.2.16}$$

at 527°C, if $K = 7.9 \times 10^4$ at this temperature.

Answer: $K_p = 1.2 \times 10^3$

Homogeneous and Heterogeneous Equilibriums

When the products and reactants of an equilibrium reaction form a single phase, whether gas or liquid, the system is a homogeneous equilibrium. In such situations, the concentrations of the reactants and products can vary over a wide range. In contrast, a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium, such as the reaction of a gas with a solid or liquid.

Because the molar concentrations of pure liquids and solids normally do not vary greatly with temperature, their concentrations are treated as constants, which allows us to simplify equilibrium constant expressions that involve pure solids or liquids.The reference states for pure solids and liquids are those forms stable at 1 bar (approximately 1 atm), which are assigned an activity of 1. (Recall from Chapter 7, for example, that the density of water, and thus its volume, changes by only a few percentage points between 0°C and 100°C.)

Consider the following reaction, which is used in the final firing of some types of pottery to produce brilliant metallic glazes:

$$CO_{2(g)} + C_{(s)} \rightleftharpoons 2CO_{(g)} \tag{14.2.19}$$

The glaze is created when metal oxides are reduced to metals by the product, carbon monoxide. The equilibrium constant expression for this reaction is as follows:

$$K = \frac{[CO]^2}{[CO_2][C]} \tag{14.2.20}$$

Because graphite is a solid, however, its molar concentration, determined from its density and molar mass, is essentially constant and has the following value:

$$[C] = \frac{2.26\ \cancel{g}/\cancel{cm^3}}{12.01\ \cancel{g}/mol} \times 1000\ \cancel{cm^3}/L = 188\ mol/L = 188\ M \tag{14.2.21}$$

We can rearrange Equation 14.2.20 so that the constant terms are on one side:

$$K[C] = K(188) = \frac{[CO]^2}{[CO_2]} \tag{14.2.22}$$

Incorporating the constant value of [C] into the equilibrium equation for the reaction in Equation 14.2.19,

$$K' = \frac{[CO]^2}{[CO_2]} \tag{14.2.23}$$

The equilibrium constant for this reaction can also be written in terms of the partial pressures of the gases:

$$K_p = \frac{(P_{CO})^2}{P_{CO_2}} \tag{14.2.24}$$

Incorporating all the constant values into K' or K_p allows us to focus on the substances whose concentrations change during the reaction.

Although the concentrations of pure liquids or solids are not written explicitly in the equilibrium constant expression, these substances must be present in the reaction mixture for chemical equilibrium to occur. Whatever the concentrations of CO and CO_2, the system described in Equation 14.2.19 will reach chemical equilibrium only if a stoichiometric amount of solid carbon or excess solid carbon has been added so that some is still present once the system has reached equilibrium. As shown in Figure 14.2.2, it does not matter whether 1 g or 100 g of solid carbon is present; in either case, the composition of the gaseous components of the system will be the same at equilibrium.

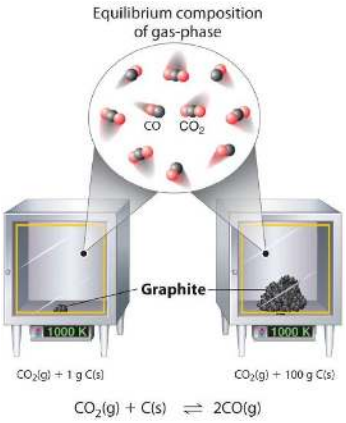


Figure 14.2.2 Effect of the Amount of Solid Present on Equilibrium in a Heterogeneous Solid–Gas System *In the system, the equilibrium composition of the gas phase at a given temperature, 1000 K in this case, is the same whether a small amount of solid carbon (left) or a large amount (right) is present.*

Example 14.2.5

Write each expression for K, incorporating all constants, and K_p for the following equilibrium reactions.

1. $PCl_{3(l)} + Cl_{2(g)} \rightleftharpoons PCl_{5(s)}$
2. $Fe_3O_{4(s)} + 4H_{2(g)} \rightleftharpoons 3Fe_{(s)} + 4H_2O_{(g)}$

Given: balanced equilibrium equations

Asked for: expressions for K and K_p

Strategy:

Find K by writing each equilibrium constant expression as the ratio of the concentrations of the products and reactants, each raised to its coefficient in the chemical equation. Then express K_p as the ratio of the partial pressures of the products and reactants, each also raised to its coefficient in the chemical equation.

Solution:

1. This reaction contains a pure solid (PCl_5) and a pure liquid (PCl_3). Their concentrations do not appear in the equilibrium constant expression because they do not change significantly. So

$$K = \frac{1}{[Cl_2]} \tag{Chapter 14.2.17}$$

and

$$K_p = \frac{1}{P_{Cl_2}} \qquad \text{(Chapter 14.2.18)}$$

2. This reaction contains two pure solids (Fe_3O_4 and Fe), which do not appear in the equilibrium constant expressions. The two gases do, however, appear in the expressions:

$$K = \frac{[H_2O]^4}{[H_2]^4} \qquad \text{(Chapter 14.2.19)}$$

Exercise

Write the expressions for K and K_p for the following reactions.

1. $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$
2. $\underset{\text{glucose}}{C_6H_{12}O_{6(s)}} + 6O_{2(g)} \rightleftharpoons 6CO_{2(g)} + 6H_2O_{(g)}$

Answer:

1. $K = [CO_2]$; and $K_p = P(CO_2)$
2. $K = \frac{[CO_2]^6[H_2O]^6}{[O_2]^6}$ and $K_p = \frac{(P_{CO_2})^6(P_{H_2O})^6}{(P_{O_2})^6}$

For reactions carried out in solution, the concentration of the solvent is omitted from the equilibrium constant expression even when the solvent appears in the balanced chemical equation for the reaction. The concentration of the solvent is also typically much greater than the concentration of the reactants or products (recall that pure water is about 55.5 M, and pure ethanol is about 17 M). Consequently, the solvent concentration is essentially constant during chemical reactions, and the solvent is therefore treated as a pure liquid. The equilibrium constant expression for a reaction contains only those species whose concentrations could change significantly during the reaction.

Note the Pattern

The concentrations of pure solids, pure liquids, and solvents are omitted from equilibrium constant expressions because they do not change significantly during reactions when enough is present to reach equilibrium.

Equilibrium Constant Expressions for the Sums of Reactions

Chemists frequently need to know the equilibrium constant for a reaction that has not been previously studied. In such cases, the desired reaction can often be written as the sum of other reactions for which the equilibrium constants are known. The equilibrium constant for the unknown reaction can then be calculated from the tabulated values for the other reactions.

To illustrate this procedure, let's consider the reaction of N_2 with O_2 to give NO_2. As we stated in Section 14.1, this reaction is an important source of the NO_2 that gives urban smog its typical brown color. The reaction normally occurs in two distinct steps. In the first reaction (1), N_2 reacts with O_2 at the high temperatures inside an internal combustion engine to give NO. The released NO then reacts with additional O_2 to give NO_2 (2). The equilibrium constant for each reaction at 100°C is also given.

1. $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \quad K_1 = 2.0 \times 10^{-25}$
2. $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)} \quad K_2 = 6.4 \times 10^{9}$
3. Summing reactions (1) and (2) gives the overall reaction of N_2 with O_2:
4. $N_{2(g)} + 2O_{2(g)} \rightleftharpoons 2NO_{2(g)} \quad K_3 = ?$

The equilibrium constant expressions for the reactions are as follows:

$$K_1 = \frac{[NO]^2}{[N_2][O_2]} \qquad K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]} \qquad K_3 = \frac{[NO_2]^2}{[N_2][O_2]^2} \qquad \text{(Chapter 14.2.20)}$$

What is the relationship between K_1, K_2, and K_3, all at 100°C? The expression for K_1 has $[NO]^2$ in the numerator, the expression for K_2 has $[NO]^2$ in the denominator, and $[NO]^2$ does not appear in the expression for K_3. Multiplying K_1 by K_2 and canceling the $[NO]^2$ terms,

$$K_1K_2 = \frac{\cancel{[NO]^2}}{[N_2][O_2]} \times \frac{[NO_2]^2}{\cancel{[NO]^2}\,[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2} = K_3 \tag{Chapter 14.2.21}$$

Thus the product of the equilibrium constant expressions for K_1 and K_2 is the same as the equilibrium constant expression for K_3:

$$K_3 = K_1K_2 = (2.0 \times 10^{-25})(6.4 \times 10^{9}) = 1.3 \times 10^{-15} \tag{Chapter 14.2.22}$$

The equilibrium constant for a reaction that is the sum of two or more reactions is equal to the product of the equilibrium constants for the individual reactions. In contrast, recall that according to Hess's Law, ΔH for the sum of two or more reactions is the *sum* of the ΔH values for the individual reactions.

Note the Pattern

To determine K for a reaction that is the sum of two or more reactions, add the reactions but multiply the equilibrium constants.

Example 14.2.6

The following reactions occur at 1200°C:

1. $CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)} \qquad K_1 = 9.17 \times 10^{-2}$
2. $CH_{4(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + 4H_{2(g)} \qquad K_2 = 3.3 \times 10^{4}$

Calculate the equilibrium constant for the following reaction at the same temperature.

3. $CO_{(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)} \qquad K_3 = ?$

Given: two balanced equilibrium equations, values of K, and an equilibrium equation for the overall reaction

Asked for: equilibrium constant for the overall reaction

Strategy:

Arrange the equations so that their sum produces the overall equation. If an equation had to be reversed, invert the value of K for that equation. Calculate K for the overall equation by multiplying the equilibrium constants for the individual equations.

Solution:

The key to solving this problem is to recognize that reaction 3 is the sum of reactions 1 and 2:

$$CO_{(g)} + \cancel{3H_{2(g)}} \rightleftharpoons \cancel{CH_{4(g)}} + H_2O_{(g)} \tag{Chapter 14.2.23}$$

$$\cancel{CH_{4(g)}} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + \cancel{3H_{2(g)}} + H_{2(g)} \tag{Chapter 14.2.24}$$

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)} \tag{Chapter 14.2.25}$$

The values for K_1 and K_2 are given, so it is straightforward to calculate K_3:

$$K_3 = K_1K_2 = (9.17 \times 10^{-2})(3.3 \times 10^{4}) = 3.03 \times 10^{3} \tag{Chapter 14.2.26}$$

Exercise

In the first of two steps in the industrial synthesis of sulfuric acid, elemental sulfur reacts with oxygen to produce sulfur dioxide. In the second step, sulfur dioxide reacts with additional oxygen to form sulfur trioxide. The reaction for each step is shown, as is the value of the corresponding equilibrium constant at 25°C. Calculate the equilibrium constant for the overall reaction at this same temperature.

1. $\frac{1}{8}S_{8(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)} \quad K_1 = 4.4 \times 10^{53}$
2. $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} \quad K_2 = 2.6 \times 10^{12}$
3. $\frac{1}{8}S_{8(s)} + \frac{3}{2}O_{2(g)} \rightleftharpoons SO_{3(g)} \quad K_3 = ?$

Answer: $K_3 = 1.1 \times 10^{66}$

Summary

The ratio of the rate constants for the forward and reverse reactions at equilibrium is the **equilibrium constant (*K*)**, a unitless quantity. The composition of the equilibrium mixture is therefore determined by the magnitudes of the forward and reverse rate constants at equilibrium. Under a given set of conditions, a reaction will always have the same *K*. For a system at equilibrium, the **law of mass action** relates *K* to the ratio of the equilibrium concentrations of the products to the concentrations of the reactants raised to their respective powers to match the coefficients in the **equilibrium equation**. The ratio is called the **equilibrium constant expression**. When a reaction is written in the reverse direction, *K* and the equilibrium constant expression are inverted. For gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products to the partial pressures of the reactants, each raised to a power matching its coefficient in the chemical equation. An equilibrium constant calculated from partial pressures (K_p) is related to *K* by the ideal gas constant (*R*), the temperature (*T*), and the change in the number of moles of gas during the reaction. An equilibrium system that contains products and reactants in a single phase is a **homogeneous equilibrium**; a system whose reactants, products, or both are in more than one phase is a **heterogeneous equilibrium**. When a reaction can be expressed as the sum of two or more reactions, its equilibrium constant is equal to the product of the equilibrium constants for the individual reactions.

Key Takeaways

- The law of mass action describes a system at equilibrium in terms of the concentrations of the products and the reactants.
- For a system involving one or more gases, either the molar concentrations of the gases or their partial pressures can be used.

Key Equations

Definition of equilibrium constant in terms of forward and reverse rate constants

Equation 14.2.5: $K = \frac{k_f}{k_r}$

Equilibrium constant expression (law of mass action)

Equation 14.2.7: $K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

Equilibrium constant expression for reactions involving gases using partial pressures

Equation 14.2.16: $K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$

Relationship between K_p and K

Equation 14.2.18: $K_p = K(RT)^{\Delta n}$

Conceptual Problems

1. For an equilibrium reaction, what effect does reversing the reactants and products have on the value of the equilibrium constant?
2. Which of the following equilibriums are homogeneous and which are heterogeneous?
   a. $2HF_{(g)} \rightleftharpoons H_{2(g)} + F_{2(g)}$
   b. $C_{(s)} + 2H_{2(g)} \rightleftharpoons CH_{4(g)}$
   c. $H_2C{=}CH_{2(g)} + H_{2(g)} \rightleftharpoons C_2H_{6(g)}$
   d. $2Hg_{(l)} + O_{2(g)} \rightleftharpoons 2HgO_{(s)}$
3. Classify each equilibrium system as either homogeneous or heterogeneous.
   a. $NH_4CO_2NH_{2(s)} \rightleftharpoons 2NH_{3(g)} + CO_{2(g)}$
   b. $C_{(s)} + O_{2(g)} \rightleftharpoons CO_{2(g)}$
   c. $2Mg_{(s)} + O_{2(g)} \rightleftharpoons 2MgO_{(s)}$
   d. $AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$
4. If an equilibrium reaction is endothermic, what happens to the equilibrium constant if the temperature of the reaction is increased? if the temperature is decreased?
5. Industrial production of NO by the reaction <math xml:id="av_1.0-15_m114" display="inline"><semantics><mrow><msub><mtext>N</mtext><mn>2</mn></msub><mtext>(g)</mtext><mo>+</mo><msub><mtext>O</mtext><mn>2</mn></msub><mtext>(g)</mtext><mo>⇌</mo><mtext>2NO(g)</mtext></mrow></semantics></math> is carried out at elevated temperatures to drive the reaction toward the formation of product. After sufficient product has formed, the reaction mixture is quickly cooled. Why?
6. How would you differentiate between a system that has reached chemical equilibrium and one that is reacting so slowly that changes in concentration are difficult to observe?
7. What is the relationship between the equilibrium constant, the concentration of each component of the system, and the rate constants for the forward and reverse reactions?
8. Write the equilibrium constant expressions for K and K_p for each reaction.
   a. $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$
   b. $PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$
   c. $2O_{3(g)} \rightleftharpoons 3O_{2(g)}$
9. Write the equilibrium constant expressions for K and K_p as appropriate for each reaction.
   a. $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$
   b. $\frac{1}{2}H_{2(g)} + 12I_{2(g)} \rightleftharpoons HI_{(g)}$
   c. $cis-stilbene_{(soln)} \rightleftharpoons trans-stilbene_{(soln)}$
10. Why is it incorrect to state that pure liquids, pure solids, and solvents are not part of an equilibrium constant expression?
11. Write the equilibrium constant expressions for K and K_p for each equilibrium reaction.
    a. $2S_{(s)} + 3O_{2(g)} \rightleftharpoons 2SO_{3(g)}$
    b. $C_{(s)} + CO_{2(g)} \rightleftharpoons 2CO_{(g)}$
    c. $2ZnS_{(s)} + 3O_{2(g)} \rightleftharpoons 2ZnO_{(s)} + 2SO_{2(g)}$
12. Write the equilibrium constant expressions for K and K_p for each equilibrium reaction.
    a. $2HgO_{(s)} \rightleftharpoons 2Hg_{(l)} + O_{2(g)}$
    b. $H_{2(g)} + I_{2(s)} \rightleftharpoons 2HI_{(g)}$
    c. $NH_4CO_2NH_{2(s)} \rightleftharpoons 2NH_{3(g)} + CO_{2(g)}$
13. At room temperature, the equilibrium constant for the reaction <math xml:id="av_1.0-15_m134" display="inline"><semantics><mrow><mn>2</mn><mtext>A(g)</mtext><mo>⇌</mo><mtext>B(g)</mtext></mrow></semantics></math> is 1. What does this indicate about the concentrations of A and B at equilibrium? Would you expect K and K_p to vary significantly from each other? If so, how would their difference be affected by temperature?

14. For a certain series of reactions, if [OH][HCO_3]/[CO_3] = K_1 and [OH][H_2CO_3]/[HCO_3] = K_2, what is the equilibrium constant expression for the overall reaction? Write the overall equilibrium equation.
15. In the equation for an enzymatic reaction, ES represents the complex formed between the substrate S and the enzyme protein E. In the final step of the following oxidation reaction, the product P dissociates from the ESO_2 complex, which regenerates the active enzyme:

$$E + S \rightleftharpoons ES \quad K_1 \qquad \text{(Chapter 14.2.27)}$$
$$ES + O_2 \rightleftharpoons ESO_2 \quad K_2 \qquad \text{(Chapter 14.2.28)}$$
$$ESO_2 \rightleftharpoons E + P \quad K_3 \qquad \text{(Chapter 14.2.29)}$$

Give the overall reaction equation and show that $K = K_1 \times K_2 \times K_3$.

Answers

1. The equilibrium constant for the reaction written in reverse: $K' = 1/K$.
2.
3. Each system is heterogeneous.
4.
5. Rapid cooling “quenches” the reaction mixture and prevents the system from reverting to the low-temperature equilibrium composition that favors the reactants.
6.
7. \(K=\dfrac{k_f}{k_r}\;\;\; K=\dfrac{[C]^c[D]^d}{[A]^a[B]^b}\])
8.
9. a. $K = \dfrac{[NO_2]^2}{[NO]^2[O_2]} \quad K_p = \dfrac{(P_{N_2O})^2}{(P_{NO})^2(P_{O_2}}$)
   b. $K = \dfrac{[HI]}{[H_2]^{1/2}[I_2]^{1/2}} \quad K_p = \dfrac{P_{HI}}{(P_{H_2})^{1/2}(P_{I_2})}$
   c. $K = \dfrac{[\text{trans-stilbene}]}{[\text{cis-stilbene}]}$
10.
11. a. $K = \dfrac{[SO_3]^2}{[O_2]^3} \quad K_p = \dfrac{(P_{SO_3})^2}{(P_{O_2})^3}$
    b. $K = \dfrac{[CO]^2}{[CO_2]} \quad K_p = \dfrac{(P_{CO})^2}{P_{CO_2}}$
    c. $K = \dfrac{[SO_2]^2}{[O_2]^3} \quad K_p = \dfrac{(P_{SO_2})^2}{(P_{O_2})^3}$
12.
13. At equilibrium,

$$[A] = \sqrt{B} \text{ and } \Delta n = -1 \text{ so } K_p = K(RT)^{\Delta n} = \frac{K}{RT}$$

the difference increases as T increases.
14.
15.

Numerical Problems

1. Explain what each of the following values for K tells you about the relative concentrations of the reactants versus the products in a given equilibrium reaction: $K = 0.892$; $K = 3.25 \times 10^{8}$; $K = 5.26 \times 10^{-11}$. Are products or reactants favored at equilibrium?
2. Write the equilibrium constant expression for each reaction. Are these equilibrium constant expressions equivalent? Explain.
   a. $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$
   b. $\frac{1}{2}N_2O_{4(g)} \rightleftharpoons NO_{2(g)}$
3. Write the equilibrium constant expression for each reaction.
   a. $\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \rightleftharpoons NH_{3(g)}$
   b. $\frac{1}{3}N_{2(g)} + H_{2(g)} \rightleftharpoons \frac{2}{3}NH_{3(g)}$

How are these two expressions mathematically related to the equilibrium constant expression for

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}?$$ (Chapter 14.2.30)

4. Write an equilibrium constant expression for each reaction.
   a. $C_{(s)} + 2H_2O_{(g)} \rightleftharpoons CO_{2(g)} + 2H_{2(g)}$
   b. $SbCl_{3(g)} + Cl_{2(g)} \rightleftharpoons SbCl_{5(g)}$
   c. $2O_{3(g)} \rightleftharpoons 3O_{2(g)}$
5. Give an equilibrium constant expression for each reaction.
   a. $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$
   b. $\frac{1}{2}H_{2(g)} + \frac{1}{2}I_{2(g)} \rightleftharpoons HI_{(g)}$
   c. $CaCO_{3(s)} + 2HOCl_{(aq)} \rightleftharpoons Ca^{2+}_{(aq)} + 2OCl^{-}_{(aq)} + H_2O_{(l)} + CO_{2(g)}$
6. Calculate K and K_p for each reaction.
   a. $2NOBr_{(g)} \rightleftharpoons 2NO_{(g)} + Br_{(g)}$ at 727°C, the equilibrium concentration of NO is 1.29 M, Br_2 is 10.52 M, and NOBr is 0.423 M.
   b. $C_{(s)} + CO_{2(g)} \rightleftharpoons 2CO_{(g)}$: at 1200 K, a 2.00 L vessel at equilibrium has partial pressures of 93.5 atm CO_2 and 76.8 atm CO, and the vessel contains 3.55 g of carbon.
7. Calculate K and K_p for each reaction.
   a. $N_2O4_{(g)} \rightleftharpoons 2NO_{2(g)}$: at the equilibrium temperature of −40°C, a 0.150 M sample of N_2O_4 undergoes a decomposition of 0.456%.
   b. $CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$: an equilibrium is reached at 227°C in a 15.5 L reaction vessel with a total pressure of 6.71 × 10^{-2} atm. It is found to contain 37.8 g of hydrogen gas, 457.7 g of carbon monoxide, and 7193 g of methanol.
8. Determine K and K_p (where applicable) for each reaction.
   a. $2H_2S_{(g)} \rightleftharpoons 2H_{2(g)} + S_{2(g)}$: at 1065°C, an equilibrium mixture consists of 1.00×10^{-3} M H_2, 1.20×10^{-3} M S_2, and 3.32×10^{-3} M H_2S.
   b. $Ba(OH)_{2(s)} \rightleftharpoons 2OH^{-}_{(aq)} + Ba^{2+}_{(aq)}$: at 25°C, a 250 mL beaker contains 0.330 mol of barium hydroxide in equilibrium with 0.0267 mol of barium ions and 0.0534 mol of hydroxide ions.
9. Determine K and K_p for each reaction.
   a. $2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$: at 500 K, a 24.3 mM sample of $NOCl$ has decomposed, leaving an equilibrium mixture that contains 72.7% of the original amount of $NOCl$.
   b. $Cl_{2(g)} + PCl_{3(g)} \rightleftharpoons PCl_{5(g)}$: at 250°C, a 500 mL reaction vessel contains 16.9 g of Cl_2 gas, 0.500 g of PCl_3, and 10.2 g of PCl_5 at equilibrium.
10. The equilibrium constant expression for a reaction is $[CO_2]^2/[SO_2]^2[O_2]$. What is the balanced chemical equation for the overall reaction if one of the reactants is Na_2CO_3(s)?
11. The equilibrium constant expression for a reaction is $[NO][H_2O]^{3/2}/[NH_3][O_2]^{5/4}$. What is the balanced chemical equation for the overall reaction?
12. Given $K = k_f/k_r$, what happens to the magnitude of the equilibrium constant if the reaction rate of the forward reaction is doubled? What happens if the reaction rate of the reverse reaction for the overall reaction is decreased by a factor of 3?
13. The value of the equilibrium constant for

$$2H_{2(g)} + S_{2(g)} \rightleftharpoons 2H_2S_{(g)}$$ (Chapter 14.2.31)

is 1.08 × 10^7 at 700°C. What is the value of the equilibrium constant for the following related reactions?
   a. $H_{2(g)} + 12S_{2(g)} \rightleftharpoons H_2S_{(g)}$
   b. $4H_{2(g)} + 2S_{2(g)} \rightleftharpoons 4H_2S_{(g)}$
   c. $H_2S_{(g)} \rightleftharpoons H_{2(g)} + 12S_{2(g)}$

Answers

1. K = 0.892: the concentrations of the products and the reactants are approximately equal at equilibrium so neither is favored; K = 3.25 × 10^8: the ratio of the concentration of the products to the reactants at equilibrium is very large so the formation of products is favored; K = 5.26 × 10^{-11}: the ratio of the concentration of the products to the reactants at equilibrium is very small so the formation of products is not favored.
2.

3. a. $K' = \dfrac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}}$

   b. $K'' = \dfrac{[NH_3]^{2/3}}{[N_2]^{1/3}[H_2]}$ $K = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$ $K' = K^{1/2}$, and $K'' = K^{1/3}$

4.

5. a. $K = \dfrac{[NO_2]^2}{[NO]^2[O_2]}$

   b. $K = \dfrac{[HI]}{[H_2]^{1/2}[I_2]^{1/2}}$

   c. $K = \dfrac{[Ca^{2+}][OCl^-]^2[P_{CO_2}]}{[HOCl]^2}$

6.

7. a. $K = 1.25 \times 10^{-5}$ $K_p = 2.39 \times 10^{-4}$

   b. $K = 9.43$ $K_p = 5.60 \times 10^{-3}$

8.

9. a. $K = \dfrac{[Cl_2][NO]^2}{[NOCl]^2} = 4.59 \times 10^{-4}$ $K_p = 1.88 \times 10^{-2}$

   b. $K = \dfrac{[PCl_5]}{[PCl_3][Cl_2]} = 28.3$ $K_p = 0.658$

10.

11. $NH_3 + \frac{5}{4}O_2 \rightleftharpoons NO + \frac{3}{2}H_2O$, which can also be written as follows:

$$4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)} \quad \text{(Chapter 14.2.32)}$$

12.

13. a. 3.29×10^{3}

    b. 1.17×10^{14}

    c. 3.04×10^{-4}

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Chapter 14.3: Solving Equilibrium Problems

Learning Objectives

- To solve quantitative problems involving chemical equilibriums

There are two fundamental kinds of equilibrium problems: (1) those in which we are given the concentrations of the reactants and the products at equilibrium (or, more often, information that allows us to calculate these concentrations), and we are asked to calculate the equilibrium constant for the reaction; and (2) those in which we are given the equilibrium constant and the initial concentrations of reactants, and we are asked to calculate the concentration of one or more substances at equilibrium. In this section, we describe methods for solving both kinds of problems.

Calculating an Equilibrium Constant from Equilibrium Concentrations



n-butane



isobutane (2-methylpropane)

We saw in the exercise in Example 6 in Section 14.2 that the equilibrium constant for the decomposition of $CaCO_3(s)$ to $CaO(s)$ and $CO_2(g)$ is $K = [CO_2]$. At 800°C, the concentration of CO_2 in equilibrium with solid $CaCO_3$ and CaO is 2.5×10^{-3} M. Thus K at 800°C is 2.5×10^{-3}. (Remember that equilibrium constants are unitless.)

A more complex example of this type of problem is the conversion of *n*-butane, an additive used to increase the volatility of gasoline, to isobutane (2-methylpropane). This reaction can be written as follows:

$$n-butane\,(g) \rightleftharpoons isobutane\,(g)$$

and the equilibrium constant K = [isobutane]/[*n*-butane]. At equilibrium, a mixture of *n*-butane and isobutane at room temperature was found to contain 0.041 M isobutane and 0.016 M *n*-butane. Substituting these concentrations into the equilibrium constant expression,

$$K = \frac{isobutane}{n-butane} = \frac{0.041\ \cancel{M}}{0.016\ \cancel{M}} = 2.6$$

Thus the equilibrium constant for the reaction as written is 2.6.

Example 14.3.1

The reaction between gaseous sulfur dioxide and oxygen is a key step in the industrial synthesis of sulfuric acid:

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$$

A mixture of SO_2 and O_2 was maintained at 800 K until the system reached equilibrium. The equilibrium mixture contained 5.0×10^{-2} M SO_3, 3.5×10^{-3} M O_2, and 3.0×10^{-3} M SO_2. Calculate K and K_p at this temperature.

Given: balanced equilibrium equation and composition of equilibrium mixture

Asked for: equilibrium constant

Strategy:

Write the equilibrium constant expression for the reaction. Then substitute the appropriate equilibrium concentrations into this equation to obtain K.

Solution:

Substituting the appropriate equilibrium concentrations into the equilibrium constant expression,

$$K = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]} = \frac{\left(5.0\times10^{-2}\right)^2}{\left(3.0\times10^{-3}\right)^2\left(3.5\times10^{-3}\right)} = 7.9 \times 10^4$$

To solve for K_p, we use Equation 14.2.18, where $\Delta n = 2 - 3 = -1$:

$$K_p = K\,(RT)^{\Delta n}$$
$$= 7.9 \times 10^4 \left[\left(0.082606\ L \cdot atm/mol \cdot \cancel{K}\right)\left(800\ \cancel{K}\right)\right]$$
$$= 1.2 \times 10^3$$

Exercise

Hydrogen gas and iodine react to form hydrogen iodide via the reaction

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$$

A mixture of H_2 and I_2 was maintained at 740 K until the system reached equilibrium. The equilibrium mixture contained 1.37×10^{-2} M HI, 6.47×10^{-3} M H_2, and 5.94×10^{-4} M I_2. Calculate K and K_p for this reaction.

Answer: $K = 48.8$; $K_p = 48.8$

Chemists are not often given the concentrations of all the substances, and they are not likely to measure the equilibrium concentrations of all the relevant substances for a particular system. In such cases, we can obtain the equilibrium concentrations from the initial concentrations of the reactants and the balanced chemical equation for the reaction, as long as the equilibrium concentration of one of the substances is known. Example 9 shows one way to do this.

Example 14.3.2

A 1.00 mol sample of NOCl was placed in a 2.00 L reactor and heated to 227°C until the system reached equilibrium. The contents of the reactor were then analyzed and found to contain 0.056 mol of Cl_2. Calculate K at this temperature. The equation for the decomposition of NOCl to NO and Cl_2 is as follows:

$$2NOCl\,(g) \rightleftharpoons 2NO\,(g) + Cl_2\,(g)$$

Given: balanced equilibrium equation, amount of reactant, volume, and amount of one product at equilibrium

Asked for: K

Strategy:

A Write the equilibrium constant expression for the reaction. Construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations (as initial concentrations plus changes in concentrations).

B Calculate all possible initial concentrations from the data given and insert them in the table.

C Use the coefficients in the balanced chemical equation to obtain the changes in concentration of all other substances in the reaction. Insert those concentration changes in the table.

D Obtain the final concentrations by summing the columns. Calculate the equilibrium constant for the reaction.

Solution:

A The first step in any such problem is to balance the chemical equation for the reaction (if it is not already balanced) and use it to derive the equilibrium constant expression. In this case, the equation is already balanced, and the equilibrium constant expression is as follows:

$$K = \frac{[NO_2]^2\,[Cl_2]}{[NOCl]^2}$$

To obtain the concentrations of NOCl, NO, and Cl_2 at equilibrium, we construct a table showing what is known and what needs to be calculated. We begin by writing the balanced chemical equation at the top of the table, followed by three lines corresponding to the initial concentrations, the changes in concentrations required to get from the initial to the final state, and the final concentrations.

$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2$			
	[NOCl]	[NO]	$[Cl_2]$
initial			
change			
final			

B Initially, the system contains 1.00 mol of NOCl in a 2.00 L container. Thus $[NOCl]_i$ = 1.00 mol/2.00 L = 0.500 M. The initial concentrations of NO and Cl_2 are 0 M because initially no products are present. Moreover, we are told that at equilibrium the system contains 0.056 mol of Cl_2 in a 2.00 L container, so $[Cl_2]_f$ = 0.056 mol/2.00 L = 0.028 M. We insert these values into the following table:

$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2$			
	[NOCl]	[NO]	$[Cl_2]$
initial	0.500	0	0
change			
final			0.028

C We use the stoichiometric relationships given in the balanced chemical equation to find the change in the concentration of Cl_2, the substance for which initial and final concentrations are known:

$\Delta[Cl_2]$ = [0.028 M (final) − 0.00 M (initial)] = +0.028 M

According to the coefficients in the balanced chemical equation, 2 mol of NO are produced for every 1 mol of Cl_2, so the change in the NO concentration is as follows:

$$\Delta[NO] = \left(\frac{0.028\ \cancel{mol\ Cl_2}}{L}\right)\left(\frac{2\ mol\ NO}{1\ \cancel{mol\ Cl_2}}\right) = 0.056\ M$$

Similarly, 2 mol of NOCl are consumed for every 1 mol of Cl_2 produced, so the change in the NOCl concentration is as follows:

$$\Delta[NOCl] = \left(\frac{0.028\ \cancel{mol\ Cl_2}}{L}\right)\left(\frac{-2\ mol\ NO}{1\ \cancel{mol\ Cl_2}}\right) = -0.056\ M$$

We insert these values into our table:

$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2$			
	[NOCl]	[NO]	$[Cl_2]$
initial	0.500	0	0
change	−0.056	+0.056	+0.028
final			0.028

D We sum the numbers in the [NOCl] and [NO] columns to obtain the final concentrations of NO and NOCl:

$[NO]_f$ = 0.000 M + 0.056 M = 0.056 M $[NOCl]_f$ = 0.500 M + (−0.056 M) = 0.444 M

We can now complete the table:

$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2$			
	[NOCl]	[NO]	$[Cl_2]$
initial	0.500	0	0
change	−0.056	+0.056	+0.028
final	0.444	0.056	0.028

We can now calculate the equilibrium constant for the reaction:

$$K = \frac{[NO_2]^2\,[Cl_2]}{[NOCl]^2} = \frac{(0.056)^2\,(0.028)^{\,2}}{0.444} = 4.5 \times 10^{-4}$$

Exercise

The German chemist Fritz Haber (1868–1934; Nobel Prize in Chemistry 1918) was able to synthesize ammonia (NH_3) by reacting 0.1248 M H_2 and 0.0416 M N_2 at about 500°C. At equilibrium, the mixture contained 0.00272 M NH_3. What is K for the reaction $N_2 + 3\,H_2 \rightleftharpoons 2NH_3$at this temperature? What is K_p?

Answer: $K = 0.105$; $K_p = 2.61 \times 10^{-5}$



The original laboratory apparatus designed by Fritz Haber and Robert Le Rossignol in 1908 for synthesizing ammonia from its elements. *A metal catalyst bed, where ammonia was produced, is in the large cylinder at the left. The Haber-Bosch process used for the industrial production of ammonia uses essentially the same process and components but on a much larger scale. Unfortunately, Haber's process enabled Germany to prolong World War I when German supplies of nitrogen compounds, which were used for explosives, had been exhausted in 1914.*

Calculating Equilibrium Concentrations from the Equilibrium Constant

To describe how to calculate equilibrium concentrations from an equilibrium constant, we first consider a system that contains only a single product and a single reactant, the conversion of *n*-butane to isobutane (Equation 14.3.3), for which $K = 2.6$ at 25°C. If we begin with a 1.00 M sample of *n*-butane, we can determine the concentration of *n*-butane and isobutane at equilibrium by constructing a table showing what is known and what needs to be calculated, just as we did in Example 14.3.2.

$$n - butane\,(g) \rightleftharpoons isobutane\,(g) \tag{14.3.3}$$

nbutane(g) ⇌isobutane(g)		
	[*n*-Butane]	[Isobutane]
initial		
change		
final		

The initial concentrations of the reactant and product are both known: $[n\text{-butane}]_i = 1.00$ M and $[\text{isobutane}]_i = 0$ M. We need to calculate the equilibrium concentrations of both *n*-butane and isobutane. Because it is generally difficult to calculate final concentrations directly, we focus on the *change* in the concentrations of the substances between the initial and the final (equilibrium) conditions. If, for example, we define the change in the concentration of isobutane (Δ[isobutane]) as $+x$, then the change in the concentration of *n*-butane is $\Delta[n\text{-butane}] = -x$. This is because the balanced chemical equation for the reaction tells us that 1 mol of *n*-butane is consumed for every 1 mol of isobutane produced. We can then express the final concentrations in terms of the initial concentrations and the changes they have undergone.

nbutane(g) ⇌isobutane(g)		
	[*n*-Butane]	[Isobutane]
initial	1.00	0
change	$-x$	$+x$
final	$(1.00 - x)$	$(0 + x) = x$

Substituting the expressions for the final concentrations of *n*-butane and isobutane from the table into the equilibrium equation,

$$K = \frac{[isobutane]}{[n-butane]} = \frac{x}{1.00 - x} = 2.6$$

Rearranging and solving for *x*,

$$x = 2.6\,(1.00 - x) = 2.6 - 2.6x$$
$$x + 2.6x = 2.6$$
$$x = 0.72$$

We obtain the final concentrations by substituting this *x* value into the expressions for the final concentrations of *n*-butane and isobutane listed in the table:

$[n\text{-butane}]_f = (1.00 - x)\ M = (1.00 - 0.72)\ M = 0.28\ M$ $[\text{isobutane}]_f = (0.00 + x)\ M = (0.00 + 0.72)\ M = 0.72\ M$

We can check the results by substituting them back into the equilibrium constant expression to see whether they give the same *K* that we used in the calculation:

$$K = \frac{[isobutane]}{[n-butane]} = \frac{0.72\ \cancel{M}}{0.28\ \cancel{M}} = 2.6$$

This is the same *K* we were given, so we can be confident of our results.

Example 14.3.3 illustrates a common type of equilibrium problem that you are likely to encounter.

Example 14.3.3

The *water–gas shift reaction* is important in several chemical processes, such as the production of H_2 for fuel cells. This reaction can be written as follows:

$$H_2\,(g) + CO_2\,(g) \rightleftharpoons H_2O\,(g) + CO\,(g)$$

K = 0.106 at 700 K. If a mixture of gases that initially contains 0.0150 M H_2 and 0.0150 M CO_2 is allowed to equilibrate at 700 K, what are the final concentrations of all substances present?

Given: balanced equilibrium equation, *K*, and initial concentrations

Asked for: final concentrations

Strategy:

A Construct a table showing what is known and what needs to be calculated. Define *x* as the change in the concentration of one substance. Then use the reaction stoichiometry to express the changes in the concentrations of the other substances in terms of *x*. From the values in the table, calculate the final concentrations.

B Write the equilibrium equation for the reaction. Substitute appropriate values from the table to obtain *x*.

C Calculate the final concentrations of all species present. Check your answers by substituting these values into the equilibrium constant expression to obtain *K*.

Solution:

A The initial concentrations of the reactants are $[H_2]_i = [CO_2]_i = 0.0150$ M. Just as before, we will focus on the *change* in the concentrations of the various substances between the initial and final states. If we define the change in the concentration of H_2O as

x, then $\Delta[H_2O] = +x$. We can use the stoichiometry of the reaction to express the changes in the concentrations of the other substances in terms of x. For example, 1 mol of CO is produced for every 1 mol of H_2O, so the change in the CO concentration can be expressed as $\Delta[CO] = +x$. Similarly, for every 1 mol of H_2O produced, 1 mol each of H_2 and CO_2 are consumed, so the change in the concentration of the reactants is $\Delta[H_2] = \Delta[CO_2] = -x$. We enter the values in the following table and calculate the final concentrations.

$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$				
	$[H_2]$	$[CO_2]$	$[H_2O]$	$[CO]$
initial	0.0150	0.0150	0	0
change	$-x$	$-x$	$+x$	$+x$
final	$(0.0150 - x)$	$(0.0150 - x)$	x	x

B We can now use the equilibrium equation and the given K to solve for x:

$$K = \frac{[H_2O]\,[CO]}{[H_2]\,[CO_2]} = \frac{(x)\,(x)}{(0.0150 - x)\,(0.0150 - x)} = \frac{x^2}{(0.0150-x)^2} = 0.160$$

We could solve this equation with the quadratic formula, but it is far easier to solve for x by recognizing that the left side of the equation is a perfect square; that is,

$$\frac{x^2}{(0.0150 - x)^2} = \left(\frac{x}{0.0150-x}\right)^2 = 0.106 \qquad \text{(Chapter 14.3.1)}$$

Taking the square root of the middle and right terms,

$$\frac{x^2}{(0.0150 - x)^2} = (0.106)^{1/2} = 0.326 \qquad \text{(Chapter 14.3.2)}$$

$$x = (0.326)(0.0150) - 0.326x \qquad \text{(Chapter 14.3.3)}$$

$$1.326x = 0.00489 \qquad \text{(Chapter 14.3.4)}$$

$$x = 0.00369 = 3.69 \times 10^{-3} \qquad \text{(Chapter 14.3.5)}$$

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f = [H_2]_i + \Delta[H_2] = (0.0150 - 0.00369)\ M = 0.0113\ M$
- $[CO_2]_f = [CO_2]_i + \Delta[CO_2] = (0.0150 - 0.00369)\ M = 0.0113\ M$
- $[H_2O]_f = [H_2O]_i + \Delta[H_2O] = (0 + 0.00369)\ M = 0.00369\ M$
- $[CO]_f = [CO]_i + \Delta[CO] = (0 + 0.00369)\ M = 0.00369\ M$

We can check our work by inserting the calculated values back into the equilibrium constant expression:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.00369)^2}{(0.0113)^2} = 0.107 \qquad \text{(Chapter 14.3.6)}$$

To two significant figures, this K is the same as the value given in the problem, so our answer is confirmed.

Exercise

Hydrogen gas reacts with iodine vapor to give hydrogen iodide according to the following chemical equation:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad \text{(Chapter 14.3.7)}$$

K = 54 at 425°C. If 0.172 M H_2 and I_2 are injected into a reactor and maintained at 425°C until the system equilibrates, what is the final concentration of each substance in the reaction mixture?

Answer: $[HI]_f$ = 0.270 M; $[H_2]_f = [I_2]_f$ = 0.037 M

In Example 14.3.3, the initial concentrations of the reactants were the same, which gave us an equation that was a perfect square and simplified our calculations. Often, however, the initial concentrations of the reactants are not the same, and/or one or more of the products may be present when the reaction starts. Under these conditions, there is usually no way to simplify the problem, and we must determine the equilibrium concentrations with other means. Such a case is described in Example 14.3.4.

Example 14.3.4

In the water–gas shift reaction shown in Example 14.3.3, a sample containing 0.632 M CO_2 and 0.570 M H_2 is allowed to equilibrate at 700 K. At this temperature, K = 0.106. What is the composition of the reaction mixture at equilibrium?

Given: balanced equilibrium equation, concentrations of reactants, and K

Asked for: composition of reaction mixture at equilibrium

Strategy:

A Write the equilibrium equation. Construct a table showing the initial concentrations of all substances in the mixture. Complete the table showing the changes in the concentrations (x) and the final concentrations.

B Write the equilibrium constant expression for the reaction. Substitute the known K value and the final concentrations to solve for x.

C Calculate the final concentration of each substance in the reaction mixture. Check your answers by substituting these values into the equilibrium constant expression to obtain K.

Solution:

A $[CO_2]_i$ = 0.632 M and $[H_2]_i$ = 0.570 M. Again, x is defined as the change in the concentration of H_2O: $\Delta[H_2O] = +x$. Because 1 mol of CO is produced for every 1 mol of H_2O, the change in the concentration of CO is the same as the change in the concentration of H_2O, so $\Delta[CO] = +x$. Similarly, because 1 mol each of H_2 and CO_2 are consumed for every 1 mol of H_2O produced, $\Delta[H_2] = \Delta[CO_2] = -x$. The final concentrations are the sums of the initial concentrations and the changes in concentrations at equilibrium.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)} \quad \text{(Chapter 14.3.8)}$$

	$[H_2]$	$[CO_2]$	$[H_2O]$	$[CO]$
initial	0.570	0.632	0	0
change	$-x$	$-x$	$+x$	$+x$
final	$(0.570 - x)$	$(0.632 - x)$	x	x

B We can now use the equilibrium equation and the known K value to solve for x:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{x^2}{(0.570 - x)(0.632 - x)} = 0.106 \quad \text{(Chapter 14.3.9)}$$

In contrast to Example 10, however, there is no obvious way to simplify this expression. Thus we must expand the expression and multiply both sides by the denominator:

$$x^2 = 0.106(0.360 - 1.20x + x^2) \quad \text{(Chapter 14.3.10)}$$

Collecting terms on one side of the equation,

$$0.894x^2 + 0.127x - 0.0382 = 0 \quad \text{(Chapter 14.3.11)}$$

This equation can be solved using the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \tag{Chapter 14.3.12}$$

$$= \frac{-0.127 \pm \sqrt{(0.127)^2 - 4(0.894)(-0.0382)}}{2(0.894)}$$

$$x = 0.148 \text{ and } -0.290 \tag{Chapter 14.3.13}$$

Only the answer with the positive value has any physical significance, so $\Delta[H_2O] = \Delta[CO] = +0.148$ M, and $\Delta[H_2] = \Delta[CO_2] = -0.148$ M.

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f [= [H_2]_i + \Delta[H_2] = 0.570\ M - 0.148\ M = 0.422M$
- $[CO_2]_f = [CO_2]_i + \Delta[CO_2] = 0.632\ M - 0.148\ M = 0.484M$
- $[H_2O]_f = [H_2O]_i + \Delta[H_2O] = 0\ M + 0.148\ M = 0.148\ M$
- $[CO]_f = [CO]_i + \Delta[CO] = 0M + 0.148\ M = 0.148M$

We can check our work by substituting these values into the equilibrium constant expression:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.148)^2}{(0.422)(0.484)} = 0.107 \tag{Chapter 14.3.14}$$

Because K is essentially the same as the value given in the problem, our calculations are confirmed.

Exercise

The exercise in Example 8 showed the reaction of hydrogen and iodine vapor to form hydrogen iodide, for which $K = 54$ at 425°C. If a sample containing 0.200 M H_2 and 0.0450 M I_2 is allowed to equilibrate at 425°C, what is the final concentration of each substance in the reaction mixture?

Answer: $[HI]_f = 0.0882$ M; $[H_2]_f = 0.156$ M; $[I_2]_f = 9.2 \times 10^{-4}$ M

In many situations it is not necessary to solve a quadratic (or higher-order) equation. Most of these cases involve reactions for which the equilibrium constant is either very small ($K \le 10^{-3}$) or very large ($K \ge 10^3$), which means that the change in the concentration (defined as x) is essentially negligible compared with the initial concentration of a substance. Knowing this simplifies the calculations dramatically, as illustrated in Example 14.3.5.

Example 14.3.5

Atmospheric nitrogen and oxygen react to form nitric oxide:

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \tag{Chapter 14.3.15}$$

$K_p = 2.0 \times 10^{-31}$ at 25°C. What is the partial pressure of NO in equilibrium with N_2 and O_2 in the atmosphere (at 1 atm, $P\{N_2\} = 0.78$ atm and $P\{O_2\} = 0.21$ atm

Given: balanced equilibrium equation and values of K_p, $P\{O_2\}$ and $P\{N_2\}$

Asked for: partial pressure of NO

Strategy:

A Construct a table and enter the initial partial pressures, the changes in the partial pressures that occur during the course of the reaction, and the final partial pressures of all substances.

B Write the equilibrium equation for the reaction. Then substitute values from the table to solve for the change in concentration (x).

C Calculate the partial pressure of NO. Check your answer by substituting values into the equilibrium equation and solving for K.

Solution:

A Because we are given K_p and partial pressures are reported in atmospheres, we will use partial pressures. The initial partial pressure of O_2 is 0.21 atm and that of N_2 is 0.78 atm. If we define the change in the partial pressure of NO as $2x$, then the change in

the partial pressure of O_2 and of N_2 is $-x$ because 1 mol each of N_2 and of O_2 is consumed for every 2 mol of NO produced. Each substance has a final partial pressure equal to the sum of the initial pressure and the change in that pressure at equilibrium.

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \quad \text{(Chapter 14.3.16)}$$

	P{N_2}	P{N_2}	P{NO}
initial P	0.78	0.21	0
change in P	$-x$	$-x$	$+2x$
final P	$(0.78 - x)$	$(0.21 - x)$	$2x$

B Substituting these values into the equation for the equilibrium constant,

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(2x)^2}{(0.78 - x)(0.21 - x)} = 2.0 \times 10^{-31} \quad \text{(Chapter 14.3.17)}$$

In principle, we could multiply out the terms in the denominator, rearrange, and solve the resulting quadratic equation. In practice, it is far easier to recognize that an equilibrium constant of this magnitude means that the extent of the reaction will be very small; therefore, the x value will be negligible compared with the initial concentrations. If this assumption is correct, then to two significant figures, $(0.78 - x) = 0.78$ and $(0.21 - x) = 0.21$. Substituting these expressions into our original equation,

$$\frac{(2x)^2}{(0.78)(0.21)} = 2.0 \times 10^{-31} \quad \text{(Chapter 14.3.18)}$$

$$\frac{4x^2}{0.16} = 2.0 \times 10^{-31} \quad \text{(Chapter 14.3.19)}$$

$$x^2 = \frac{0.33 \times 10^{-31}}{4} \quad \text{(Chapter 14.3.20)}$$

$$x = 9.1 \times 10^{-17} \quad \text{(Chapter 14.3.21)}$$

C Substituting this value of x into our expressions for the final partial pressures of the substances,

- $P_{NO} = 2x\ atm = 1.8 \times 10^{-16}\ atm$
- $P_{N_2} = (0.78 - x)\ atm = 0.78\ atm$
- $P_{O_2} = (0.21 - x)\ atm = 0.21\ atm$

From these calculations, we see that our initial assumption regarding x was correct: given two significant figures, 2.0×10^{-16} is certainly negligible compared with 0.78 and 0.21. When can we make such an assumption? As a general rule, if x is less than about 5% of the total, or $10^{-3} > K > 10^3$, then the assumption is justified. Otherwise, we must use the quadratic formula or some other approach. The results we have obtained agree with the general observation that toxic NO, an ingredient of smog, does not form from atmospheric concentrations of N_2 and O_2 to a substantial degree at 25°C. We can verify our results by substituting them into the original equilibrium equation:

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(1.8 \times 10^{-16})^2}{(0.78)(0.21)} = 2.0 times 10^{-31} \quad \text{(Chapter 14.3.22)}$$

The final K_p agrees with the value given at the beginning of this example.

Exercise

Under certain conditions, oxygen will react to form ozone, as shown in the following equation:

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)} \quad \text{(Chapter 14.3.23)}$$

$K_p = 2.5 \times 10^{-59}$ at 25°C. What ozone partial pressure is in equilibrium with oxygen in the atmosphere P(O_2) =0.21 atm?

Answer: 4.8×10^{-31} atm

Another type of problem that can be simplified by assuming that changes in concentration are negligible is one in which the equilibrium constant is very large ($K \geq 10^3$). A large equilibrium constant implies that the reactants are converted almost entirely to products, so we can assume that the reaction proceeds 100% to completion. When we solve this type of problem, we view the system as equilibrating from the *products* side of the reaction rather than the reactants side. This approach is illustrated in Example 14.3.6.

Example 14.3.6

The chemical equation for the reaction of hydrogen with ethylene (C_2H_4) to give ethane (C_2H_6) is as follows:

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)} \quad \text{(Chapter 14.3.24)}$$

$K = 9.6 \times 10^{18}$ at 25°C. If a mixture of 0.200 M H_2 and 0.155 M C_2H_4 is maintained at 25°C in the presence of a powdered nickel catalyst, what is the equilibrium concentration of each substance in the mixture?

Given: balanced chemical equation, K, and initial concentrations of reactants

Asked for: equilibrium concentrations

Strategy:

A Construct a table showing initial concentrations, concentrations that would be present if the reaction were to go to completion, changes in concentrations, and final concentrations.

B Write the equilibrium constant expression for the reaction. Then substitute values from the table into the expression to solve for x (the change in concentration).

C Calculate the equilibrium concentrations. Check your answers by substituting these values into the equilibrium equation.

Solution:

A From the magnitude of the equilibrium constant, we see that the reaction goes essentially to completion. Because the initial concentration of ethylene (0.155 M) is less than the concentration of hydrogen (0.200 M), ethylene is the limiting reactant; that is, no more than 0.155 M ethane can be formed from 0.155 M ethylene. If the reaction were to go to completion, the concentration of ethane would be 0.155 M and the concentration of ethylene would be 0 M. Because the concentration of hydrogen is greater than what is needed for complete reaction, the concentration of unreacted hydrogen in the reaction mixture would be 0.200 M − 0.155 M = 0.045 M. The equilibrium constant for the forward reaction is very large, so the equilibrium constant for the reverse reaction must be very small. The problem then is identical to that in Example 12. If we define $-x$ as the change in the ethane concentration for the reverse reaction, then the change in the ethylene and hydrogen concentrations is $+x$. The final equilibrium concentrations are the sums of the concentrations for the forward and reverse reactions.

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)} \quad \text{(Chapter 14.3.25)}$$

	$[H_2]$	$[C_2H_4]$	$[C_2H_6]$
initial	0.200	0.155	0
assuming 100% reaction	0.045	0	0.155
change	$+x$	$+x$	$-x$
final	$(0.045 + x)$	$(0 + x)$	$(0.155 - x)$

B Substituting values into the equilibrium constant expression,

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155 - x}{(0.045 + x)x} = 9.6 \times 10^{18} \quad \text{(Chapter 14.3.26)}$$

Once again, the magnitude of the equilibrium constant tells us that the equilibrium will lie far to the right as written, so the reverse reaction is negligible. Thus x is likely to be very small compared with either 0.155 M or 0.045 M, and the equation can be simplified [(0.045 + x) = 0.045 and (0.155 − x) = 0.155] as follows:

$$K = \frac{0.155}{0.045x} = 9.6 \times 10^{18} \quad \text{(Chapter 14.3.27)}$$

$$x = 3.6 \times 10^{-19} \quad \text{(Chapter 14.3.28)}$$

C The small x value indicates that our assumption concerning the reverse reaction is correct, and we can therefore calculate the final concentrations by evaluating the expressions from the last line of the table:

- $[C_2H_6]_f = (0.155 - x)\ M = 0.155\ M$
- $[C_2H_4]_f = x\ M = 3.6 \times 10^{-19} M$
- $[H_2]_f = (0.045 + x)\ M = 0.045\ M$

We can verify our calculations by substituting the final concentrations into the equilibrium constant expression:

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155}{(0.045)(3.6 \times 10^{-19})} = 9.6 \times 10^{18} \quad \text{(Chapter 14.3.29)}$$

This K value agrees with our initial value at the beginning of the example.

Exercise

Hydrogen reacts with chlorine gas to form hydrogen chloride:

$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)} \quad \text{(Chapter 14.3.30)}$$

K_p = 4.0 × 10^{31} at 47°C. If a mixture of 0.257 M H_2 and 0.392 M Cl_2 is allowed to equilibrate at 47°C, what is the equilibrium composition of the mixture?

Answer:

- $[H_2]_f = 4.8 \times 10^{-32}\ M$
- $[Cl_2]_f = 0.135\ M$
- $[HCl]_f = 0.514\ M$

Summary

When an equilibrium constant is calculated from equilibrium concentrations, molar concentrations or partial pressures are substituted into the equilibrium constant expression for the reaction. Equilibrium constants can be used to calculate the equilibrium concentrations of reactants and products by using the quantities or concentrations of the reactants, the stoichiometry of the balanced chemical equation for the reaction, and a tabular format to obtain the final concentrations of all species at equilibrium.

Key Takeaway

- Various methods can be used to solve the two fundamental types of equilibrium problems: (1) those in which we calculate the concentrations of reactants and products at equilibrium and (2) those in which we use the equilibrium constant and the initial concentrations of reactants to determine the composition of the equilibrium mixture.

Conceptual Problems

1. Describe how to determine the magnitude of the equilibrium constant for a reaction when not all concentrations of the substances are known.
2. Calculations involving systems with very small or very large equilibrium constants can be dramatically simplified by making certain assumptions about the concentrations of products and reactants. What are these assumptions when K is (a) very large and (b) very small? Illustrate this technique using the system A + 2B ⇌ C for which you are to calculate the concentration of the product at equilibrium starting with only A and B. Under what circumstances should simplifying assumptions not be used?

Numerical Problems

1. In the equilibrium reaction A + B ⇌C, what happens to K if the concentrations of the reactants are doubled? tripled? Can the same be said about the equilibrium reaction A ⇌B + C?
2. The following table shows the reported values of the equilibrium P{O_2} at three temperatures for the reaction $Ag_2O(s)$ ⇌ 2 Ag(s) + 1/2 $O_2(g)$ for which $\Delta H°$ = 31 kJ/mol. Are these data consistent with what you would expect to occur? Why or why not?

T (°C)	P(O_2) mm Hg
150	182
184	143
191	126

3. Given the equilibrium system $N_2O_4(g)$ ⇌ 2 $NO_2(g)$, what happens to K_p if the initial pressure of N_2O_4 is doubled? If K_p is 1.7 × 10^{-1} at 2300°C, and the system initially contains 100% N_2O_4 at a pressure of 2.6 × 10^2 atm, what is the equilibrium pressure of each component?
4. At 430°C, 4.20 mol of HI in a 9.60 L reaction vessel reaches equilibrium according to the following equation: $H_2(g)$ + $I_2(g)$ ⇌2HI(g) At equilibrium, [H_2] = 0.047 M and [HI] = 0.345 M. What are K and K_p for this reaction?
5. Methanol, a liquid used as an automobile fuel additive, is commercially produced from carbon monoxide and hydrogen at 300°C according to the following reaction: CO(g) + 2$H_2(g)$ ⇌ $CH_3OH(g)$ and K_p = 1.3 × 10^{-4}. If 56.0 g of CO is mixed with excess hydrogen in a 250 mL flask at this temperature, and the hydrogen pressure is continuously maintained at 100 atm, what would be the maximum percent yield of methanol? What pressure of hydrogen would be required to obtain a minimum yield of methanol of 95% under these conditions?
6. Starting with pure A, if the total equilibrium pressure is 0.969 atm for the reactionA(s ⇌ 2 B(g) + C(g), what is K_p?
7. The decomposition of ammonium carbamate to NH_3 and CO_2 at 40°C is written as $NH_4CO_2NH_2(s)$ ⇌ 2$NH_3(g)$ + CO_2 If the partial pressure of NH_3 at equilibrium is 0.242 atm, what is the equilibrium partial pressure of CO_2? What is the total gas pressure of the system? What is K_p?
8. At 375 K, K_p for the reaction $SO_2Cl_2(g)$ ⇌ $SO_2(g)$ + Cl_2g) is 2.4, with pressures expressed in atmospheres. At 303 K, K_p is 2.9 × 10^{-2}.
    1. What is K for the reaction at each temperature?
    2. If a sample at 375 K has 0.100 M Cl_2 and 0.200 M SO_2 at equilibrium, what is the concentration of SO_2Cl_2?
    3. If the sample given in part b is cooled to 303 K, what is the pressure inside the bulb?
9. For the gas-phase reaction aA ⇌ bB, show that $K_p = K(RT)^{\Delta n}$ assuming ideal gas behavior.
10. For the gas-phase reaction I_2 ⇌2I, show that the total pressure is related to the equilibrium pressure by the following equation:

$$P_T = \sqrt{K_p P_{I_2}} + P_{I_2} \qquad \textbf{(Chapter 14.3.31)}$$

11. Experimental data on the system Br2(l) ⇌ Br_2(aq) are given in the following table. Graph [Br_2] versus moles of Br_2(l) present; then write the equilibrium constant expression and determine K.

Grams Br_2 in 100 mL Water	$[Br_2]$ (M)
1.0	0.0626
2.5	0.156
3.0	0.188
4.0	0.219
4.5	0.219

12. Data accumulated for the reaction n-butane(g) ⇌ isobutane(g) at equilibrium are shown in the following table. What is the equilibrium constant for this conversion? If 1 mol of *n*-butane is allowed to equilibrate under the same reaction conditions, what is the final number of moles of *n*-butane and isobutane?

Moles *n*-butane	Moles Isobutane
0.5	1.25
1.0	2.5
1.50	3.75

13. Solid ammonium carbamate ($NH_4CO_2NH_2$) dissociates completely to ammonia and carbon dioxide when it vaporizes:

$$[NH_4CO_2NH_{2(s)} \rightleftharpoons 2NH_{3(g)}+CO_{2(g)}\]$$

At 25°C, the total pressure of the gases in equilibrium with the solid is 0.116 atm. What is the equilibrium partial pressure of each gas? What is K_p? If the concentration of CO_2 is doubled and then equilibrates to its initial equilibrium partial pressure $+x$ atm, what change in the NH_3 concentration is necessary for the system to restore equilibrium?

14. The equilibrium constant for the reaction $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ is $K_p = 2.2 \times 10^{-10}$ at 100°C. If the initial concentration of $COCl_2$ is 3.05×10^{-3} M, what is the partial pressure of each gas at equilibrium at 100°C? What assumption can be made to simplify your calculations?

15. Aqueous dilution of IO_4^- results in the following reaction:

$$IO_{4(aq)}^- + 2H_2O_{(l)} \rightleftharpoons H_4IO_{6(aq)}^- \quad \textbf{(Chapter 14.3.32)}$$

and $K = 3.5 \times 10^{-2}$. If you begin with 50 mL of a 0.896 M solution of IO_4^- that is diluted to 250 mL with water, how many moles of $H_4IO_6^-$ are formed at equilibrium?

16. Iodine and bromine react to form IBr, which then sublimes. At 184.4°C, the overall reaction proceeds according to the following equation:

$$I_{2(g)} + Br_{2(g)} \rightleftharpoons 2IBr_{(g)} \quad \textbf{(Chapter 14.3.33)}$$

$K_p = 1.2 \times 10^2$. If you begin the reaction with 7.4 g of I_2 vapor and 6.3 g of Br_2 vapor in a 1.00 L container, what is the concentration of IBr(g) at equilibrium? What is the partial pressure of each gas at equilibrium? What is the total pressure of the system?

17. For the reaction

$$C_{(s)} + 12N_{2(g)} + \frac{5}{2}H_{2(g)} \rightleftharpoons CH3NH2(g) \quad \textbf{(Chapter 14.3.34)}$$

$K = 1.8 \times 10^{-6}$. If you begin the reaction with 1.0 mol of N_2, 2.0 mol of H_2, and sufficient C(s) in a 2.00 L container, what are the concentrations of N_2 and CH_3NH_2 at equilibrium? What happens to K if the concentration of H_2 is doubled?

Contributors

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Modified by Joshua Halpern (Howard University), Scott Sinex, and Scott Johnson (PGCC)

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Chapter 14.4: Non-equilibrium Conditions

Learning Objectives

- To predict in which direction a reaction will proceed.

In Section 14.3, we saw that knowing the magnitude of the equilibrium constant under a given set of conditions allows chemists to predict the extent of a reaction. Often, however, chemists must decide whether a system has reached equilibrium or if the composition of the mixture will continue to change with time. In this section, we describe how to quantitatively analyze the composition of a reaction mixture to make this determination.

The Reaction Quotient

To determine whether a system has reached equilibrium, chemists use a quantity called the reaction quotient (Q). The expression for the reaction quotient has precisely the same form as the equilibrium constant expression, except that Q may be derived from a set of values measured at *any* time during the reaction of *any* mixture of the reactants and the products, regardless of whether the system is at equilibrium. Therefore, for the following general reaction:

$$aA + bB \rightarrow cC + dD \tag{Chapter 14.4.1}$$

the reaction quotient is defined as follows:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{14.4.1}$$

The reaction quotient Q_p analogous to K_p, can be written for any reaction that involves gases by using the partial pressures of the components.

To understand how information is obtained using a reaction quotient, consider the dissociation of dinitrogen tetroxide to nitrogen dioxide,

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \tag{Chapter 14.4.2}$$

for which $K = 4.65 \times 10^{-3}$ at 298 K. We can write Q for this reaction as follows:

$$Q = \frac{[NO_2]^2}{[N_2O_4]} \tag{14.4.2}$$

The following table lists data from three experiments in which samples of the reaction mixture were obtained and analyzed at equivalent time intervals, and the corresponding values of Q were calculated for each. Each experiment begins with different proportions of product and reactant:

Experiment	$[NO_2]$ (M)	$[N_2O_4]$ (M)	$Q = [NO_2]^2/[N_2O_4]$
1	0	0.0400	$\frac{0^2}{0.0400} = 0$
2	0.0600	0	$\frac{(0.0600)^2}{0} = \text{undefined}$
3	0.0200	0.0600	$\frac{(0.0200)^2}{0.0600} = 6.67 \times 10^{-3}$

As these calculations demonstrate, Q can have any numerical value between 0 and infinity (undefined); that is, Q can be greater than, less than, or equal to K.

Comparing the magnitudes of Q and K enables us to determine whether a reaction mixture is already at equilibrium and, if it is not, predict how its composition will change with time to reach equilibrium (i.e., whether the reaction will proceed to the right or to the left as written). All you need to remember is that the composition of a system not at equilibrium will change in a way that makes Q approach K. If $Q = K$, for example, then the system is already at equilibrium, and no further change in the composition of the

system will occur unless the conditions are changed. If $Q < K$, then the ratio of the concentrations of products to the concentrations of reactants is *less* than the ratio at equilibrium. Therefore, the reaction will proceed to the right as written, forming products at the expense of reactants. Conversely, if $Q > K$, then the ratio of the concentrations of products to the concentrations of reactants is *greater* than at equilibrium, so the reaction will proceed to the left as written, forming reactants at the expense of products. These points are illustrated graphically in Figure 14.4.1

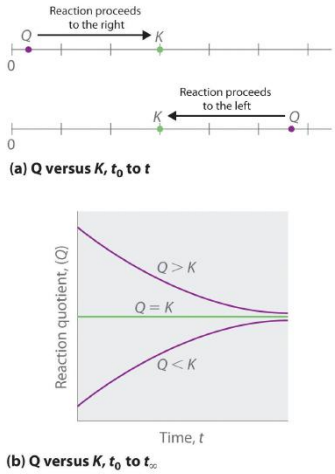


Figure 14.4.1 Two Different Ways of Illustrating How the Composition of a System Will Change Depending on the Relative Values of Q and K*(a) Both Q and K are plotted as points along a number line: the system will always react in the way that causes Q to approach K. (b) The change in the composition of a system with time is illustrated for systems with initial values of Q > K, Q < K, and Q = K.*

Note the Pattern

If $Q < K$, the reaction will proceed to the right as written. If $Q > K$, the reaction will proceed to the left as written. If $Q = K$, then the system is at equilibrium.

Example 14.4.1

At elevated temperatures, methane (CH_4) reacts with water to produce hydrogen and carbon monoxide in what is known as a *steam-reforming* reaction:

$$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)} \qquad \text{(Chapter 14.4.3)}$$

$K = 2.4 \times 10^{-4}$ at 900 K. Huge amounts of hydrogen are produced from natural gas in this way and are then used for the industrial synthesis of ammonia. If 1.2×10^{-2} mol of CH_4, 8.0×10^{-3} mol of H_2O, 1.6×10^{-2} mol of CO, and 6.0×10^{-3} mol of H_2 are placed in a 2.0 L steel reactor and heated to 900 K, will the reaction be at equilibrium or will it proceed to the right to produce CO and H_2 or to the left to form CH_4 and H_2O?

Given: balanced chemical equation, *K*, amounts of reactants and products, and volume

Asked for: direction of reaction

Strategy:

A Calculate the molar concentrations of the reactants and the products.

B Use Equation 14.4.1 to determine *Q*. Compare *Q* and *K* to determine in which direction the reaction will proceed.

Solution:

A We must first find the initial concentrations of the substances present. For example, we have 1.2×10^{-2} mol of CH_4 in a 2.0 L container, so

$$[CH_4] = \frac{1.2 \times 10^{-2} mol}{2.0\ L} = 6.0 \times 10^{-3} M \tag{Chapter 14.4.4}$$

We can calculate the other concentrations in a similar way:

- $[H_2O] = 4.0 \times 10^{-3} M$,
- $[CO] = 8.0 \times 10^{-3} M$, and
- $[H_2] = 3.0 \times 10^{-3} M$.

B We now compute Q and compare it with K:

$$Q = \frac{[CO][H_2]^3}{[CH_4][H_2O} = \frac{(8.0 \times 10^{-3})(3.0 \times 10^{-3})^3}{(6.0 \times 10^{-3})(4.0 \times 10^{-3})} = 9.0 \times 10^{-6} \tag{Chapter 14.4.5}$$

Because $K = 2.4 \times 10^{-4}$, we see that $Q < K$. Thus the ratio of the concentrations of products to the concentrations of reactants is less than the ratio for an equilibrium mixture. The reaction will therefore proceed to the right as written, forming H_2 and CO at the expense of H_2O and CH_4.

Exercise

In the water–gas shift reaction introduced in Example 10, carbon monoxide produced by steam-reforming reaction of methane reacts with steam at elevated temperatures to produce more hydrogen:

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)} \tag{Chapter 14.4.6}$$

K = 0.64 at 900 K. If 0.010 mol of both CO and H_2O, 0.0080 mol of CO_2, and 0.012 mol of H_2 are injected into a 4.0 L reactor and heated to 900 K, will the reaction proceed to the left or to the right as written?

Answer: Q = 0.96 ($Q > K$), so the reaction will proceed to the left, and CO and H_2O will form.

Predicting the Direction of a Reaction with a Graph

By graphing a few equilibrium concentrations for a system at a given temperature and pressure, we can readily see the range of reactant and product concentrations that correspond to equilibrium conditions, for which $Q = K$. Such a graph allows us to predict what will happen to a reaction when conditions change so that Q no longer equals K, such as when a reactant concentration or a product concentration is increased or decreased.

Lead carbonate decomposes to lead oxide and carbon dioxide according to the following equation:

$$PbCO_{3(s)} \rightleftharpoons PbO_{(s)} + CO_{2(g)} \tag{14.4.3}$$

Because $PbCO_3$ and PbO are solids, the equilibrium constant is simply $K = [CO_2]$. At a given temperature, therefore, any system that contains solid $PbCO_3$ and solid PbO will have exactly the same concentration of CO_2 at equilibrium, regardless of the ratio or the amounts of the solids present. This situation is represented in Figure 14.4.2, which shows a plot of $[CO_2]$ versus the amount of $PbCO_3$ added. Initially, the added $PbCO_3$ decomposes completely to CO_2 because the amount of $PbCO_3$ is not sufficient to give a CO_2 concentration equal to K. Thus the left portion of the graph represents a system that is *not* at equilibrium because it contains only CO_2(g) and PbO(s). In contrast, when just enough $PbCO_3$ has been added to give $[CO_2] = K$, the system has reached equilibrium, and adding more $PbCO_3$ has no effect on the CO_2 concentration: the graph is a horizontal line. Thus any CO_2 concentration that is not on the horizontal line represents a nonequilibrium state, and the system will adjust its composition to achieve equilibrium, provided enough $PbCO_3$ and PbO are present. For example, the point labeled A in Figure 14.4.2 lies above the horizontal line, so it corresponds to a $[CO_2]$ that is greater than the equilibrium concentration of CO_2 ($Q > K$). To reach equilibrium, the system must decrease $[CO_2]$, which it can do only by reacting CO_2 with solid PbO to form solid $PbCO_3$. Thus the

reaction in Equation 14.4.3 will proceed to the left as written, until $[CO_2] = K$. Conversely, the point labeled *B* in Figure 14.4.2 lies below the horizontal line, so it corresponds to a $[CO_2]$ that is less than the equilibrium concentration of CO_2 ($Q < K$). To reach equilibrium, the system must increase $[CO_2]$, which it can do only by decomposing solid $PbCO_3$ to form CO_2 and solid PbO. The reaction in Equation 14.4.2 will therefore proceed to the right as written, until $[CO_2] = K$.

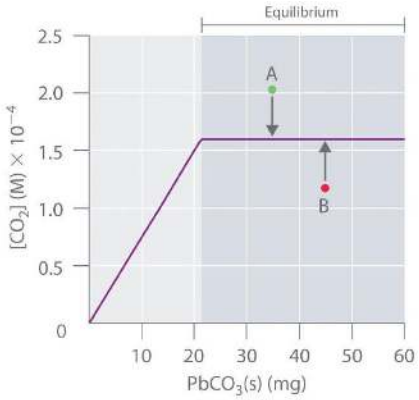


Figure 14.4.2 The Concentration of Gaseous CO_2 in a Closed System at Equilibrium as a Function of the Amount of Solid $PbCO_3$ Added *Initially the concentration of $CO_2(g)$ increases linearly with the amount of solid $PbCO_3$ added, as $PbCO_3$ decomposes to $CO_2(g)$ and solid PbO. Once the CO_2 concentration reaches the value that corresponds to the equilibrium concentration, however, adding more solid $PbCO_3$ has no effect on $[CO_2]$, as long as the temperature remains constant.*

In contrast, the reduction of cadmium oxide by hydrogen gives metallic cadmium and water vapor:

$$CdO_{(s)} + H_{2(g)} \rightleftharpoons Cd_{(s)} + H_2O_{(g)} \tag{14.4.4}$$

and the equilibrium constant *K* is $[H_2O]/[H_2]$. If $[H_2O]$ is doubled at equilibrium, then $[H_2]$ must also be doubled for the system to remain at equilibrium. A plot of $[H_2O]$ versus $[H_2]$ at equilibrium is a straight line with a slope of *K* (Figure 14.4.3). Again, only those pairs of concentrations of H_2O and H_2 that lie on the line correspond to equilibrium states. Any point representing a pair of concentrations that does not lie on the line corresponds to a nonequilibrium state. In such cases, the reaction in Equation 14.4.4 will proceed in whichever direction causes the composition of the system to move toward the equilibrium line. For example, point *A* in Figure 14.4.3 lies below the line, indicating that the $[H_2O]/[H_2]$ ratio is less than the ratio of an equilibrium mixture ($Q < K$). Thus the reaction in Equation 14.4.3 will proceed to the right as written, consuming H_2 and producing H_2O, which causes the concentration ratio to move up and to the left toward the equilibrium line. Conversely, point *B* in Figure 14.4.3 lies above the line, indicating that the $[H_2O]/[H_2]$ ratio is greater than the ratio of an equilibrium mixture ($Q > K$). Thus the reaction in Equation 14.4.4 will proceed to the left as written, consuming H_2O and producing H_2, which causes the concentration ratio to move down and to the right toward the equilibrium line.

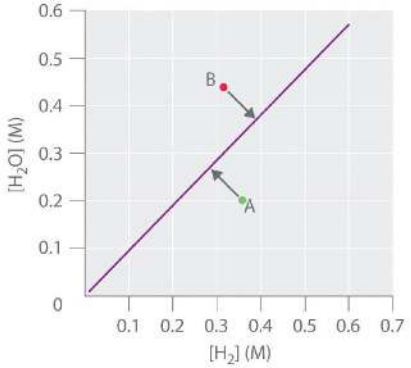


Figure 14.4.3 The Concentration of Water Vapor versus the Concentration of Hydrogen for the CdO(s) + $H_2(g)$ ⇌Cd(s) + $H_2O(g)$ System at Equilibrium*For any equilibrium concentration of $H_2O(g)$, there is only one equilibrium concentration of $H_2(g)$. Because the magnitudes of the two concentrations are directly proportional, a large $[H_2O]$ at equilibrium requires a large $[H_2]$ and vice versa. In this case, the slope of the line is equal to K.*

In another example, solid ammonium iodide dissociates to gaseous ammonia and hydrogen iodide at elevated temperatures:

$$NH_4I_{(s)} \rightleftharpoons NH_{3(g)} + HI_{(g)} \tag{14.4.5}$$

For this system, K is equal to the product of the concentrations of the two products: $[NH_3][HI]$. If we double the concentration of NH_3, the concentration of HI must decrease by approximately a factor of 2 to maintain equilibrium, as shown in Figure 14.4.4. As a result, for a given concentration of either HI or NH_3, only a *single* equilibrium composition that contains equal concentrations of both NH_3 and HI is possible, for which $[NH_3] = [HI] = K^{1/2}$. Any point that lies below and to the left of the equilibrium curve (such as point A in Figure 14.4.4) corresponds to $Q < K$, and the reaction in Equation 14.4.5 will therefore proceed to the right as written, causing the composition of the system to move toward the equilibrium line. Conversely, any point that lies above and to the right of the equilibrium curve (such as point B in Figure 14.4.4) corresponds to $Q > K$, and the reaction in Equation 14.4.5 will therefore proceed to the left as written, again causing the composition of the system to move toward the equilibrium line. By graphing equilibrium concentrations for a given system at a given temperature and pressure, we can predict the direction of reaction of that mixture when the system is not at equilibrium.

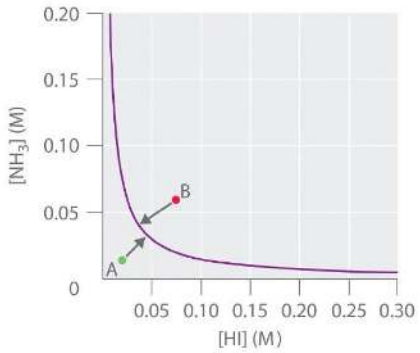


Figure 14.4.4 The Concentration of $NH_3(g)$ versus the Concentration of HI(g) for the $NH_4I(s)$ ⇌ $NH_3(g)$ + HI(g) System at Equilibrium*Only one equilibrium concentration of $NH_3(g)$ is possible for any given equilibrium concentration of HI(g). In this case, the two are inversely proportional. Thus a large [HI] at equilibrium requires a small $[NH_3]$ at equilibrium and vice versa.*

Le Châtelier's Principle

When a system at equilibrium is perturbed in some way, the effects of the perturbation can be predicted qualitatively using Le Châtelier's principle (named after the French chemist Henri Louis Le Châtelier, 1850–1936).The name is pronounced "Luh SHOT-lee-ay." This principle can be stated as follows: *if a stress is applied to a system at equilibrium, the composition of the system will change to counteract the applied stress.* Stress occurs when any change in a system affects the magnitude of Q or K. In Equation 14.4.5, for example, increasing $[NH_3]$ produces a stress on the system that requires a decrease in [HI] for the system to return to equilibrium. As a further example, consider esters, which are one of the products of an equilibrium reaction between a carboxylic acid and an alcohol. Esters are responsible for the scents we associate with fruits (such as oranges and bananas), and they are also used as scents in perfumes. Applying a stress to the reaction of a carboxylic acid and an alcohol will change the composition of the system, leading to an increase or a decrease in the amount of ester produced. In Section 14.5 and Section 14.6 , we explore how chemists control reactions conditions to affect equilibrium concentrations.

Note the Pattern

In all reactions, if a stress is applied to a system at equilibrium, the composition of the system will change to counteract the applied stress (Le Châtelier's principle).

Example 14.4.2

Write an equilibrium constant expression for each reaction and use this expression to predict what will happen to the concentration of the substance in bold when the indicated change is made if the system is to maintain equilibrium.

1. $2HgO(s) \rightleftharpoons 2Hg(l) + \mathbf{O_2(g)}$: the amount of HgO is doubled.
2. $NH_4HS(s) \rightleftharpoons \mathbf{NH_3(g)} + H_2S(g)$: the concentration of H_2S is tripled.
3. ***n*-butane(g)** ⇌ isobutene(g): the concentration of isobutane is halved.

Given: equilibrium systems and changes

Asked for: equilibrium constant expressions and effects of changes

Strategy:

Write the equilibrium constant expression, remembering that pure liquids and solids do not appear in the expression. From this expression, predict the change that must occur to maintain equilibrium when the indicated changes are made.

Solution:

1. Because HgO(s) and Hg(l) are pure substances, they do not appear in the equilibrium constant expression. Thus, for this reaction, $K = [O_2]$. The equilibrium concentration of O_2 is a constant and does not depend on the amount of HgO present. Hence adding more HgO will not affect the equilibrium concentration of O_2, so no compensatory change is necessary.
2. NH_4HS does not appear in the equilibrium constant expression because it is a solid. Thus $K = [NH_3][H_2S]$, which means that the concentrations of the products are inversely proportional. If adding H_2S triples the H_2S concentration, for example, then the NH_3 concentration must decrease by about a factor of 3 for the system to remain at equilibrium so that the product of the concentrations equals K.
3. For this reaction, K = [isobutane]/[*n*-butane], so halving the concentration of isobutane means that the *n*-butane concentration must also decrease by about half if the system is to maintain equilibrium.

Exercise

Write an equilibrium constant expression for each reaction. What must happen to the concentration of the substance in bold when the indicated change occurs if the system is to maintain equilibrium?

1. $HBr(g) + NaH(s) \rightleftharpoons NaBr(s) + \mathbf{H_2(g)}$: the concentration of HBr is decreased by a factor of 3.
2. $6Li(s) + \mathbf{N_2(g)} \rightleftharpoons 2Li_3N(s)$: the amount of Li is tripled.
3. $\mathbf{SO_2(g)} + Cl_2(g) \rightleftharpoons SO_2Cl_2(l)$: the concentration of Cl_2 is doubled.

Answer:

1. $K = [H_2]/[HBr]$; $[H_2]$ must decrease by about a factor of 3.
2. $K = 1/[N_2]$; solid lithium does not appear in the equilibrium constant expression, so no compensatory change is necessary.
3. $K = 1/[SO_2][Cl_2]$; $[SO_2]$ must decrease by about half.

Summary

The **reaction quotient (*Q* or Q_p)** has the same form as the equilibrium constant expression, but it is derived from concentrations obtained at any time. When a reaction system is at equilibrium, *Q* = *K*. Graphs derived by plotting a few equilibrium concentrations for a system at a given temperature and pressure can be used to predict the direction in which a reaction will proceed. Points that do not lie on the line or curve represent nonequilibrium states, and the system will adjust, if it can, to achieve equilibrium. **Le Châtelier's principle** states that if a stress is applied to a system at equilibrium, the composition of the system will adjust to counteract the stress.

Key Takeaway

- The reaction quotient (*Q*) is used to determine whether a system is at equilibrium and if it is not, to predict the direction of reaction.

Key Equation

Reaction quotient

Equation 14.4.1:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad \textbf{(Chapter 14.4.7)}$$

Conceptual Problems

1. During a set of experiments, graphs were drawn of [reactants] versus [products] at equilibrium. Using Figure 14.4.3 and Figure 14.4.4 as your guides, sketch the shape of each graph using appropriate labels.
   a. $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$
   b. $2MgO_{(s)} \rightleftharpoons 2Mg_{(s)} + O_{2(g)}$
   c. $2O_{3(g)} \rightleftharpoons 3O_{2(g)}$
   d. $2PbS_{(s)} + 3O_{2(g)} \rightleftharpoons 2PbO_{(s)} + 2SO_{2(g)}$
2. Write an equilibrium constant expression for each reaction system. Given the indicated changes, how must the concentration of the species in bold change if the system is to maintain equilibrium?
   a. $2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + \mathbf{H_2O(g)}$: $[CO_2]$ is doubled.
   b. $\mathbf{N_2F_4(g)} \rightleftharpoons 2NF_2(g)$: [NF] is decreased by a factor of 2.
   c. $H_2(g) + I_2(g) \rightleftharpoons \mathbf{2HI(g)}$: $[I_2]$ is doubled.
3. Write an equilibrium constant expression for each reaction system. Given the indicated changes, how must the concentration of the species in bold change if the system is to maintain equilibrium?
   a. $CS_2(g) + \mathbf{4H_2(g)} \rightleftharpoons CH_4(g) + 2H_2S(g)$: $[CS_2]$ is doubled.
   b. $\mathbf{PCl_5(g)} \rightleftharpoons PCl_3(g) + Cl_2(g)$: $[Cl_2]$ is decreased by a factor of 2.
   c. $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + \mathbf{6H_2O(g)}$: [NO] is doubled.

Answer

1.
2.
3. a. $K = \frac{[CH_4][H_2S]^2}{[CS_2][H_2]^4}$; doubling $[CS_2]$ would require decreasing $[H_2]$ by a factor of $2\sqrt{4} \cong 1.189$.
   b. $K = \frac{[PCl_3]}{[Cl_2][PCl_5]}$; if $[Cl_2]$ is halved, $[PCl_5]$ must also be halved.

c. $K = \frac{[NO]^4[H_2O]^6}{[NH_3][O_2]^5}$; if $[NO]$ is doubled, $[H_2O]$ is multiplied by 22/3≅1.587.

Numerical Problems

1. The data in the following table were collected at 450°C for the reaction

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

	Equilibrium Partial Pressure (atm)		
P (atm)	NH_3	N_2	H_2
30 (equilibrium)	1.740	6.588	21.58
100	15.20	19.17	65.13
600	321.6	56.74	220.8

The reaction equilibrates at a pressure of 30 atm. The pressure on the system is first increased to 100 atm and then to 600 atm. Is the system at equilibrium at each of these higher pressures? If not, in which direction will the reaction proceed to reach equilibrium?

2. For the reaction 2A ⇌ B + 3 C, *K* at 200°C is 2.0. A 6.00 L flask was used to carry out the reaction at this temperature. Given the experimental data in the following table, all at 200°C, when the data for each experiment were collected, was the reaction at equilibrium? If it was not at equilibrium, in which direction will the reaction proceed?

Experiment	A	B	C
1	2.50 M	2.50 M	2.50 M
2	1.30 atm	1.75 atm	14.15 atm
3	12.61 mol	18.72 mol	6.51 mol

3. The following two reactions are carried out at 823 K:

$$CoO_{(s)} + H_{2(g)} \rightleftharpoons Co_{(s)} + H_2O_{(g)} \text{ with } K = 67$$
$$CoO_{(s)} + CO_{(g)} \rightleftharpoons Co_{(s)} + CO_{2(g)} \text{ with } K = 490$$

   a. Write the equilibrium expression for each reaction.
   b. Calculate the partial pressure of both gaseous components at equilibrium in each reaction if a 1.00 L reaction vessel initially contains 0.316 mol of H_2 or CO plus 0.500 mol CoO.
   c. Using the information provided, calculate K_p for the following reaction:

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$$ **(Chapter 14.4.8)**

   d. Describe the shape of the graphs of [reactants] versus [products] as the amount of CoO changes.

4. Hydrogen iodide ($HI)_2$ is synthesized via $H_2(g)_3$+ $I_2(g)$ ⇌ 2HI(g), for which K_p = 54.5 at 425°C. Given a 2.0 L vessel containing 1.12×10 mol of H_2 and 1.8×10 mol of I_2 at equilibrium, what is the concentration of HI? Excess hydrogen is added to the vessel so that the vessel now contains 3.64×10 mol of H_2. Calculate *Q* and then predict the direction in which the reaction will proceed. What are the new equilibrium concentrations?

Answers

1. Not at equilibrium; in both cases, the sum of the equilibrium partial pressures is *less* than the total pressure, so the reaction will proceed to the right to decrease the pressure.
2.
3. a. $K = [H_2O][H_2]$; K=[CO2][CO]

b. $P_{H_2O} = 21.0\ atm$; $P_{H_2} = 0.27\ atm$; $P_{CO_2} = 21.3\ atm$; $P_{CO} = 0.07\ atm$

c. $K_p = 0.14$

d. The amount of CoO has no effect on the shape of a graph of products versus reactants *as long as some solid CoO is present*.

4.

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- Anonymous

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Chapter 14.5: Factors That Affect Equilibrium

Learning Objectives

- To predict the effects of stresses on a system at equilibrium.

Chemists use various strategies to increase the yield of the desired products of reactions. When synthesizing an ester, for example, how can a chemist control the reaction conditions to obtain the maximum amount of the desired product? Only three types of stresses can change the composition of an equilibrium mixture: (1) a change in the concentrations (or partial pressures) of the components by adding or removing reactants or products, (2) a change in the total pressure or volume, and (3) a change in the temperature of the system. In this section, we explore how changes in reaction conditions can affect the equilibrium composition of a system. We will explore each of these possibilities in turn.

Changes in Concentration

If we add a small volume of carbon tetrachloride (CCl_4) solvent to a flask containing crystals of iodine, we obtain a saturated solution of I_2 in CCl_4, along with undissolved crystals:

$$I_{2(s)} \rightleftharpoons I_{2(soln)} \tag{14.5.1}$$

The system reaches equilibrium, with $K = [I_2]$. If we add more CCl_4, thereby diluting the solution, Q is now less than K. Le Châtelier's principle tells us that the system will react to relieve the stress—but how? Adding solvent stressed the system by decreasing the concentration of dissolved I_2. Hence more crystals will dissolve, thereby increasing the concentration of dissolved I_2 until the system again reaches equilibrium if enough solid I_2 is available (Figure 14.5.1). By adding solvent, we drove the reaction shown in Equation 14.5.1 to the right as written.

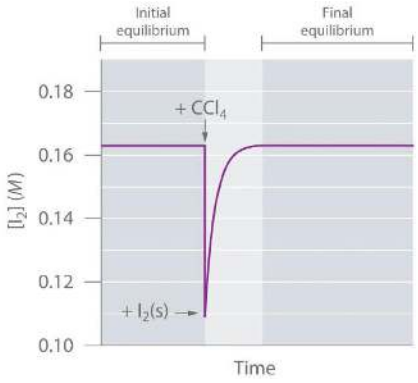


Figure 14.5.1 The Concentration of Dissolved I_2 as a Function of Time Following the Addition of More Solvent to a Saturated Solution in Contact with Excess Solid I_2 *The concentration of I_2 decreases initially due to dilution but returns to its original value as long as solid I_2 is present.*

We encounter a more complex system in the reaction of hydrogen and nitrogen to form ammonia:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \tag{14.5.2}$$

The K_p for this reaction is 2.14×10^{-2} at about 540 K. Under one set of equilibrium conditions, the partial pressure of ammonia is $P(NH_3) = 0.454$ atm, that of hydrogen is $P(H_2) = 2.319$ atm, and that of nitrogen is $P(N_2) = 0.773$ atm. If an additional 1 atm of hydrogen is added to the reactor to give $P(H_2) = 3.319$ atm, how will the system respond? Because the stress is an increase in $P(H_2)$ the system must respond in some way that decreases the partial pressure of hydrogen to counteract the stress. The reaction will therefore proceed to the right as written, consuming H_2 and N_2 and forming additional NH_3. Initially, the partial pressures of H_2 and N_2 will decrease, and the partial pressure of NH_3 will increase until the system eventually reaches a new equilibrium composition, which will have a net increase in $P(H_2)$

We can confirm that this is indeed what will happen by evaluating Q_p under the new conditions and comparing its value with K_p. The equations used to evaluate K_p and Q_p have the same form: substituting the values after adding hydrogen into the expression for Q_p results in the following:

$$Q_p = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3} = \frac{(0.454)^2}{(0.773)(2.319 + 1.00)^3} = 7.29 \times 10^{-3} \tag{Chapter 14.5.1}$$

Thus $Q_p < K_p$, which tells us that the ratio of products to reactants is less than at equilibrium. To reach equilibrium, the reaction must proceed to the right as written: the partial pressures of the products will increase, and the partial pressures of the reactants will decrease. Q_p will thereby increase until it equals K_p, and the system will once again be at equilibrium. Changes in the partial pressures of the various substances in the reaction mixture (Equation 14.5.2) as a function of time are shown in Figure 14.5.2.

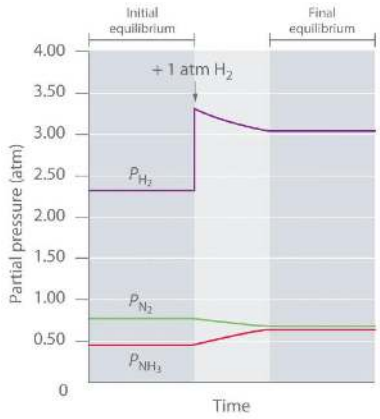


Figure 14.5.2 The Partial Pressures of H_2, N_2, and NH_3 as a Function of Time Following the Addition of More H_2 to an Equilibrium Mixture *Some of the added hydrogen is consumed by reacting with nitrogen to produce more ammonia, allowing the system to reach a new equilibrium composition.*

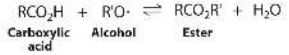
We can force a reaction to go essentially to completion, regardless of the magnitude of K, by continually removing one of the products from the reaction mixture. Consider, for example, the *methanation* reaction, in which hydrogen reacts with carbon monoxide to form methane and water:

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)} \tag{14.5.3}$$

This reaction is used for the industrial production of methane, whereas the reverse reaction is used for the production of H_2 (Example 14). The expression for Q has the following form:

$$Q = \frac{[CH_4][H_2O]}{[CO][H_2]^3} \tag{14.5.4}$$

Regardless of the magnitude of K, if either H_2O or CH_4 can be removed from the reaction mixture so that $[H_2O]$ or $[CH_4]$ is approximately zero, then $Q \approx 0$. In other words, when product is removed, the system is stressed ($Q << K$), and more product will form to counter the stress. Because water (bp = 100°C) is much less volatile than methane, hydrogen, or carbon monoxide (all of which have boiling points below −100°C), passing the gaseous reaction mixture through a cold coil will cause the water vapor to condense to a liquid that can be drawn off. Continuing to remove water from the system forces the reaction to the right as the system attempts to equilibrate, thus enriching the reaction mixture in methane. This technique, referred to as *driving a reaction to completion*, can be used to force a reaction to completion even if K is relatively small. For example, esters are usually synthesized by removing water. The products of the condensation reaction are shown here. In Chapter 16, we will describe the thermodynamic basis for the change in the equilibrium position caused by changes in the concentrations of reaction components.



Example 14.5.1

For each equilibrium system, predict the effect of the indicated stress on the specified quantity.

1. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$:
   (1) the effect of removing O_2 on $P(SO_2)$
   (2) the effect of removing O_2 on $P(SO_3)$
2. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$:
   (1) the effect of removing CO_2 on the amount of $CaCO_3$;
   (2) the effect of adding $CaCO_3$ on $P(CO_2)$

Given: balanced chemical equations and changes

Asked for: effects of indicated stresses

Strategy:

Use Q and K to predict the effect of the stress on each reaction.

Solution:

1. (1) Removing O_2 will decrease $P(O_2)$thereby decreasing the denominator in the reaction quotient and making $Q_p > K_p$. The reaction will proceed to the left as written, increasing the partial pressures of SO_2 and O_2 until Q_p once again equals K_p.
   (2) Removing O_2 will decrease $P(O_2)$ and thus increase Q_p, so the reaction will proceed to the left. The partial pressure of SO_3 will decrease.
2. K_p and Q_p are both equal to $P(CO_2)$.
   (1) Removing CO_2 from the system causes more $CaCO_3$ to react to produce CO_2, which increases $P(CO_2)$ to the partial pressure required by K_p. (2) Adding (or removing) solid $CaCO_3$ has no effect on $P(CO_2)$ because it does not appear in the expression for K_p (or Q_p).

Exercise

For each equilibrium system, predict the effect that the indicated stress will have on the specified quantity.

1. $H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$:
   1. the effect of adding CO on $[H_2]$;
   2. the effect of adding CO_2 on $[H_2]$
2. $CuO_{(s)} + CO_{(g)} \rightleftharpoons Cu_{(s)} + CO_{2(g)}$:
   1. the effect of adding CO on the amount of Cu;
   2. the effect of adding CO_2 on $[CO]$

Answer:

1. (1) $[H_2]$ increases; (2) $[H_2]$ decreases.
2. (1) the amount of Cu increases; (2) [CO] increases.

Changes in Total Pressure or Volume

Because liquids are relatively incompressible, changing the pressure above a liquid solution has little effect on the concentrations of dissolved substances. Consequently, changes in external pressure have very little effect on equilibrium systems that contain only solids or liquids. In contrast, because gases are highly compressible, their concentrations vary dramatically with pressure. From the ideal gas law, $PV = nRT$, described in Section 6.3, the concentration (C) of a gas is related to its pressure as follows:

$$C = \frac{n}{V} = \frac{P}{RT} \tag{14.5.5}$$

Hence the concentration of any gaseous reactant or product is directly proportional to the applied pressure (P) and inversely proportional to the total volume (V). Consequently, the equilibrium compositions of systems that contain gaseous substances are quite sensitive to changes in pressure, volume, and temperature.

These principles can be illustrated using the reversible dissociation of gaseous N_2O_4 to gaseous NO_2 (Equation 14.1.1).

$$N_2O_4 \rightleftharpoons 2NO_2 \tag{15.1.1}$$

The syringe shown in Figure 14.5.3 initially contains an equilibrium mixture of colorless N_2O_4 and red-brown NO_2. Decreasing the volume by 50% causes the mixture to become darker because all concentrations have doubled. Decreasing the volume also constitutes a stress, however, as we can see by examining the effect of a change in volume on Q. At equilibrium,

$$Q = K = \frac{[NO_2]^2}{[N_2O_4]} \tag{14.5.6a}$$

If the volume is decreased by half, the concentrations of the substances in the mixture are doubled, so the new reaction quotient is as follows:

$$Q = \frac{(2[NO_2]_i)^2}{2[N_2O_4]_i} = \frac{4([NO_2]_i)^2}{2[N_2O_4]_i} = 2K \tag{14.5.6b}$$

Because Q is now greater than K, the system is no longer at equilibrium. The stress can be relieved if the reaction proceeds to the left, consuming 2 mol of NO_2 for every 1 mol of N_2O_4 produced. This will decrease the concentration of NO_2 and increase the concentration of N_2O_4, causing Q to decrease until it once again equals K. Thus, as shown in part (c) in Figure 14.5.3, the intensity of the brown color due to NO_2 decreases with time following the change in volume.

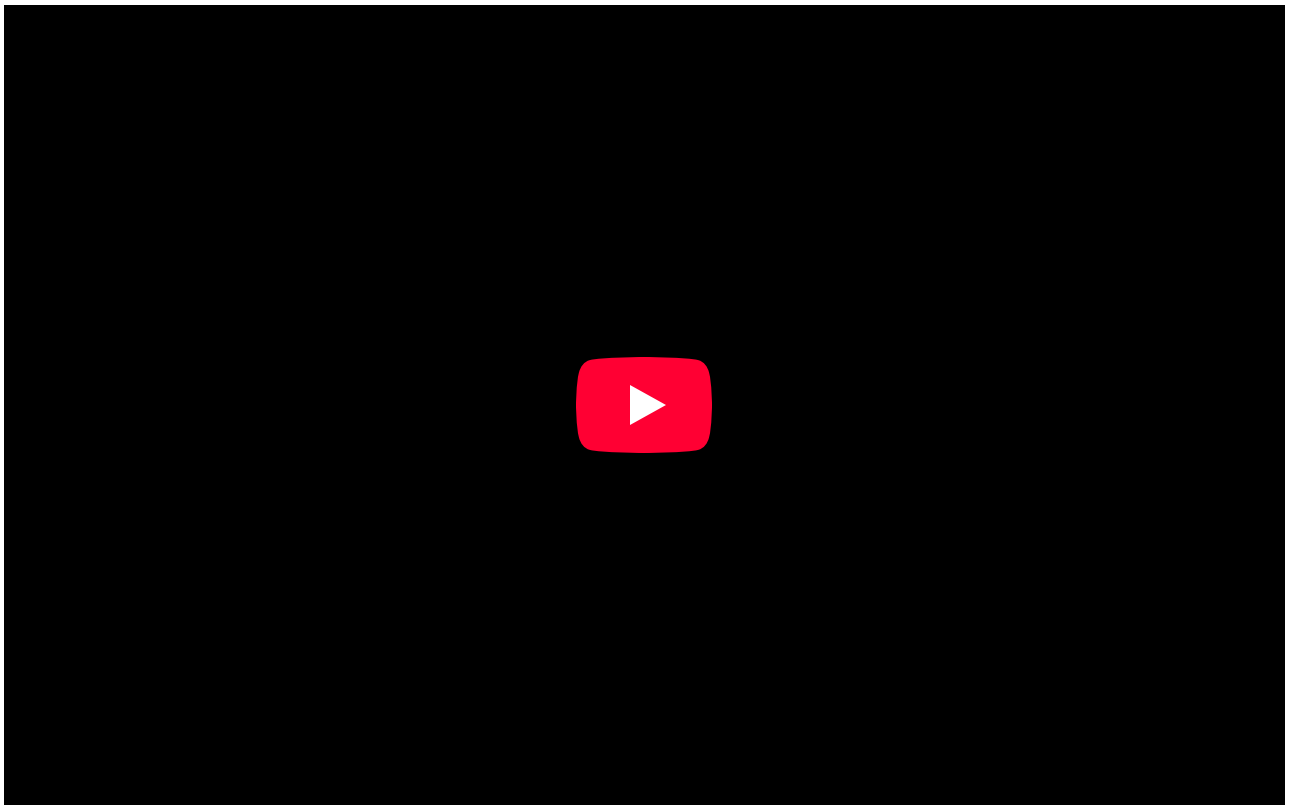




Figure 14.5.3 The Effect of Changing the Volume (and Thus the Pressure) of an Equilibrium Mixture of N_2O_4 and NO_2 at Constant Temperature *(a) The syringe with a total volume of 15 mL contains an equilibrium mixture of N_2O_4 and NO_2; the red-brown color is proportional to the NO_2 concentration. (b) If the volume is rapidly decreased by a factor of 2 to 7.5 mL, the initial effect is to double the concentrations of all species present, including NO_2. Hence the color becomes more intense. (c) With time, the system adjusts its composition in response to the stress as predicted by Le Châtelier's principle, forming colorless N_2O_4 at the expense of red-brown NO_2, which decreases the intensity of the color of the mixture. Video from joan-ramon i pinazo*

Note the Pattern

Increasing the pressure of a system (or decreasing the volume) favors the side of the reaction that has fewer gaseous molecules and vice versa.

In general, *if a balanced chemical equation contains different numbers of gaseous reactant and product molecules, the equilibrium will be sensitive to changes in volume or pressure*. Increasing the pressure on a system (or decreasing the volume) will favor the side of the reaction that has fewer gaseous molecules and vice versa.

Example 14.5.2

For each equilibrium system, write the reaction quotient for the system if the pressure is decreased by a factor of 2 (i.e., if the volume is doubled) at constant temperature and then predict the direction of the reaction.

1. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
2. $C_2H_{2(g)} + C_2H_{6(g)} \rightleftharpoons 2C_2H_{4(g)}$
3. $2NO_{2(g)} \rightleftharpoons 2NO_{(g)} + O_{2(g)}$

Given: balanced chemical equations

Asked for: direction of reaction if pressure is halved

Strategy:

Use Le Châtelier's principle to predict the effect of the stress.

Solution:

1. Two moles of gaseous products are formed from 4 mol of gaseous reactants. Decreasing the pressure will cause the reaction to shift to the left because that side contains the larger number of moles of gas. Thus the pressure increases, counteracting the stress. K for this reaction is $[NH_3]^2/[N_2][H_2]^3$. When the pressure is

decreased by a factor of 2, the concentrations are halved, which means that the new reaction quotient is as follows:

$$Q = \frac{[1/2\ NH_3]^2}{[1/2\ N_2][1/2H_2]^3} = \frac{1/4\ [NH_3]^2}{1/16\ [N_2][H_2]^3} = 4K \qquad \text{(Chapter 14.5.2)}$$

2. Two moles of gaseous products form from 2 mol of gaseous reactants. Decreasing the pressure will have no effect on the equilibrium composition because both sides of the balanced chemical equation have the same number of moles of gas. Here $K = [C_2H_4]^2/[C_2H_2][C_2H_6]$. The new reaction quotient is as follows:

$$Q = \frac{[C_2H_4]^2}{[C_2H_2][C_2H_6]} = \frac{[1/2C_2H_4]^2}{[1/2C_2H_2][1/2C_2H_6]} = \frac{1/4[C_2H_4]^2}{1/4[C_2H_2][C_2H_6]} = K \qquad \text{(Chapter 14.5.3)}$$

3. Three moles of gaseous products are formed from 2 mol of gaseous reactants. Decreasing the pressure will favor the side that contains more moles of gas, so the reaction will shift toward the products to increase the pressure. For this reaction $K = [NO]^2[O_2]/[NO_2]^2$. Under the new reaction conditions the reaction quotient is as follows:

$$Q = \frac{[1/2NO]^2[1/2O_2]}{[1/2NO_2]^2} = \frac{1/8[NO]^2[O_2]}{1/4[NO_2]^2} = 1/2K \qquad \text{(Chapter 14.5.4)}$$

Exercise

For each equilibrium system, write a new reaction quotient for the system if the pressure is increased by a factor of 2 (i.e., if the volume is halved) at constant temperature and then predict the direction in which the reaction will shift.

1. $H_2O_{(g)} + CO_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$
2. $H_{2(g)} + C_2H_{4(g)} \rightleftharpoons C_2H_{6(g)}$
3. $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

Answer:

1. $Q = K$; no effect
2. $Q = 1/2\ K$; to the right
3. $Q = 1/2\ K$; to the right

Changes in Temperature

In all the cases we have considered so far, the magnitude of the equilibrium constant, K or K_p, was constant. Changes in temperature can, however, change the value of the equilibrium constant without immediately affecting the reaction quotient ($Q \neq K$). In this case, the system is no longer at equilibrium; the composition of the system will change until Q equals K at the new temperature.

To predict how an equilibrium system will respond to a change in temperature, we must know something about the enthalpy change of the reaction (ΔH_{rxn}). As you will learn in the next chapter, Chapter 15, heat is released to the surroundings in an exothermic reaction ($\Delta H_{rxn} < 0$), and heat is absorbed from the surroundings in an endothermic reaction ($\Delta H_{rxn} > 0$). We can express these changes in the following way:

- Exothermic (ΔH<0):

$$\text{reactants} \rightleftharpoons \text{products} + \text{heat} \qquad (14.5.7)$$

- Endothermic (ΔH>0):

$$\text{reactants} + \text{heat} \rightleftharpoons \text{products} \qquad (14.5.8)$$

Thus heat can be thought of as a product in an exothermic reaction and as a reactant in an endothermic reaction. Increasing the temperature of a system corresponds to adding heat. Le Châtelier's principle predicts that an exothermic reaction will shift to the left (toward the reactants) if the temperature of the system is increased (heat is added). Conversely, an endothermic reaction will shift to the right (toward the products) if the temperature of the system is increased. If a reaction is thermochemically neutral ($\Delta H_{rxn} = 0$), then a change in temperature will not affect the equilibrium composition.

We can examine the effects of temperature on the dissociation of N_2O_4 to NO_2, for which ΔH = +58 kJ/mol. This reaction can be written as follows:

$$58\ kJ + N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \tag{14.5.9}$$

Increasing the temperature (adding heat to the system) is a stress that will drive the reaction to the right, as illustrated in Figure 14.5.4. Thus increasing the temperature increases the ratio of NO_2 to N_2O_4 at equilibrium, which increases K.



Figure 14.5.4 The Effect of Temperature on the Equilibrium between Gaseous N_2O_4 and NO_2 *The value of* ***K*** *changes with temperature of the same 99.9% pure* ***NO_2/N_2O_4*** *sealed in an ampoule. From left to right -196° C, 0° C, 23° C, 35° C, 50° C. In the endothermic reaction , the equilibrium position can be shifted by changing the temperature. When heat is added and the temperature increases, the reaction shifts to the right and the flask turns reddish brown due to an increase in* ***NO_2***. *When heat is removed and the temperature decreases, the reaction shifts to the left and flask turns colorless due to an increase in* ***N_2O_4***. *This demonstrates Le Chatelier's Principle because the equilibrium shifts in the direction that consumes energy. Figure used with permission from Wikipedia.*

The effect of increasing the temperature on a system at equilibrium can be summarized as follows: *increasing the temperature increases the magnitude of the equilibrium constant for an endothermic reaction, decreases the equilibrium constant for an exothermic reaction, and has no effect on the equilibrium constant for a thermally neutral reaction*. Table 14.5.1 shows the temperature dependence of the equilibrium constants for the synthesis of ammonia from hydrogen and nitrogen, which is an exothermic reaction with $\Delta H°$ = −91.8 kJ/mol. The values of both K and K_p decrease dramatically with increasing temperature, as predicted for an exothermic reaction.

Table 14.5.1 Temperature Dependence of K and K_p for $N_2(g) + 3\ H_2\ (g) \rightleftharpoons 2\ NH_3(g)$

Temperature (K)	K	K_p
298	3.3×10^{8}	5.6×10^{5}
400	3.9×10^{4}	3.6×10^{1}
450	2.6×10^{3}	1.9
500	1.7×10^{2}	1.0×10^{-1}
550	2.6×10^{1}	1.3×10^{-2}
600	4.1	1.7×10^{-3}

Note the Pattern

Increasing the temperature causes endothermic reactions to favor products and exothermic reactions to favor reactants.

Example 14.5.3

For each equilibrium reaction, predict the effect of decreasing the temperature:

1. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad \Delta H_{rxn} = -91.8 \ kJ/mol$
2. $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)} \quad \Delta H_{rxn} = 178 \ kJ/mol$

Given: balanced chemical equations and values of ΔH_{rxn}

Asked for: effects of decreasing temperature

Strategy:

Use Le Châtelier's principle to predict the effect of decreasing the temperature on each reaction.

Solution:

1. The formation of NH_3 is exothermic, so we can view heat as one of the products:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + 91.8 \ kJ \qquad \text{(Chapter 14.5.5)}$$

2. If the temperature of the mixture is decreased, heat (one of the products) is being removed from the system, which causes the equilibrium to shift to the right. Hence the formation of ammonia is favored at lower temperatures.

3. The decomposition of calcium carbonate is endothermic, so heat can be viewed as one of the reactants:

$$CaCO_{3(s)} + 178 \ kJ \rightleftharpoons CaO_{(s)} + CO_{2(g)} \qquad \text{(Chapter 14.5.6)}$$

If the temperature of the mixture is decreased, heat (one of the reactants) is being removed from the system, which causes the equilibrium to shift to the left. Hence the thermal decomposition of calcium carbonate is less favored at lower temperatures.

Exercise

For each equilibrium system, predict the effect of increasing the temperature on the reaction mixture:

1. $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ with $\Delta H_{rxn} = -198 \ kJ/mol$
2. $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ with $\Delta H_{rxn} = +181 \ kJ/mol$

Answer:

1. Reaction shifts to the left.
2. Reaction shifts to the right.

Summary

Three types of stresses can alter the composition of an equilibrium system: adding or removing reactants or products, changing the total pressure or volume, and changing the temperature of the system. A reaction with an unfavorable equilibrium constant can be driven to completion by continually removing one of the products of the reaction. Equilibriums that contain different numbers of gaseous reactant and product molecules are sensitive to changes in volume or pressure; higher pressures favor the side with fewer gaseous molecules. Removing heat from an exothermic reaction favors the formation of products, whereas removing heat from an endothermic reaction favors the formation of reactants.

Key Takeaway

- Equilibriums are affected by changes in concentration, total pressure or volume, and temperature.

Conceptual Problems

1. If an equilibrium reaction is endothermic in the forward direction, what is the expected change in the concentration of each component of the system if the temperature of the reaction is increased? If the temperature is decreased?
2. Write the equilibrium equation for the following system:

   \[4NH_{3(g)} +5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}\

   Would you expect the equilibrium to shift toward the products or reactants with an increase in pressure? Why?
3. The reaction rate approximately doubles for every 10°C rise in temperature. What happens to K?
4. The formation of $A_2B_2(g)$ via the equilibrium reaction $2AB(g) \rightleftharpoons A_2B_2(g)$ is exothermic. What happens to the ratio k_f/k_r if the temperature is increased? If both temperature and pressure are increased?
5. In each system, predict the effect that the indicated change will have on the specified quantity at equilibrium:
   a. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$:
   H_2 is removed; what is the effect on $P(I_2)$?
   b. $2NOBr_{(g)} \rightleftharpoons 2NO_{(g)} + Br_{2(g)}$
   If Br_2 is removed; what is the effect on P_{NOBr}?
   c. $2NaHCO_{3(s)} \rightleftharpoons Na_2CO_{3(g)} + CO_{2(g)} + H_2O_{(g)}$
   If CO_2 is removed; what is the effect on $P(NaHCO_3)$?
6. What effect will the indicated change have on the specified quantity at equilibrium?
   a. $NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$
   If NH_4Cl is increased; what is the effect on P_{HCl}?
   b. $2H2O_{(g)} \rightleftharpoons 2H_{2(g)} + O_{2(g)}$
   If O_2 is added; what is the effect on $P(H_2)$?<
   c. $PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$
   If Cl_2 is removed; what is the effect on $P(PCl_5)$?

Numerical Problems

1. For each equilibrium reaction, describe how Q and K change when the pressure is increased, the temperature is increased, the volume of the system is increased, and the concentration(s) of the reactant(s) is increased.
   a. $A(g) \rightleftharpoons B(g)$ $\Delta H = -20.6$ kJ/mol
   b. $2A(g) \rightleftharpoons B(g)$ $\Delta H = -0.3$ kJ/mol

c. $A(g) + B(g) \rightleftharpoons 2C(g)$ $\Delta H = 46$ kJ/mol

2. For each equilibrium reaction, describe how Q and K change when the pressure is decreased, the temperature is increased, the volume of the system is decreased, and the concentration(s) of the reactant(s) is increased.
   a. $2A(g) \rightleftharpoons B(g)$ $\Delta H = -80$ kJ/mol
   b. $A(g) \rightleftharpoons 2B(g)$ $\Delta H = 0.3$ kJ/mol
   c. $2A(g) \rightleftharpoons 2B(g) + C(g)$ $\Delta H = 46$ kJ/mol
3. Le Châtelier's principle states that a system will change its composition to counteract stress. For the system $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$, write the equilibrium constant expression K_p. What changes in the values of Q and K would you anticipate when (a) the volume is doubled, (b) the pressure is increased by a factor of 2, and (c) $COCl_2$ is removed from the system?
4. For the equilibrium system $3O_2(g) \rightleftharpoons 2\ O_3(g)$, $\Delta H° = 284$ kJ, write the equilibrium constant expression K_p. What happens to the values of Q and K if the reaction temperature is increased? What happens to these values if both the temperature and pressure are increased?
5. Carbon and oxygen react to form CO_2 gas via $C(s) + O_2(g) \rightleftharpoons CO_2(g)$, for which $K = 1.2 \times 10^{69}$. Would you expect K to increase or decrease if the volume of the system were tripled? Why?
6. The reaction $COCl_2(g) \rightleftharpoons CO(g) + Cl_2\ (g)$ has $K = 2.2 \times 10^{-10}$ at 100°C. Starting with an initial $P(\ COCl_2)$ of 1.0 atm, you determine the following values of P_{CO} at three successive time intervals: 6.32×10^{-6} atm, 1.78×10^{-6} atm, and 1.02×10^{-5} atm. Based on these data, in which direction will the reaction proceed after each measurement? If chlorine gas is added to the system, what will be the effect on Q?
7. The following table lists experimentally determined partial pressures at three temperatures for the reaction $Br_2(g) \rightleftharpoons 2\ Br(g)$

T (K)	1123	1173	1273
$P(Br_2)$ (atm)	3.000	0.3333	6.755×10^{-2}
P(Br) (atm)	3.477×10^{-2}	2.159×10^{-2}	2.191×10^{-2}

   Is this an endothermic or an exothermic reaction? Explain your reasoning.
8. The dissociation of water vapor proceeds according to the following reaction:$H_2O(g) \rightleftharpoons 1/2\ O_2(g) + H_2\ (g)$. At 1300 K, there is 0.0027% dissociation, whereas at 2155 K, the dissociation is 1.18%. Calculate K and K_p. Is this an endothermic reaction or an exothermic reaction? How do the magnitudes of the two equilibriums compare? Would increasing the pressure improve the yield of H_2 gas at either temperature? (Hint: assume that the system initially contains 1.00 mol of H_2O in a 1.00 L container.)
9. When 1.33 mol of CO_2 and 1.33 mol of H_2 are mixed in a 0.750 L container and heated to 395°C, they react according to the following equation: $CO_2(g) + H_2\ (g) \rightleftharpoons CO(g) + H_2O(g)$ If $K = 0.802$, what are the equilibrium concentrations of each component of the equilibrium mixture? What happens to K if H_2O is removed during the course of the reaction?
10. The equilibrium reaction $H_2(g) + Br_2(g) \rightleftharpoons 2\ HBr(g)$ has $K_p = 2.2 \times 10^{9}$ at 298 K. If you begin with 2.0 mol of Br_2 and 2.0 mol of H_2 in a 5.0 L container, what is the partial pressure of HBr at equilibrium? What is the partial pressure of H_2 at equilibrium? If H_2 is removed from the system, what is the effect on the partial pressure of Br_2?
11. Iron(II) oxide reacts with carbon monoxide according to the following equation: $FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$ At 800°C, $K = 0.34$; at 1000°C, $K = 0.40$.
    a. A 20.0 L container is charged with 800.0 g of CO_2, 1436 g of FeO, and 1120 g of iron. What are the equilibrium concentrations of all components of the mixture at each temperature?
    b. What are the partial pressures of the gases at each temperature?
    c. If CO were removed, what would be the effect on $P(CO_2)$ at each temperature?
12. The equilibrium constant K for the reaction $C(s) + CO_2\ g) >\rightleftharpoons 2\ CO(g)$ is 1.9 at 1000 K and 0.133 at 298 K.
    a. If excess C is allowed to react with 25.0 g of CO_2 in a 3.00 L flask, how many grams of CO are produced at each temperature?
    b. What are the partial pressures of each gas at 298 K? at 1000 K?
    c. Would you expect K to increase or decrease if the pressure were increased at constant temperature and volume?
13. Data for the oxidation of methane, $CH_4(g) + 2\ O_2(g) \rightleftharpoons CO_2(g) + 2\ H_2O(g)$, in a closed 5.0 L vessel are listed in the following table. Fill in the blanks and determine the missing values of Q and K (indicated by ?) as the reaction is driven to

completion.

	CH_4	O_2	CO_2	H_2O	Q	K
initial (moles)	0.45	0.90	0	0	?	
at equilibrium						1.29
add 0.50 mol of methane	0.95				?	
new equilibrium						?
remove water				0	?	
new equilibrium						1.29

Answers

1.
2.
3. $K_p = P(COCl_2)/($
   $P(CO)\ P(Cl_2))$
   P
   None of the changes would affect *K*; (a) *Q* doubles; (b) *Q* is halved; *Q* decreases.
4.
5. *K* would not change; it does not depend on volume.
6.
7.
8.
9. $[CO] = [H_2O] = 0.839$ M, $[CO_2] = [H_2] = 0.930$ M; no effect on *K*
10.
11. a. At 800°C, $[CO] = 0.678$ M, $[CO_2] = 0.231$ M; at 1000°C, $[CO] = 0.645$ M, $[CO_2] = 0.264$ M
    b. At 800°C, $PCO = 59.7$ atm, $P(CO_2) = 20.3$ atm; at 1000°C, $P(CO) = 67.4$ atm, $P(CO_2) = 27.6$ atm.
    c. Removing CO would cause the reaction to shift to the right, causing $P(CO_2)$ to decrease.
12.
13.

	CH_4	O_2	CO_2	H_2O	Q	K
initial (moles)	0.45	0.90	0	0	**0**	1.29
at equilibrium	0.215	0.43	0.235	0.47	*K*	1.29
add 0.50 mol of methane	0.715	0.43	0.235	0.47	**0.39**	1.29
new equilibrium	0.665	0.33	0.285	0.57	*K*	**1.29**
remove water	0.665	0.33	0.285	0	**0**	1.29
new equilibrium	0.57	0.14	0.38	0.19	*K*	1.29

Contributors

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Modified by Joshua Halpern (Howard University), Scott Sinex, and Scott Johnson (PGCC)

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Chapter 14.6: Controlling the Products of Reactions

Learning Objectives

- To understand different ways to control the products of a reaction.

Whether in the synthetic laboratory or in industrial settings, one of the primary goals of modern chemistry is to control the identity and quantity of the products of chemical reactions. For example, a process aimed at synthesizing ammonia is designed to maximize the amount of ammonia produced using a given amount of energy. Alternatively, other processes may be designed to minimize the creation of undesired products, such as pollutants emitted from an internal combustion engine. To achieve these goals, chemists must consider the competing effects of the reaction conditions that they can control.

One way to obtain a high yield of a desired compound is to make the reaction rate of the desired reaction much faster than the reaction rates of any other possible reactions that might occur in the system. Altering reaction conditions to control reaction rates, thereby obtaining a single product or set of products, is called kinetic control A second approach, called thermodynamic control, consists of adjusting conditions so that at equilibrium only the desired products are present in significant quantities.

The Haber-Bosch Process for Synthesis of Ammonia

An example of thermodynamic control is the Haber-Bosch process. Karl Bosch (1874–1940) was a German chemical engineer who was responsible for designing the process that took advantage of Fritz Haber's discoveries regarding the N_2 + H_2/NH_3 equilibrium to make ammonia synthesis via this route cost-effective. He received the Nobel Prize in Chemistry in 1931 for his work. The industrial process is called either the Haber process or the Haber-Bosch process. used to synthesize ammonia via the following reaction:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \tag{14.6.1a}$$

with

$$\Delta H_{rxn} = -91.8\ kJ/mol \tag{14.6.1b}$$

Because the reaction converts 4 mol of gaseous reactants to only 2 mol of gaseous product, Le Châtelier's principle predicts that the formation of NH_3 will be favored when the pressure is increased. The reaction is exothermic, however (ΔH_{rxn} = −91.8 kJ/mol), so the equilibrium constant decreases with increasing temperature, which causes an equilibrium mixture to contain only relatively small amounts of ammonia at high temperatures (Figure 14.6.1). Taken together, these considerations suggest that the maximum yield of NH_3 will be obtained if the reaction is carried out at as low a temperature and as high a pressure as possible. Unfortunately, at temperatures less than approximately 300°C, where the equilibrium yield of ammonia would be relatively high, the reaction is too *slow* to be of any commercial use. The industrial process therefore uses a mixed oxide (Fe_2O_3/K_2O) catalyst that enables the reaction to proceed at a significant rate at temperatures of 400°C–530°C, where the formation of ammonia is less unfavorable than at higher temperatures.

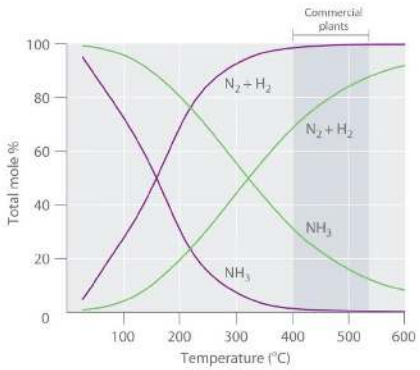


Figure 14.6.1 Effect of Temperature and Pressure on the Equilibrium Composition of Two Systems that Originally Contained a 3:1 Mixture of Hydrogen and Nitrogen *At all temperatures, the total pressure in the systems was initially either 4 atm (purple curves) or 200 atm (green curves). Note the dramatic decrease in the proportion of NH_3 at equilibrium at higher temperatures in*

both cases, as well as the large increase in the proportion of NH_3 at equilibrium at any temperature for the system at higher pressure (green) versus lower pressure (purple). Commercial plants that use the Haber-Bosch process to synthesize ammonia on an industrial scale operate at temperatures of 400°C–530°C (indicated by the darker gray band) and total pressures of 130–330 atm.

Because of the low value of the equilibrium constant at high temperatures (e.g., K = 0.039 at 800 K), there is no way to produce an equilibrium mixture that contains large proportions of ammonia at high temperatures. We can, however, control the temperature and the pressure while using a catalyst to convert a fraction of the N_2 and H_2 in the reaction mixture to NH_3, as is done in the Haber-Bosch process. This process also makes use of the fact that the product—ammonia—is less volatile than the reactants. Because NH_3 is a liquid at room temperature at pressures greater than 10 atm, cooling the reaction mixture causes NH_3 to condense from the vapor as liquid ammonia, which is easily separated from unreacted N_2 and H_2. The unreacted gases are recycled until complete conversion of hydrogen and nitrogen to ammonia is eventually achieved. Figure 14.6.2 is a simplified layout of a Haber-Bosch process plant.

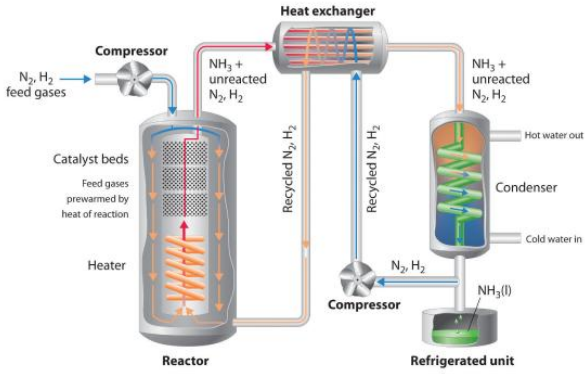


Figure 14.6.2 A Schematic Diagram of an Industrial Plant for the Production of Ammonia via the Haber-Bosch Process *A 3:1 mixture of gaseous H_2 and N_2 is compressed to 130–330 atm, heated to 400°C–530°C, and passed over an Fe_2O_3/K_2O catalyst, which results in partial conversion to gaseous NH_3. The resulting mixture of gaseous NH_3, H_2, and N_2 is passed through a heat exchanger, which uses the hot gases to prewarm recycled N_2 and H_2, and a condenser to cool the NH_3, giving a liquid that is readily separated from unreacted N_2 and H_2. (Although the normal boiling point of NH_3 is −33°C, the boiling point increases rapidly with increasing pressure, to 20°C at 8.5 atm and 126°C at 100 atm.) The unreacted N_2 and H_2 are recycled to form more*

Below are videos showing how the process is carried out. The first step is generation of hydrogen gas by reaction of methane and steam on a nickel catalyst.

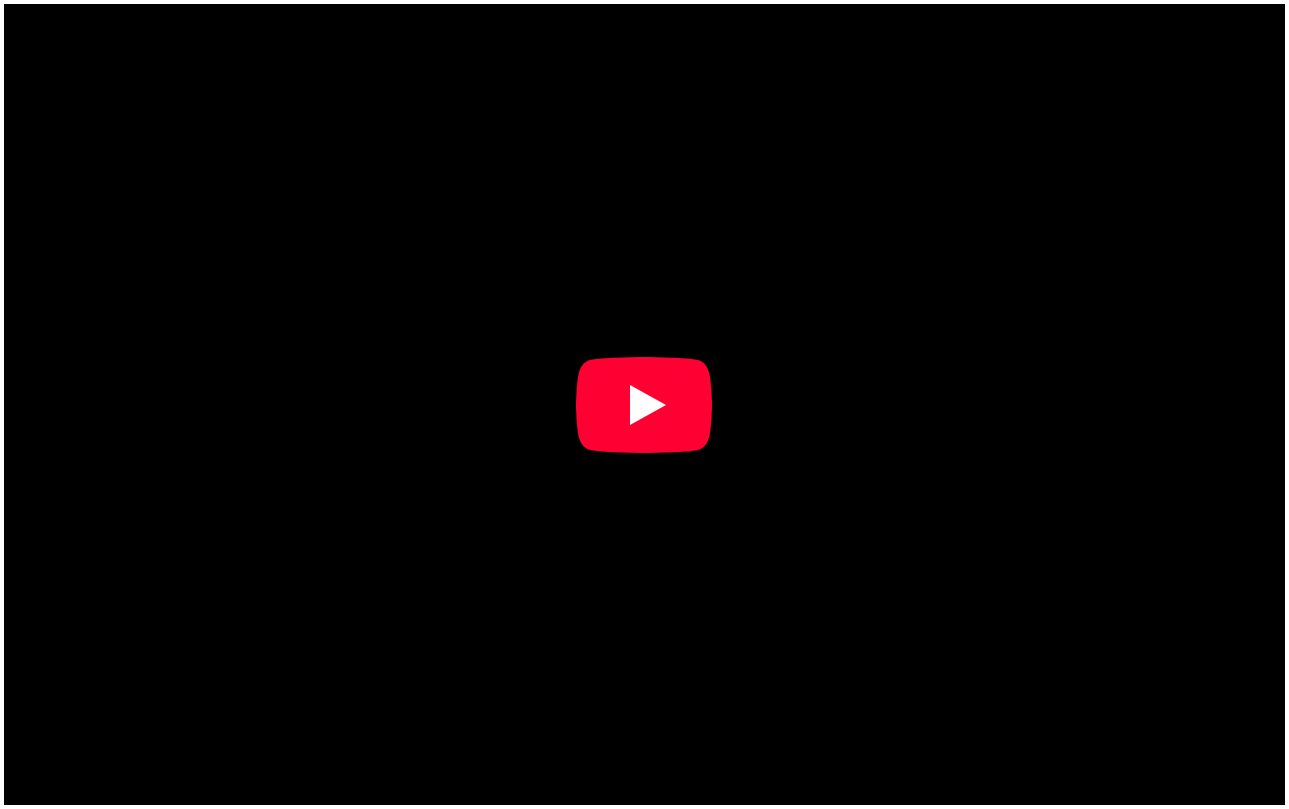
$$CH_4(g) + H_2O(g) <=> CO(g) + 3H_2(g) \tag{14.6.2a}$$

followed by

$$CO(g) + H_2O(g) <=> CO_2(g) + H_2(g) \tag{14.6.2b}$$

Any remaining methane is converted to carbon dioxide by reaction with air leaving a mix of pure nitrogen, hydrogen and carbon dioxide, The carbon dioxide then has to be scrubbed out from the gas mixture leaving a 3:1 mixture of hydrogen gas and nitrogen which is fed into the ammonia converter. Formation of ammonia requires a catalyst to break the nitrogen bond. On the iron catalyst the N_2 and H_2 atomize and react to form an equilibrium mixture of NH_3, N_2 and H_2, which is about 15% ammonia. The gas in the reactor flows continually through an external cooler which condenses the ammonia and returns the remaining N_2 and H_2 to the reactor which further react to form more ammonia.

The first video below, from BASF, shows a schematic version of the Haber-Bosch process.



video we can write the seven reactions that are involved in the process where ad indicates that the molecule or ı the catalyst

$$H_2 \rightleftharpoons 2H^{ad}$$

$$N_2 \rightleftharpoons N_{2ad}$$

$$N_{2ad} \rightleftharpoons 2N_{ad}$$

$$H_{ad} + N_{ad} \rightleftharpoons NH_{ad}$$

$$NH_{ad} + H_{ad} \rightleftharpoons NH_{2ad}$$

$$NH_{2ad} + H_{ad} \rightleftharpoons NH_{3ad}$$

$$NH_{3ad} \rightleftharpoons NH_3$$

Reaction 14.6.3 is much the slowest, and therefore the rate determining step. Figure 14.6.3 summarizes the reaction scheme

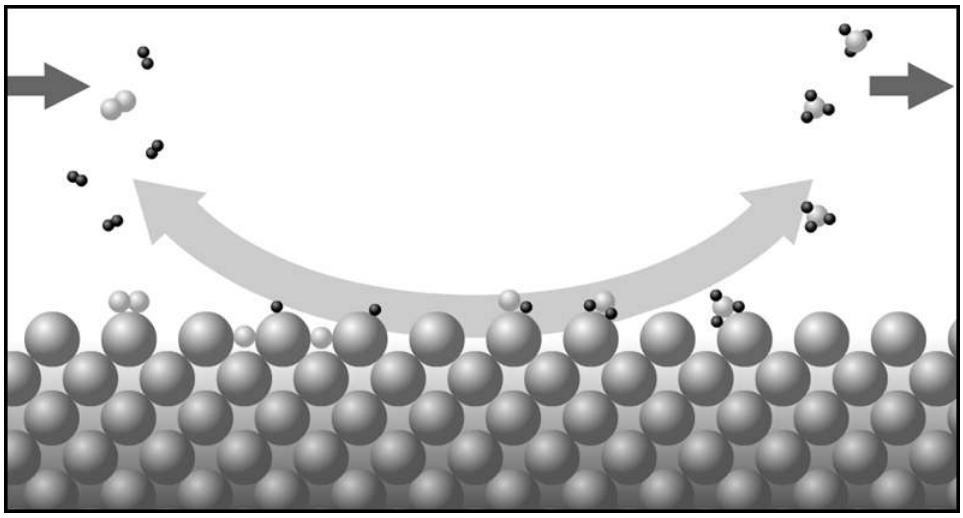


Figure 14.6.3: *A representation of the reactions Eqs. 14.6.3a - 14.6.3g with H_2 and N_2 coming in from the left and being adsorbed on the catalyst. The H_2 and N_2 then atomize on the surface of the catalyst, followed by a set of sequential reactions forming NH, NH_2 and finally NH_3 which desorbs from the catalyst as shown on the right*

Gerhard Ertl worked out the energetics of the reaction shown in Figure 14.6.4 below shows the amount of energy per mole needed on the catalyst and that which would be needed in the gas phase. Ertl's Nobel Prize speech about his work on the catalytic reactions forming ammonia and other catalytic reactions can be viewed on line

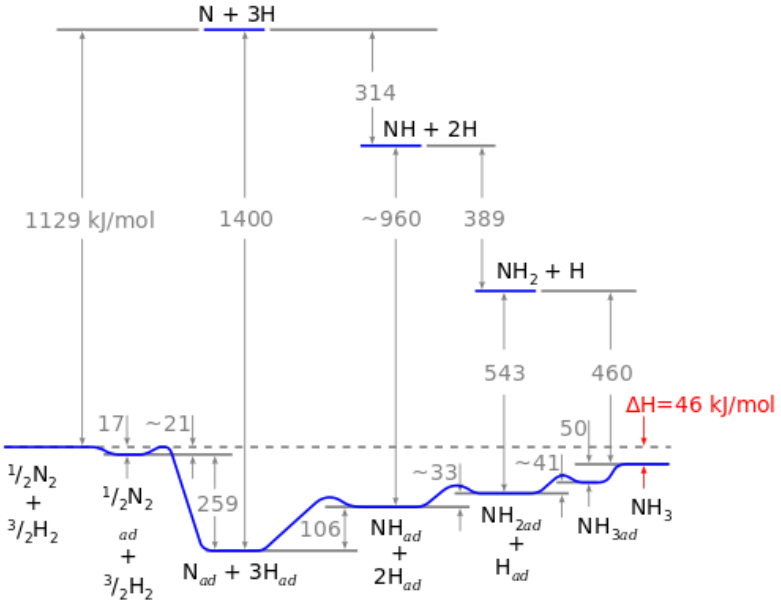
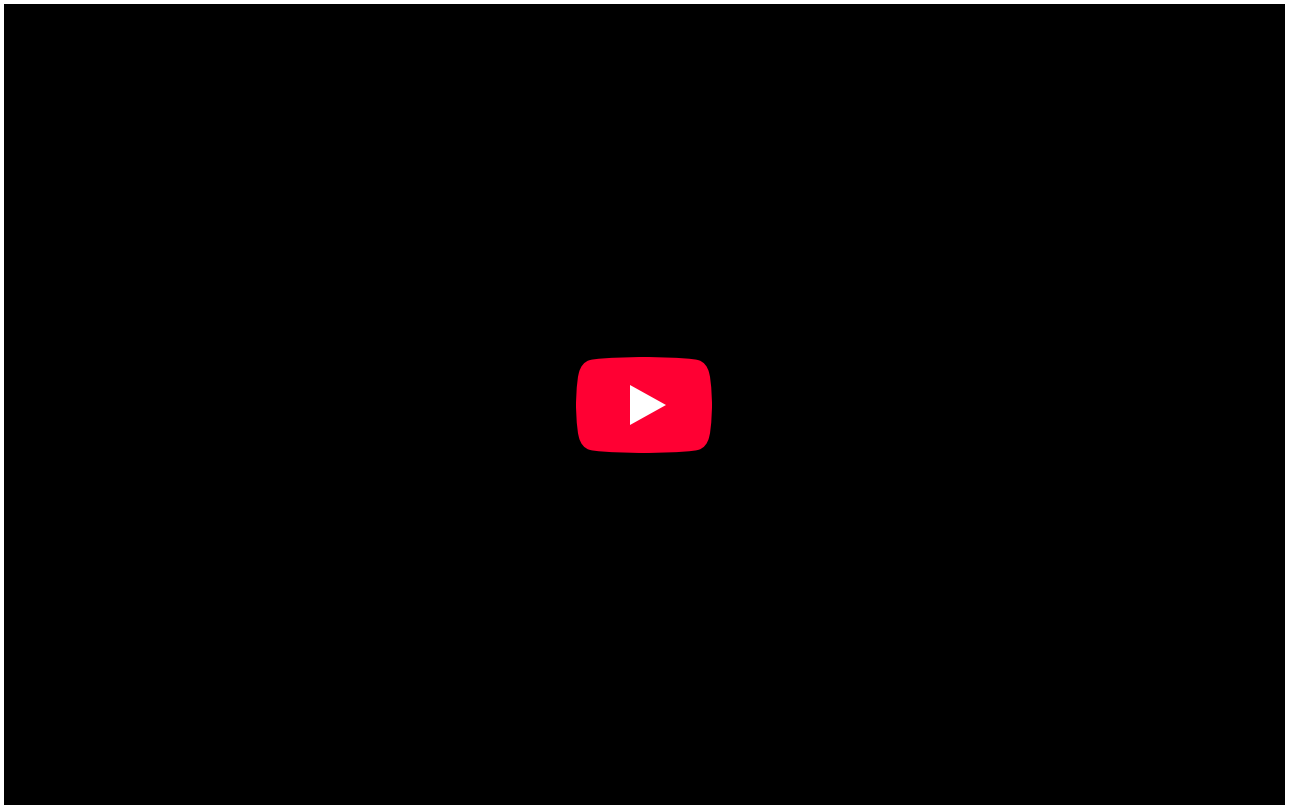
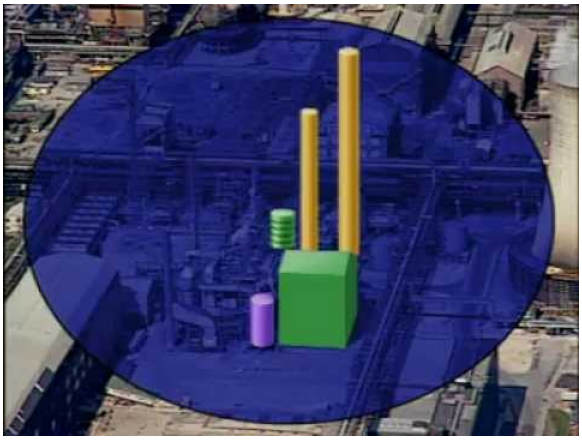


Figure 14.6.4: *Ertl's group was able to measure the energy needed for each step of the Bosch-Haber process as opposed to the energy that would be needed in the gas phase*

The second video from the Royal Society of Chemistry gives you a tour through a ammonia plant.





The Sohio Acrylonitrile Process

The Sohio acrylonitrile process, in which propene and ammonia react with oxygen to form acrylonitrile, is an example of a kinetically controlled reaction:

$$\mathrm{CH_2{=}CHCH_{3(g)} + NH_{3(g)} + \tfrac{3}{2}\,O_{2(g)} \rightleftharpoons CH_2{=}CHC{\equiv}N_{(g)} + 3\,H_2O_{(g)}} \tag{14.6.4}$$

Like most oxidation reactions of organic compounds, this reaction is highly exothermic ($\Delta H° = -519$ kJ/mol) and has a very large equilibrium constant ($K = 1.2 \times 10^{94}$). Nonetheless, the reaction shown in Equation 14.6.2 is not the reaction a chemist would expect to occur when propene or ammonia is heated in the presence of oxygen. Competing combustion reactions that produce CO_2 and N_2 from the reactants, such as those shown in Equation 14.6.5 and Equation 14.6.6, are even more exothermic and have even larger equilibrium constants, thereby reducing the yield of the desired product, acrylonitrile:

$$\mathrm{CH_2{=}CHCH_{3(g)} + \tfrac{9}{2}\,O_{2(g)} \rightleftharpoons 3\,CO_{2(g)} + 3\,H_2O_{(g)}} \tag{14.6.5a}$$

with

$$\Delta H^\circ = -1926.1\ kJ/mol \tag{14.6.5b}$$

and

$$K = 4.5 \times 10^{338} \tag{14.6.5c}$$

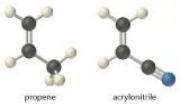
$$2\,NH_{3(g)} + 3\,O_{2(g)} \rightleftharpoons N_{2(g)} + 6\,H_2O_{(g)} \tag{14.6.6a}$$

with

$$\Delta H^\circ = -1359.2\ kJ/mol, \tag{14.6.6b}$$

and

$$K = 4.4 \times 10^{234} \tag{14.6.6c}$$



In fact, the formation of acrylonitrile in Equation 14.6.4. is accompanied by the release of approximately 760 kJ/mol of heat due to partial combustion of propene during the reaction.

The Sohio process uses a catalyst that selectively accelerates the rate of formation of acrylonitrile without significantly affecting the reaction rates of competing combustion reactions. Consequently, acrylonitrile is formed more rapidly than CO_2 and N_2 under the optimized reaction conditions (approximately 1.5 atm and 450°C). The reaction mixture is rapidly cooled to prevent further oxidation or combustion of acrylonitrile, which is then washed out of the vapor with a liquid water spray. Thus controlling the kinetics of the reaction causes the desired product to be formed under conditions where equilibrium is not established. In industry, this reaction is carried out on an enormous scale. Acrylonitrile is the building block of the polymer called *polyacrylonitrile*, found in all the products referred to collectively as *acrylics*, whose wide range of uses includes the synthesis of fibers woven into clothing and carpets.

Note the Pattern

Controlling the amount of product formed requires that both thermodynamic and kinetic factors be considered.

Example 14.6.1

Recall that methanation is the reaction of hydrogen with carbon monoxide to form methane and water:

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)} \tag{Chapter 14.6.1}$$

This reaction is the reverse of the steam reforming of methane described in Example 14. The reaction is exothermic (ΔH° = −206 kJ/mol), with an equilibrium constant at room temperature of $K_p = 7.6 \times 10^{24}$. Unfortunately, however, CO and H_2 do not react at an appreciable rate at room temperature. What conditions would you select to maximize the amount of methane formed per unit time by this reaction?

Given: balanced chemical equation and values of ΔH° and K

Asked for: conditions to maximize yield of product

Strategy:

Consider the effect of changes in temperature and pressure and the addition of an effective catalyst on the reaction rate and equilibrium of the reaction. Determine which combination of reaction conditions will result in the maximum production of methane.

Solution:

The products are highly favored at equilibrium, but the rate at which equilibrium is reached is too slow to be useful. You learned in Chapter 13 that the reaction rate can often be increased dramatically by increasing the temperature of the reactants. Unfortunately, however, because the reaction is quite exothermic, an increase in temperature will shift the

equilibrium to the left, causing more reactants to form and relieving the stress on the system by absorbing the added heat. If we increase the temperature too much, the equilibrium will no longer favor methane formation. (In fact, the equilibrium constant for this reaction is very temperature sensitive, decreasing to only 1.9×10^{-3} at 1000°C.) To increase the reaction rate, we can try to find a catalyst that will operate at lower temperatures where equilibrium favors the formation of products. Higher pressures will also favor the formation of products because 4 mol of gaseous reactant are converted to only 2 mol of gaseous product. Very high pressures should not be needed, however, because the equilibrium constant favors the formation of products. Thus optimal conditions for the reaction include carrying it out at temperatures greater than room temperature (but not too high), adding a catalyst, and using pressures greater than atmospheric pressure.

Industrially, catalytic methanation is typically carried out at pressures of 1–100 atm and temperatures of 250°C–450°C in the presence of a nickel catalyst. (At 425°C°C, K_p is 3.7×10^{3}, so the formation of products is still favored.) The synthesis of methane can also be favored by removing either H_2O or CH_4 from the reaction mixture by condensation as they form.

Exercise

As you learned in Example 10, the water–gas shift reaction is as follows:

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)} \qquad \text{(Chapter 14.6.2)}$$

K_p = 0.106 and ΔH = 41.2 kJ/mol at 700 K. What reaction conditions would you use to maximize the yield of carbon monoxide?

Answer: high temperatures to increase the reaction rate and favor product formation, a catalyst to increase the reaction rate, and atmospheric pressure because the equilibrium will not be greatly affected by pressure

Summary

Changing conditions to affect the reaction rates to obtain a single product is called **kinetic control** of the system. In contrast, **thermodynamic control** is adjusting the conditions to ensure that only the desired product or products are present in significant concentrations at equilibrium.

Key Takeaway

- Both kinetic and thermodynamic factors can be used to control reaction products.

Conceptual Problems

1. A reaction mixture will produce either product A or B depending on the reaction pathway. In the absence of a catalyst, product A is formed; in the presence of a catalyst, product B is formed. What conclusions can you draw about the forward and reverse rates of the reaction that produces A versus the reaction that produces B in (a) the absence of a catalyst and (b) the presence of a catalyst?
2. Describe how you would design an experiment to determine the equilibrium constant for the synthesis of ammonia:

   $$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \text{(Chapter 14.6.3)}$$

   The forward reaction is exothermic ($\Delta H°$ = −91.8 kJ). What effect would an increase in temperature have on the equilibrium constant?
3. What effect does a catalyst have on each of the following?
   a. the equilibrium position of a reaction
   b. the rate at which equilibrium is reached
   c. the equilibrium constant?
4. How can the ratio Q/K be used to determine in which direction a reaction will proceed to reach equilibrium?

5. Industrial reactions are frequently run under conditions in which competing reactions can occur. Explain how a catalyst can be used to achieve reaction selectivity. Does the ratio Q/K for the selected reaction change in the presence of a catalyst?

Numerical Problems

1. The oxidation of acetylene via $2C_2H_2$ (g) + $5O_2$(g) ⇌ 4 CO_2(g) + 2 H_2O(l) has $\Delta H°$ = −2600 kJ. What strategy would you use with regard to temperature, volume, and pressure to maximize the yield of product?
2. The oxidation of carbon monoxide via CO(g) + 1/2 O_2(g) ⇌ CO_2(g) has $\Delta H°$ = −283 kJ. If you were interested in maximizing the yield of CO_2, what general conditions would you select with regard to temperature, pressure, and volume?
3. You are interested in maximizing the product yield of the system $2SO_2$(g) + O_2 (g) ⇌ 2 SO_3 (g) K = 280 and $\Delta H°$ = −158 kJ. What general conditions would you select with regard to temperature, pressure, and volume? If SO_2 has an initial concentration of 0.200 M and the amount of O_2 is stoichiometric, what amount of SO_3 is produced at equilibrium?

Answer

1. Use low temperature and high pressure (small volume).
2.
3.

Contributors

- Anonymous

Modified by Joshua Halpern (Howard University), Scott Sinex, and Scott Johnson (PGCC)

Haber Bosch process videos from BASF and the Royal Society for Chemistry on YouTube

Figure 14.6.3 is from the ESA, now available on the internet wayback machine

Figure 14.6.4 is from the Wikipedia Commons

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Chapter 14.7: End of Chapter Materials

APPLICATION PROBLEMS

Problems marked with a ♦ involve multiple concepts.

1. ♦ The total concentrations of dissolved Al in a soil sample represent the sum of "free" Al^{3+} and bound forms of Al that are stable enough to be considered definite chemical species. The distribution of aluminum among its possible chemical forms can be described using equilibrium constants such as the following:

   $K_1 = [AlOH^{2+}]/[Al^{3+}][OH^-] = 1.0 \times 10^9$

   $K_2 = [AlSO_4^+]/[Al^{3+}][SO_4^{2-}] = 1.0 \times 10^3$

   $K_3 = [AlF^{2+}]/[Al^{3+}][F^-] = 1.0 \times 10^7$

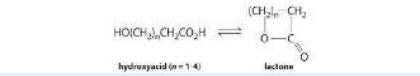
   a. Write an equilibrium equation for each expression.

   b. Which anion has the highest affinity for Al^{3+}: OH^-, SO_4^{2-}, or F^-? Explain your reasoning.

   c. A 1.0 M solution of Al^{3+} is mixed with a 1.0 M solution of each of the anions. Which mixture has the lowest Al^{3+} concentration?

2. Many hydroxy acids form lactones (cyclic esters) that contain a 5- or 6-membered ring. Common hydroxy acids found in nature are glycolic acid, a constituent of cane sugar juice; lactic acid, which has the characteristic odor and taste of sour milk; and citric acid, found in fruit juices. The general reaction for lactone formation can be written as follows:

   hydroxy acid ⇌ lactone + H_2O

   Use the information in the following table to calculate the equilibrium constant for lactone formation for each hydroxy acid given and determine which ring size is most stable.

		At Equilibrium	
Hydroxy Acid Formula	**Size of Lactone Ring (atoms)**	**Hydroxy Acid (M)**	**Lactone (M)**
$HOCH_2CH_2COOH$	4	4.99×10^{-3}	5.00×10^{-5}
$HOCH_2CH_2CH_2COOH$	5	8.10×10^{-5}	2.19×10^{-4}
$HOCH_2CH_2CH_2CH_2COOH$	6	5.46×10^{-2}	5.40×10^{-9}
$HOCH_2CH_2CH_2CH_2CH_2COOH$	7	9.90×10^{-3}	1.00×10^{-4}

3. ♦ Phosphorus pentachloride, an important reagent in organic chemistry for converting alcohols to alkyl chlorides (ROH → RCl), is hydrolyzed in water to form phosphoric acid and hydrogen chloride. In the gaseous state, however, PCl_5 can decompose at 250°C according to $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, for which $K = 0.0420$.

   a. Are products or reactants favored in the decomposition of $PCl_5(g)$?

   b. If a 2.00 L flask containing 104.1 g PCl_5 is heated to 250°C, what is the equilibrium concentration of each species in this reaction?

   c. What effect would an increase in pressure have on the equilibrium position? Why?

   d. If a 1.00×10^3 L vessel containing 2.00×10^3 kg of PCl_3 with a constant chlorine pressure of 2.00 atm is allowed to reach equilibrium, how many kilograms of PCl_5 are produced? What is the percent yield of PCl_5?

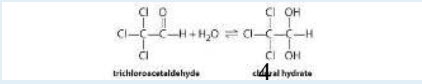
4. ♦ Carbon disulfide (CS_2) is used in the manufacture of rayon and in electronic vacuum tubes. However, extreme caution must be used when handling CS_2 in its gaseous state because it is extremely toxic and can cause fatal convulsions. Chronic toxicity is marked by psychic disturbances and tremors. CS_2 is used to synthesize H_2S at elevated T via the following reaction:

   $$CS_2(g) + 4\,H_2(g) \rightleftharpoons CH_4(g) + 2H_2S(g), K = 3.3 \times 10^4$$

   a. If the equilibrium concentration of methane in this reaction is 2.5×10^{-2} M and the initial concentration of each reactant is 0.1635 M, what is the concentration of H_2S at equilibrium?

b. Exposure to CS_2 concentrations greater than 300 ppm for several hours can start to produce adverse effects. After working for several hours in a laboratory that contains large quantities of CS_2, you notice that the fume hoods were off and there was not enough ventilation to remove any CS_2 vapor. Given the equilibrium $CS_2(l) \rightleftharpoons CS_2(g)$, where $T = 20°C$ and $K_p = 0.391$, determine whether you are in any danger.

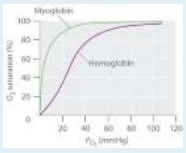
5. ♦ Chloral hydrate, a sedative commonly referred to as "knockout drops," is in equilibrium with trichloroacetaldehyde in highly concentrated aqueous solutions:



The equilibrium constant for this reaction as written is 3×10^{4}. Are the products or the reactants favored? Write an equilibrium expression for this reaction. How could you drive this reaction to completion?

6. Hydrogen cyanide is commercially produced in the United States by the following reaction: $CH_4(g) + NH_3(g) + 3/2\ O2(g) \rightleftharpoons HCN(g) + 3H_2O(g)$ where HCN is continuously removed from the system. This reaction is carried out at approximately 1100°C in the presence of a catalyst; however, the high temperature causes other reactions to occur. Why is it necessary to run this reaction at such an elevated temperature? Does the presence of the catalyst affect the equilibrium position?

7. ♦ Hemoglobin transports oxygen from the lungs to the capillaries and consists of four subunits, each capable of binding a single molecule of O_2. In the lungs, $P(O_2)$ is relatively high (100 mmHg), so hemoglobin becomes nearly saturated with O_2. In the tissues, however, $P(O_2)$ is relatively low (40 mmHg), so hemoglobin releases about half of its bound oxygen. Myoglobin, a protein in muscle, resembles a single subunit of hemoglobin. The plots show the percent O_2 saturation versus $P(O_2)$ for hemoglobin and myoglobin. Based on these plots, which molecule has the higher affinity for oxygen? What advantage does hemoglobin have over myoglobin as the oxygen transporter? Why is it advantageous to have myoglobin in muscle tissue? Use equilibrium to explain why it is more difficult to exercise at high altitudes where the partial pressure of oxygen is lower.



8. ♦ Sodium sulfate is widely used in the recycling industry as well as in the detergent and glass industries. This compound combines with H_2SO_4 via $Na_2SO_4(s) + H_2SO_4(g) \rightleftharpoons 2NaHSO_4(s)$ Sodium hydrogen sulfate is used as a cleaning agent because it is water soluble and acidic.
   a. Write an expression for K for this reaction.
   b. Relate this equilibrium constant to the equilibrium constant for the related reaction: $2Na_2SO_4(s) + 2H_2SO_4(g) \rightleftharpoons 4NaHSO_4(s)$
   c. The dissolution of Na_2SO_4 in water produces the equilibrium reaction $SO_4^{2-}(aq) + H_2O(l) \rightleftharpoons HSO_4^{-}(aq) + OH^{-}(aq)$ with $K = 8.33 \times 10^{-13}$. What is the concentration of OH^- in a solution formed from the dissolution of 1.00 g of sodium sulfate to make 150.0 mL of aqueous solution? Neglect the autoionization of water in your answer.

9. ♦ One of the Venera orbiter satellites measured S_2 concentrations at the surface of Venus. The resulting thermochemical data suggest that S_2 formation at the planet's surface occurs via the following equilibrium reaction: $4CO(g) + 2SO_2(g) \rightleftharpoons 4CO_2(g) + S_2(g)$. Write an expression for K for this reaction and then relate this expression to those for the following reactions:
   a. $2CO(g) + SO_2(g) \rightleftharpoons 2CO_2(g) + 1/2\ S_2(g)$
      $CO(g) + 1/2\ SO_2(g) \rightleftharpoons CO_2(g) + 1/4\ S_2(g)$
   b. At 450°C, the equilibrium pressure of CO_2 is 85.0 atm, SO_2 is 1.0 atm, CO is 1.0 atm, and S_2 is 3.0×10^{-8} atm. What are K and K_p at this temperature? What is the concentration of S_2?

10. ♦ Until the early part of the 20th century, commercial production of sulfuric acid was carried out by the "lead-chamber" process, in which SO_2 was oxidized to H_2SO_4 in a lead-lined room. This process may be summarized by the following sequence of reactions:
   a. $NO(g) + NO_2(g) + 2H_2SO_4(l) \rightleftharpoons 2NOHSO_4(s) + H_2O(l)$ K1
      $2NOHSO_4(s) + SO_2(g) + 2H_2O(l) \rightleftharpoons 3H_2SO_4(l) + 2NO(g)$ K2

a. Write the equilibrium constant expressions for reactions 1 and 2 and the sum of the reactions (reaction 3).
b. Show that $K_3 = K_1 \times K_2$.
c. If insufficient water is added in reaction 2 such that the reaction becomes $NOHSO_4(s) + 1/2\ SO_2(g) + H_2O(l) \rightleftharpoons 3/2H_2SO_4(l) + NO(g)$ does K_3 still equal $K_1 \times K_2$?
d. Based on part c, write the equilibrium constant expression for K_2.

11. Phosgene (carbonic dichloride, $COCl_2$) is a colorless, highly toxic gas with an odor similar to that of moldy hay. Used as a lethal gas in war, phosgene can be immediately fatal; inhalation can cause either pneumonia or pulmonary edema. For the equilibrium reaction $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ K_p is 0.680 at −10°C. If the initial pressure of $COCl_2$ is 0.681 atm, what is the partial pressure of each component of this equilibrium system? Is the formation of products or reactant favored in this reaction?
12. ♦ British bituminous coal has a high sulfur content and produces much smoke when burned. In 1952, burning of this coal in London led to elevated levels of smog containing high concentrations of sulfur dioxide, a lung irritant, and more than 4000 people died. Sulfur dioxide emissions can be converted to SO_3 and ultimately to H_2SO_4, which is the cause of acid rain. The initial reaction is $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ for which $K_p = 44$.
    a. Given this K_p, are product or reactants favored in this reaction?
    b. What is the partial pressure of each species under equilibrium conditions if the initial pressure of each reactant is 0.50 atm?
    c. Would an increase in pressure favor the formation of product or reactants? Why?
13. Oxyhemoglobin is the oxygenated form of hemoglobin, the oxygen-carrying pigment of red blood cells. Hemoglobin is built from α and β protein chains. Assembly of the oxygenated (oxy) and deoxygenated (deoxy) β-chains has been studied with the following results:
    $4\beta(oxy) \rightleftharpoons \beta4(oxy) \quad K=9.07\times10^{15}$
    $4\beta(deoxy) \rightleftharpoons \beta4(deoxy) \quad K=9.20\times10^{13}$
    Is it more likely that hemoglobin β chains assemble in an oxygenated or deoxygenated state? Explain your answer.
14. ♦ Inorganic weathering reactions can turn silicate rocks, such as diopside ($CaMgSi_2O_6$), to carbonate via the following reaction:
    $$CaMgSi_2O_6 + CO_2(g) \rightleftharpoons MgSiO_3(s) + CaCO_3(s) + SiO_2(s)$$
    Write an expression for the equilibrium constant. Although this reaction occurs on both Earth and Venus, the high surface temperature of Venus causes the reaction to be driven in one direction on that planet. Predict whether high temperatures will drive the reaction to the right or the left and then justify your answer. The estimated partial pressure of carbon dioxide on Venus is 85 atm due to the dense Venusian atmosphere. How does this pressure influence the reaction?
15. Silicon and its inorganic compounds are widely used to manufacture textile glass fibers, cement, ceramic products, and synthetic fillers. Two of the most important industrially utilized silicon halides are $SiCl_4$ and $SiHCl_3$, formed by reaction of elemental silicon with HCl at temperatures greater than 300°C:
    $$Si(s) + 4HCl(g) \rightleftharpoons SiCl_4(g) + 2H_2(g)$$
    $$Si(g) + 3HCl(g) \rightleftharpoons SiHCl_3(g) + H_2(g)$$
    Which of these two reactions is favored by increasing [HCl]? by decreasing the volume of the system?
16. ♦ The first step in the utilization of glucose in humans is the conversion of glucose to glucose-6-phosphate via the transfer of a phosphate group from ATP (adenosine triphosphate), which produces glucose-6-phosphate and ADP (adenosine diphosphate):
    $$glucose + ATP \rightleftharpoons glucose\text{-}6\text{-}phosphate + ADP \quad K=680 \text{ at } 25°C$$
    a. Is the formation of products or reactants favored in this reaction?
    b. Would K increase, decrease, or remain the same if the glucose concentration were doubled?
    c. If $-RT \ln K = -RT' \ln K'$, what would K be if the temperature were decreased to 0°C?
    d. Is the formation of products favored by an increase or a decrease in the temperature of the system?
17. In the presence of O_2, the carbon atoms of glucose can be fully oxidized to CO_2 with a release of free energy almost 20 times greater than that possible under conditions in which O_2 is not present. In many animal cells, the TCA cycle (tricarboxylic acid cycle) is the second stage in the complete oxidation of glucose. One reaction in the TCA cycle is the conversion of citrate to isocitrate, for which $K = 0.08$ in the forward direction. Speculate why the cycle continues despite this unfavorable value of K. What happens if the citrate concentration increases?

18. ♦ Soil is an open system, subject to natural inputs and outputs that may change its chemical composition. Aqueous-phase, adsorbed, and solid-phase forms of Al(III) are of critical importance in controlling the acidity of soils, although industrial effluents, such as sulfur and nitrogen oxide gases, and fertilizers containing nitrogen can also have a large effect. Dissolution of the mineral gibbsite, which contains Al^{3+} in the form $Al(OH)_3(s)$, occurs in soil according to the following reaction:

$$Al(OH)_3(s)+3H^+(aq) \rightleftharpoons Al^{3+}(aq)+3H_2O(l)$$

When gibbsite is in a highly crystalline state, K = 9.35 for this reaction at 298 K. In the microcrystalline state, K = 8.11. Is this change consistent with the increased surface area of the microcrystalline state?

ANSWERS

1.
2.
3. a. reactant
   b. $[Cl_2] = [PCl_3] = 0.0836$ M; $[PCl_5] = 0.166$ M
   c. increasing pressure favors reactant (PCl_5)
   d. 1.59×10^3 kg; 52.5%
4.
5. Products are favored;

$$K = \frac{[chloralhydrate]}{[Cl_3CHO]\,[H_2O]} \qquad \text{(Chapter 14.7.1)}$$

   high concentrations of water will favor chloral hydrate formation.
6.
7.
8.
9. $K = \dfrac{[CO_2]^4\,[S_2]}{[CO]^4\,[SO_2]^2}$
   a. $K' = \dfrac{[CO_2]^2\,[S_2]^{1/2}}{[CO]^2\,[SO_2]} = K^{1/2}$
   b. $K'' = \dfrac{[CO_2]\,[S_2]^{1/4}}{[CO]\,[SO_2]^{1/2}} = K^{1/4}$
   c. $K_p = 1.6$; $K = 93$; $[S_2] = 5.1 \times 10^{-10}$ M
10.
11. $P(CO) = P(Cl_2) = 0.421$ atm; $P(COCl_2) = 0.260$ atm reactants are slightly favored.
12.
13.
14.
15. Both reactions are favored by increasing [HCl] and decreasing volume.
16.
17.
18.

Contributors

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Modified by Joshua Halpern (Howard University), Scott Sinex, and Scott Johnson (PGCC)

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CHAPTER OVERVIEW

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Chapter 15.0: Introduction

In Section 11.3 , you learned that applying a small amount of heat to solid ammonium dichromate initiates a vigorous reaction that produces chromium(III) oxide, nitrogen gas, and water vapor. These are not the only products of this reaction that interest chemists, however; the reaction also releases energy in the form of heat and light. So our description of this reaction was incomplete. A complete description of a chemical reaction includes not only the identity, amount, and chemical form of the reactants and products but also the quantity of energy produced or consumed. In combustion reactions, heat is always a product; in other reactions, heat may be produced or consumed.

This chapter introduces you to thermochemistry, a branch of chemistry that describes the energy changes that occur during chemical reactions. In some situations, the energy produced by chemical reactions is actually of greater interest to chemists than the material products of the reaction. For example, the controlled combustion of organic molecules, primarily sugars and fats, within our cells provides the energy for physical activity, thought, and other complex chemical transformations that occur in our bodies. Similarly, our energy-intensive society extracts energy from the combustion of fossil fuels, such as coal, petroleum, and natural gas, to manufacture clothing and furniture, heat your home in winter and cool it in summer, and power the car or bus that gets you to class and to the movies. By the end of this chapter, you will know enough about thermochemistry to explain why ice cubes cool a glass of soda, how instant cold packs and hot packs work, and why swimming pools and waterbeds are heated. You will also understand what factors determine the caloric content of your diet and why even “nonpolluting” uses of fossil fuels may be affecting the environment.



Figure 15.0.1 Thermodynamic spontaneity. *The highly exothermic and dramatic thermite reaction is thermodynamically spontaneous. Reactants of aluminum and a metal oxide, usually iron, which are stable at room temperature, are ignited either in the presence of heat or by the reaction of potassium permanganate and glycerin. The resulting products are aluminum oxide, free and molten elemental metal, and a great deal of heat, which makes this an excellent method for on-site welding. Because this reaction has its own oxygen supply, it can be used for underwater welding as well.*

Let's go to video



Mo Joshua Halpern Howard University

Thermite video from kosasihiskandarsjah on YouTube

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Chapter 15.1 Energy Changes in Chemical Reactions

Learning Objectives

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

In this section, we describe forms of energy and discuss the relationship between energy, heat, and work.

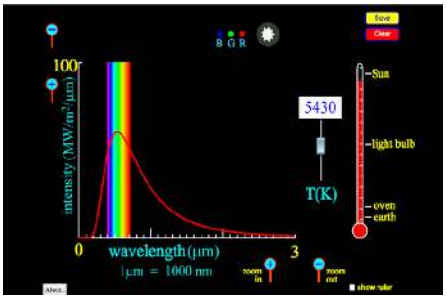
Forms of Energy

Sources of energy include electrical, nuclear, and chemical. **Electrical energy** results from the flow of electrically charged particles, either ions or electrons, in one direction under the influence of electrical or magnetic fields. **Nuclear** is the energy holding the nucleus of atoms together and can be released or absorbed by nuclear reactions. These reactions can transmute the nucleus, changing either the mass number or the atomic number of the nucleus. Similarly, **chemical energy** is the energy stored in molecular bonds. In a chemical reaction bonds are broken and formed. Breaking bonds requires energy, making bonds produces energy.

Types of energy include radiant, thermal, kinetic and potential energy. When charged particles move they emit electromagnetic radiation which we call **radiant energy**. This also includes quantum state changes in atoms and molecules which result in the emission/absorption of light. Any solid or liquid above absolute zero also emits radiant energy, called black body radiation, driven by internal motion of electrons, molecules or nuclei. This average energy and the distribution of potential and kinetic energies is characterized by the temperature of the black body and the motion is described as thermal . The intensity is governed by the Stefan-Boltzmann law, where E is the energy emitted per unit surface area.

$$E = \sigma T^4$$

The nature of this spectrum can be investigated using the following applet from PhET (you may need JAVA to see this)



Click to Run

Figure 15.1.1: An applet from PhET demonstrating the spectral distribution of black body emission as a function of temperature *The envelope of the solar spectrum is a black body spectrum of about 5500 K with sharp lines characteristic of atomic spectra, such as the lines of the hydrogen atomic spectrum. Radiant energy spans the spectrum from X-ray to microwave and beyond.*

Kinetic energy is due to the motion of an object. The energy tied up in chemical bonds is a form of potential energy which can be released when the bonds are broken in a reaction and the energy is converted into thermal energy, e.g. randomly directed kinetic energy. Chemical energy can also be converted to radiant energy; one common example is the light emitted by fireflies, which is produced from a chemical reaction.

Energy can be converted from one form to another or from one object to another. For example, when you climb a ladder to a high diving board, your body uses chemical energy produced by the combustion of organic molecules. As you climb, the chemical energy is converted to *mechanical work* to overcome the force of gravity. When you reach the top, your potential energy with respect to the water is increased, and when you dive off that potential energy is converted to kinetic energy as you move towards the water.

Although energy can be converted from one form to another, *the total amount of energy in the universe remains constant*. This is known as the Law of Conservation of EnergyThe total amount of energy in the universe remains constant. Energy can be neither created nor destroyed, but it can be converted from one form to another. If thermal energy is exchanged in any part of the process the Law of Conservation of Energy is also known as the First Law of Thermodynamics.

Energy, Work, and Heat

One definition of energy is the capacity to do work. The easiest form of work to visualize is mechanical workThe energy required to move an object a distance d when opposed by a force F, (Figure 15.1.2, which is the energy required to move an object a distance d when opposed by a force F, such as gravity:

$$\begin{aligned} work &= force \times distance \\ w &= Fd \end{aligned}$$

Consider the mechanical work required for you to lift a barbell. Energy is expended to overcome the force of gravity. The amount of work done (w) and thus the energy required depends on three things: (1) the height the barbell is lifted to (the distance d); (2) the mass, which must be raised that distance against the downward acceleration due to gravity; and (3) the details of how you lift the barbell.

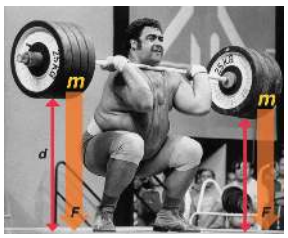


Figure 15.1.2 An Example of Mechanical Work *One form of energy is mechanical work, the energy required to move an object of mass m a distance d when opposed by a force F, such as gravity.*

Defining heat and thermal energy is a bit more complex. To start we will take a molecular viewpoint using the kinetic theory of gases as explained in Section 6.6. For an ideal gas the total internal energy is the sum of the kinetic energies of all of the molecules Per mole we showed in Section 6.6 that the energy E is related to the temperature T by

$$E = \frac{3}{2}RT$$

Rearranging Equation 15.1.3, we find that the temperature of an ideal gas is related to the average kinetic energy of an individual molecule by

$$T = \frac{1}{3R} M v_{rms}^2$$

where R, the gas constant, is 8.314 J/mole-K and M is the molar mass of the gas molecules. From this, the temperature of the gas is directly proportional to the average kinetic energy.

For a real gas where the molecules attract each other, the thermal energy would be the sum of all of the kinetic energy plus the energy associated with the molecular attraction. A liquid would be the same, except that the potential energy associated with the molecular attraction would exceed the kinetic energy associated with the moving molecules (otherwise the liquid would turn into a gas).

The energy associated with the internal motions and bonding of the constituent atoms, nuclei and electrons is the **internal energy**

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

Temperature is related to heat flow by the Zeroth Law of Thermodynamics which states that if two bodies are in thermodynamic equilibrium with a third one, they are in thermodynamic equilibrium with each other. At equilibrium there will be no transfer of heat between the three bodies and they will all be at the same temperature. If we use a thermometer as the third body, the temperature registered by the thermometer will be the same for the two other bodies because they are all in thermodynamic equilibrium with each other.

In Section 6.6 we discussed how to use the kinetic theory to determine the total internal energy of a gas. For more complex systems this can be done using Statistical Mechanics which allows calculation of the distribution of energy among molecules in gases, liquids and solids. Thermodynamics does not allow calculation of internal energy but it does allow measuring changes in internal energy.

The internal energy of an object can be changed only by the transfer of energy to or from another object. Consider, for example, the chemical energy stored in a fully charged battery. As shown in Figure 15.1.3 , this energy can be used primarily to perform work (e.g., run an electric fan) or to generate light and heat (e.g., illuminating a light bulb). When the battery is fully discharged in either case, the total change in energy is the same, even though the fraction released as work or heat will vary depending on whether you are using an LED (less heat generated) or an incandescent bulb (heating the bulb filament by passing a current through it generates blackbody radiation). The sum of the heat produced and the work performed equals the change in energy (ΔE):

$$\begin{aligned} Energy\ Change(\Delta E) &= work + heat \\ \Delta E &= q + w \end{aligned}$$

This is the First Law of Thermodynamics. Energy can be transferred only in the form of heat, work performed on or by an object, or some combination of heat and work. The total change of energy is equal to the sum of the total heat transferred and work done. Heat added to the system is positive and heat taken away from the system is negative. Work done on the system is positive and work the system does is negative.

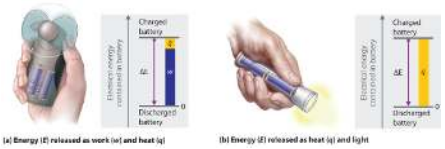


Figure 15.1.3 Energy Transfer: *Discharging a fully charged battery releases the same amount of energy whether the battery is used to run a fan (a) or illuminate a light bulb (b). In (a), most of the energy is used to perform work, which turns the blades of the fan and thus moves the air; only a small portion of the energy is released as heat by the electric motor. In (b), all the energy is released as heat and light; no work is done.*

In the next section we will discuss the difference between thermodynamic quantities that are properties of the state that a body is in. That means that to calculate the change in internal energy, ΔE, for some process it is not necessary to know how the changes have occurred but simply what the initial and final states are. The internal energy, E, and the change of internal energy in any process, ΔE, are called **state functions**.

Because work occurs only when an object, such as a person, or a substance, such as water, moves against an opposing force, work requires that a system and its surroundings be connected. In contrast, the flow of *heat*, the transfer of energy due to differences in temperature between two objects, represents a thermal connection between a system and its surroundings. This connection can also involve radiative transfer, as the transfer of energy from the Sun to the Earth. Thus doing work causes a physical displacement, whereas the flow of heat causes a temperature change. The units of work and heat must be the same because both processes result in the transfer of energy. In the SI system, those units are joules (J), the same unit used for energy. There is no difference between an energy change brought about by doing work on a system and an equal energy change brought about by heating it.

The quantity of work, *w* and heat, *q*, in any process are determined by the details of how the work is done, for example, was the work done at constant pressure, was heat flow between the surroundings allowed or not, was the temperature held constant or not. The heat and work in any process depend on the details, and heat and work are called **path functions**.

The differential form of the First Law of Thermodynamics is

$$\begin{aligned} Energy\ Change(dE) &= work + heat \\ dE &= \delta q + \delta w \end{aligned}$$

where dE indicates that energy is a perfect differential and δq and δw are inexact differentials. The differential form of fundamental equations such as the First Law is discussed in detail by Andreana Rosniks at another ChemWiki page, and will also be treated in this and the next chapter.

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

Because all forms of energy can be interconverted, energy in any form can be expressed using the same units as kinetic energy. The SI unit of energy, the joule (J), named after the British physicist James Joule (1818–1889). A joule is defined as 1 kilogram·meter^2/second^2 (kg·m^2/s^2). Because a joule is such a small quantity of energy, chemists usually express energy in kilojoules (1 kJ = 10^3 J).

Kinetic Energy

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

$$KE = \tfrac{1}{2} m v^2$$

PV Work

There are many kinds of work, including mechanical work, electrical work, and work against a gravitational or a magnetic field. Here we will consider only mechanical work, focusing on the work done during changes in the pressure or the volume of a gas. To describe this *pressure–volume work* (*PV* work), we will use such imaginary oddities as frictionless pistons, which involve no component of resistance, and ideal gases, which have no attractive or repulsive interactions.

Imagine an ideal gas, confined by a frictionless piston, with internal pressure P_{int} and initial volume V_i (Figure 15.1.4). If $P_{ext} = P_{int}$, the system is at equilibrium; the piston does not move, and no work is done. If the external pressure on the piston (P_{ext}) is less than P_{int}, however, then the ideal gas inside the piston will expand, forcing the piston to perform work on its surroundings; that is, the final volume (V_f) will be greater than V_i. If $P_{ext} > P_{int}$, then the gas will be compressed, and the surroundings will perform work on the system.

$$w = Fd = P_{ext} A dh$$



Figure 15.1.4 *PV* Work *Using a frictionless piston, if the external pressure is less than P_{int} (a), the ideal gas inside the piston will expand, forcing the piston to perform work on its surroundings. The final volume (V_f) will be greater than V_i. Alternatively, if the external pressure is greater than P_{int} (b), the gas will be compressed, and the surroundings will perform work on the system.*

The change in the volume of the cylinder (dV) as the piston moves a distance d is d$V = Adh$, as shown in Figure 15.1.4. The work performed is thus

$$w = P_{ext}dV$$

The units of work obtained using this definition are correct for energy: pressure is force per unit area (newton/m^2) and volume has units of cubic meters, so

$$w = \frac{F}{A}dV = \frac{newton}{m^2} \times m^3 = newton \times m = Joule$$

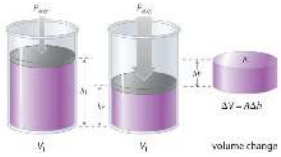


Figure 15.1.6 Work Performed with a Change in Volume *The change in the volume (ΔV) of the cylinder housing a piston is $\Delta V = A\Delta h$ as the piston moves. The work performed by the surroundings on the system as the piston moves inward is given by $w = P_{ext}\Delta V$.*

If we use atmospheres for P and liters for V, we obtain units of L·atm for work. These units correspond to units of energy, as shown in the different values of the ideal gas constant R:

$$R= \dfrac{0.08206 \; L \cdot \; atm}{mol\cdot K}= \dfrac{8.314 \; J}{mol\cdot K}$$

Thus 0.08206 L·atm = 8.314 J and 1 L·atm = 101.3 J. (For more information on the ideal gas law, see Chapter 6.)

Whether work is defined as having a positive sign or a negative sign is a matter of convention.Chemists, define heat flow *from* a system *to* its surroundings as negative. Using that same sign convention, we define work done *by* a system *on* its surroundings as having a negative sign because it results in a transfer of energy from a system to its surroundings.This is an arbitrary convention and one that is not universally used. Some engineering disciplines are more interested in the work done *on* the surroundings than in the work done *by* the system and therefore use the opposite convention. Because $\Delta V > 0$ for an expansion, Equation 15.1.9 must be written with a negative sign to describe *PV* work done *by* the system as negative:

$$w = -P_{ext}\Delta V$$

The work done by a gas expanding against an external pressure is therefore negative, corresponding to work done *by* a system *on* its surroundings. Conversely, when a gas is compressed by an external pressure, $\Delta V < 0$ and the work is positive because work is being done *on* a system *by* its surroundings.

In contrast to internal energy, work is not a state function. We can see this by examining Figure 15.1.7, in which two different, two-step pathways take a gaseous system from an initial state to a final state with corresponding changes in temperature. In pathway A, the volume of a gas is initially increased while its pressure stays constant (step 1); then its pressure is decreased while the volume remains constant (step 2). In pathway B, the order of the steps is reversed. The temperatures, pressures, and volumes of the initial and final states are identical in both cases, but the amount of work done, indicated by the shaded areas in the figure, is substantially different. As we can see, the amount of work done depends on the pathway taken from (V_1, P_1) to (V_2, P_2), which means that work is not a state function.

Note the Pattern

Internal energy is a state function, whereas work is not.

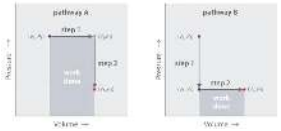


Figure 15.1.7 Work Is Not a State Function *In pathway A, the volume of a gas is initially increased while its pressure stays constant (step 1). Its pressure is then decreased while the volume remains constant (step 2). Pathway B reverses these steps. Although (V_1, P_1) and (V_2, P_2) are identical in both cases, the amount of work done (shaded area) depends on the pathway taken.*

Note the Pattern

The units of energy are the same for all forms of energy.

Energy can also be expressed in the non-SI units of calories (cal)A non-SI unit of energy: 1 cal = 4.184 J exactly., where 1 cal was originally defined as the amount of energy needed to raise the temperature of exactly 1 g of water from 14.5°C to 15.5°C.We specify the exact temperatures because the amount of energy needed to raise the temperature of 1 g of water 1°C varies slightly with elevation. To three significant figures, however, this amount is 1.00 cal over the temperature range 0°C–100°C. The name is derived from the Latin *calor*, meaning “heat.” Although energy may be expressed as either calories or joules, calories were defined in terms of heat, whereas joules were defined in terms of motion. Because calories and joules are both units of energy, however, the calorie is now defined in terms of the joule:

$$1\ cal = 4.184\ Jexactly$$

$$1\ J = 0.2390\ cal$$

In this text, we will use the SI units—joules (J) and kilojoules (kJ). Engineers, of course, often use calories and (shudder) British thermal units (BTU) and other customary energy units

Example 15.1.1

1. If the mass of a baseball is 149 g, what is the kinetic energy of a fastball clocked at 100 mi/h?

Given: mass and velocity or height

Asked for: kinetic energy

Strategy:

Use Equation 15.1.7 to calculate the kinetic energy

Solution:

1. The kinetic energy of an object is given by $1/2\ mv^2$ In this case, we know both the mass and the velocity, but we must convert the velocity to SI units and then plug the answer into the formulat for kinetic energy

Key Equations

general definition of work

Equation 15.1.2: $w = Fd$

relationship between energy, heat, and work

Equation 15.1.5: $\Delta E = q + w$

kinetic energy

Equation 15.1.7: $KE = 1/2\ mv^2$

Pressure volume work

Equation 15.1.9: $w = -P_{ext}dV$

Summary

Thermochemistry is a branch of chemistry that qualitatively and quantitatively describes the energy changes that occur during chemical reactions. **Energy** is the capacity to do work. **Mechanical work** is the amount of energy required to move an object a given distance when opposed by a force. **Thermal energy** is due to the random motions of atoms, molecules, or ions in a substance. The **temperature** of an object is a measure of the amount of thermal energy it contains. **Heat (*q*)** is the transfer of thermal energy from a hotter object to a cooler one. Energy can take many forms; most are different varieties of **potential energy (*PE*)**, energy caused by the relative position or orientation of an object. **Kinetic energy (*KE*)** is the energy an object possesses due to its motion. Energy can be converted from one form to another, but the **law of conservation of energy** states that energy can be neither created nor destroyed.

When thermal energy is transferred the law of conservation of energy is called the first law of thermodynamics.

The most common units of energy are the **joule (J)**, defined as 1 $(kg \cdot m^2)/s^2$, and the **calorie**, defined as the amount of energy needed to raise the temperature of 1 g of water by 1°C (1 cal = 4.184 J).

Key Takeaway

- All forms of energy can be interconverted. Three things can change the energy of an object: the transfer of heat, work performed on or by an object, or some combination of heat and work.

Conceptual Problems

1. What is the relationship between mechanical work and energy?
2. Does a person with a mass of 50 kg climbing a height of 15 m do work? Explain your answer. Does that same person do work while descending a mountain?
3. If a person exerts a force on an immovable object, does that person do work? Explain your answer.
4. Explain the differences between electrical energy, nuclear energy, and chemical energy.
5. The chapter describes thermal energy, radiant energy, electrical energy, nuclear energy, and chemical energy. Which form(s) of energy are represented by each of the following?
    1. sunlight
    2. the energy produced by a cathode ray tube, such as that found in a television
    3. the energy emitted from radioactivity
    4. the energy emitted from a burning candle
    5. the energy associated with a steam engine
    6. the energy emitted by a cellular phone
    7. the energy associated with a stick of dynamite
6. Describe the various forms of energy that are interconverted when a flashlight is switched on.
7. Describe the forms of energy that are interconverted when the space shuttle lifts off.
8. Categorize each of the following as representing kinetic energy or potential energy.
    1. the energy associated with a laptop computer sitting on the edge of a desk
    2. shoveling snow
    3. water pouring out of a fire hydrant
    4. the energy released by an earthquake
    5. the energy in a volcano about to erupt
    6. the energy associated with a coiled spring
9. Are the units for potential energy the same as the units for kinetic energy? Can an absolute value for potential energy be obtained? Explain your answer.
10. Categorize each of the following as representing kinetic energy or potential energy.
    1. water cascading over Niagara Falls
    2. a beaker balanced on the edge of a sink
    3. the energy released during a mudslide
    4. rollerblading
    5. the energy in a block of ice on a rooftop before a thaw
11. Why does hammering a piece of sheet metal cause the metal to heat up?

3. Technically, the person is not doing any work, since the object does not move.

Answers

1.
4.
5.
6.
7.
8.
9.
10.

11. The kinetic energy of the hammer is transferred to the metal.

Numerical Problems

Please be sure you are familiar with the topics discussed in Essential Skills 4 (Section 5.6 "Essential Skills 4") before proceeding to the Numerical Problems.

1. Describe the mathematical relationship between (a) the thermal energy stored in an object and that object's mass and (b) the thermal energy stored in an object and that object's temperature.
2. How much energy (in kilojoules) is released or stored when each of the following occurs?
    1. A 230 lb football player is lifted to a height of 4.00 ft.
    2. An 11.8 lb cat jumps from a height of 6.50 ft.
    3. A 3.75 lb book falls off of a shelf that is 5.50 ft high.
3. Calculate how much energy (in kilojoules) is released or stored when each of the following occurs:
    1. A 130 lb ice skater is lifted 7.50 ft off the ice.
    2. A 48 lb child jumps from a height of 4.0 ft.
    3. An 18.5 lb light fixture falls from a 10.0 ft ceiling.
4. A car weighing 1438 kg falls off a bridge that is 211 ft high. Ignoring air resistance, how much energy is released when the car hits the water?
5. A 1 tn roller coaster filled with passengers reaches a height of 28 m before accelerating downhill. How much energy is released when the roller coaster reaches the bottom of the hill? Assume no energy is lost due to friction.

Answers

1. 1. The thermal energy content of an object is directly proportional to its mass.
    2. The thermal energy content of an object is directly proportional to its temperature.
2.
3. 1. 1.3 kJ stored
    2. 0.26 kJ released
    3. 0.251 kJ released
4.
5. 250 kJ released

Contributors

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Chapter 15.2: The First Law of Thermodynamics

Learning Objectives

- To calculate changes in internal energy.

The relationship between the energy change of a system and that of its surroundings is given by the first law of thermodynamics, which states that the *energy of the universe is constant*. We can express this law mathematically as follows:

$$\Delta E_{univ} = \Delta E_{sys} + \Delta E_{surr} = 0$$

$$\Delta E_{sys} = -\Delta E_{surr}$$

where the subscripts *univ*, *sys*, and *surr* refer to the universe, the system, and the surroundings, respectively. Remembering that energy is a state function we can equally well use The change in energy of a system is identical in magnitude but opposite in sign to the change in energy of its surroundings.

An important factor that determines the outcome of a chemical reaction is the tendency of all systems, chemical or otherwise, to move toward the lowest possible overall energy state. As a brick dropped from a rooftop falls, its potential energy is converted to kinetic energy; when it reaches ground level, it has achieved a state of lower potential energy. Anyone nearby will notice that energy is transferred to the surroundings as the noise of the impact reverberates and the dust rises when the brick hits the ground. Similarly, if a spark ignites a mixture of isooctane and oxygen in an internal combustion engine, carbon dioxide and water form spontaneously, while potential energy (in the form of the relative positions of atoms in the molecules) is released to the surroundings as heat and work. The internal energy content of the CO_2/H_2O product mixture is less than that of the isooctane/O_2 reactant mixture. The two cases differ, however, in the form in which the energy is released to the surroundings. In the case of the falling brick, the energy is transferred as work done on whatever happens to be in the path of the brick; in the case of burning isooctane, the energy can be released as solely heat (if the reaction is carried out in an open container) or as a mixture of heat and work (if the reaction is carried out in the cylinder of an internal combustion engine). Because heat and work are the only two ways in which energy can be transferred between a system and its surroundings, any change in the internal energy of the system is the sum of the heat transferred (q) and the work done (w):

$$dE_{sys} = \delta q + \delta w$$

Although q and w are not state functions on their own, their sum (ΔE_{sys}) is independent of the path taken and is therefore a state function. A major task for the designers of any machine that converts energy to work is to maximize the amount of work obtained and minimize the amount of energy released to the environment as heat. An example is the combustion of coal to produce electricity. Although the maximum amount of energy available from the process is fixed by the energy content of the reactants and the products, the fraction of that energy that can be used to perform useful work is not fixed, as discussed in Section 16.3. Because we focus almost exclusively on the changes in the energy of a system, we will not use “sys” as a subscript unless we need to distinguish explicitly between a system and its surroundings.

Note the Pattern

The tendency of all systems, chemical or otherwise, is to move toward the state with the lowest possible energy.

Note the Pattern

Although q and w are not state functions, their sum (ΔE_{sys}) is independent of the path taken and therefore is a state function.

Example 15.2.1

A sample of an ideal gas in the cylinder of an engine is compressed from 400 mL to 50.0 mL during the compression stroke against a constant pressure of 8.00 atm. At the same time, 140 J of energy is transferred from the gas to the

surroundings as heat. What is the total change in the internal energy (ΔE) of the gas in joules?

Given: initial volume, final volume, external pressure, and quantity of energy transferred as heat

Asked for: total change in internal energy

Strategy:

A Determine the sign of q to use in Equation 15.2.2.

B From Equation 15.1.9, calculate w from the values given. Substitute this value into Equation 15.2.2 to calculate ΔE.

Solution:

A From Equation 15.2.2, we know that $\Delta E = q + w$. We are given the magnitude of q (140 J) and need only determine its sign. Because energy is transferred from the system (the gas) to the surroundings, q is negative by convention.

B Because the gas is being compressed, we know that work is being done *on* the system, so w must be positive. From Equation 15.1.9,

$$w = -P_{ext}\Delta V = --(8.0\ \cancel{atm})\left(0.0500\ \cancel{L} - 0.400\ \cancel{L}\right)\left(\frac{101.3\ J}{\cancel{L}\cdot\cancel{atm}}\right) = 284\ J$$

Thus

$$\Delta E = q + w = -140\ J + 284\ J = 144\ J$$

In this case, although work is done *on* the gas, increasing its internal energy, heat flows *from* the system *to* the surroundings, decreasing its internal energy by 144 J. The work done and the heat transferred can have opposite signs.

Exercise

A sample of an ideal gas is allowed to expand from an initial volume of 0.200 L to a final volume of 3.50 L against a constant external pressure of 0.995 atm. At the same time, 117 J of heat is transferred from the surroundings to the gas. What is the total change in the internal energy (ΔE) of the gas in joules?

Answer: −216 J

Note the Pattern

By convention, both heat flow and work have a negative sign when energy is transferred from a system to its surroundings and vice versa.

Enthalpy

To further understand the relationship between heat flow (q) and the resulting change in internal energy (ΔE), we can look at two sets of limiting conditions: reactions that occur at constant volume and reactions that occur at constant pressure. We will assume that PV work is the only kind of work possible for the system, so we can substitute its definition from Equation 15.1.9 into Equation 15.2.2 to obtain the following:

$$dE = q - pdV$$

where the subscripts have been deleted.

If the reaction occurs in a closed vessel, the volume of the system is fixed, and dV is zero. Under these conditions, the heat flow (often given the symbol q_v to indicate constant volume) must equal dE:

$$\underset{\text{constant volume}}{\delta q_v = dE}$$

No *PV* work can be done, and the change in the internal energy of the system is equal to the amount of heat transferred from the system to the surroundings or vice versa.

Many chemical reactions are not, however, carried out in sealed containers at constant volume but in open containers at a more or less constant pressure of about 1 atm. The heat flow under these conditions is given the symbol q_p to indicate constant pressure. Replacing q in Equation 15.2.3 by q_p and rearranging to solve for q_p,

$$\underset{\text{constant pressure}}{\delta q_p = dE + PdV}$$

Thus, at constant pressure, the heat flow for any process is equal to the change in the internal energy of the system plus the *PV* work done.

Because conditions of constant pressure are so important in chemistry, a new state function called enthalpy (*H*) is defined as $H = E + PV$. At constant pressure, the change in the enthalpy of a system is as follows:

$$dH = dE + d(PV) = dE + PdV + VdP$$

Comparing the previous two equations shows that at constant pressure, the change in the enthalpy of a system is equal to the heat flow: $\Delta H = q_p$. This expression is consistent with a definition of enthalpy as the heat absorbed or produced during any process that occurs at constant pressure.

Note the Pattern

At constant pressure, the change in the enthalpy of a system is equal to the heat flow: $\Delta H = q_p$.

Example 15.2.2

The molar enthalpy of fusion for ice at 0.0°C and a pressure of 1.00 atm is 6.01 kJ, and the molar volumes of ice and water at 0°C are 0.0197 L and 0.0180 L, respectively. Calculate ΔH and ΔE for the melting of ice at 0.0°C. (For more information on enthalpy,

Given: enthalpy of fusion for ice, pressure, and molar volumes of ice and water

Asked for: ΔH and ΔE for ice melting at 0.0°C

Strategy:

A Determine the sign of q and set this value equal to ΔH.

B Calculate $\Delta(PV)$ from the information given.

C Determine ΔE by substituting the calculated values into Equation 15.2.6.

Solution:

A Because 6.01 kJ of heat is absorbed from the surroundings when 1 mol of ice melts, q = +6.01 kJ. When the process is carried out at constant pressure, $q = q_p = \Delta H$ = 6.01 kJ.

B To find ΔE using Equation 15.2.6, we need to calculate $\Delta(PV)$. The process is carried out at a constant pressure of 1.00 atm, so

$\Delta PV = P\Delta V = P(V_f - V)$=\left (1.00\;atm \right)\left (0.0180\;L-0.0197\lL \right)

$$= \left(-1.7 \times 10{-}3 \ \cancel{L \cdot atm}\right)\left(101.3 \ J/\cancel{L \cdot atm}\right)$$

C Substituting the calculated values of ΔH and $P\Delta V$ into Equation 15.2.6,

$$\Delta E = \Delta H - P\Delta V = -6010\ J - (-0.0017\ J) = 6010\ J = 6.01\ kJ$$

Exercise

At 298 K and 1 atm, the conversion of graphite to diamond requires the input of 1.850 kJ of heat per mole of carbon. The molar volumes of graphite and diamond are 0.00534 L and 0.00342 L, respectively. Calculate ΔH and ΔE for the conversion of C (graphite) to C (diamond) under these conditions.

Answer: ΔH = 1.85 kJ/mol; ΔE = 1.85 kJ/mol

The Relationship between ΔH and ΔE

If ΔH for a reaction is known, we can use the change in the enthalpy of the system (Equation 15.2.6) to calculate its change in internal energy. When a reaction involves only solids, liquids, liquid solutions, or any combination of these, the volume does not change appreciably ($\Delta V = 0$). Under these conditions, we can simplify Equation 15.2.6 to $\Delta H = \Delta E$. If gases are involved, however, ΔH and ΔE can differ significantly. We can calculate ΔE from the measured value of ΔH by using the right side of Equation 15.2.6 together with the ideal gas law, $PV = nRT$. Recognizing that $\Delta(PV) = \Delta(nRT)$, we can rewrite Equation 15.2.6 as follows:

$$\Delta H = DeltaE + \Delta\left(PV\right) = DeltaE + \Delta\left(nRT\right)$$

At constant temperature, $\Delta(nRT) = RT\Delta n$, where Δn is the difference between the final and initial numbers of moles of gas. Thus

$$\Delta E = \Delta H - RT\Delta n$$

For reactions that result in a net production of gas, $\Delta n > 0$, so $\Delta E < \Delta H$. Conversely, endothermic reactions ($\Delta H > 0$) that result in a net consumption of gas have $\Delta n < 0$ and $\Delta E > \Delta H$. The relationship between ΔH and ΔE for systems involving gases is illustrated in Example 4.

Note the Pattern

For reactions that result in a net production of gas, $\Delta E < \Delta H$. For endothermic reactions that result in a net consumption of gas, $\Delta E > \Delta H$.

Example 15.2.3

The combustion of graphite to produce carbon dioxide is described by the equation C (graphite, s) + O_2(g) → CO_2(g). At 298 K and 1.0 atm, ΔH = −393.5 kJ/mol of graphite for this reaction, and the molar volume of graphite is 0.0053 L. What is ΔE for the reaction?

Given: balanced chemical equation, temperature, pressure, ΔH, and molar volume of reactant

Asked for: ΔE

Strategy:

A Use the balanced chemical equation to calculate the change in the number of moles of gas during the reaction.

B Substitute this value and the data given into Equation 15.2.8 to obtain ΔE.

Solution:

A In this reaction, 1 mol of gas (CO_2) is produced, and 1 mol of gas (O_2) is consumed. Thus $\Delta n = 1 - 1 = 0$.

B Substituting this calculated value and the given values into Equation 15.2.8,

$$\Delta E = \Delta H - RT\Delta n = (-393.5\ kJ/mol) - [8.314\ J/mol \cdot K]\,(298\ K)\,(0)$$

$$= (-393.5\ kJ/mol) - (0\ J/mol) = -393.5\ kJ$$

To understand why only the change in the volume of the gases needs to be considered, notice that the molar volume of graphite is only 0.0053 L. A change in the number of moles of gas corresponds to a volume change of 22.4 L/mol of gas at standard temperature and pressure (STP), so the volume of gas consumed or produced in this case is (1)(22.4 L) = 22.4 L, which is much, much greater than the volume of 1 mol of a solid such as graphite.

Exercise

Calculate ΔE for the conversion of oxygen gas to ozone at 298 K: $3O_2(g) \rightarrow 2O_3(g)$. The value of ΔH for the reaction is 285.4 kJ.

Answer: 288 kJ

As the exercise in Example 4 illustrates, the magnitudes of ΔH and ΔE for reactions that involve gases are generally rather similar, even when there is a net production or consumption of gases.

Summary

The **first law of thermodynamics** states that the energy of the universe is constant. The change in the internal energy of a system is the sum of the heat transferred and the work done. At constant pressure, heat flow (q) and internal energy (E) are related to the system's **enthalpy (H)**. The heat flow is equal to the change in the internal energy of the system plus the PV work done. When the volume of a system is constant, changes in its internal energy can be calculated by substituting the ideal gas law into the equation for ΔE.

Key Takeaway

- Enthalpy is a state function, and the change in enthalpy of a system is equal to the sum of the change in the internal energy of the system and the PV work done.

Key Equations

Internal energy change

Equation 15.2.2: $\Delta E_{sys} = q + w$

Enthalpy change

Equation 15.2.6: $\Delta H = \Delta E + \Delta(PV)$

Relationship between ΔH and ΔE for an ideal gas

Equation 15.2.8: $\Delta E = \Delta H - RT\Delta n$

Conceptual Problems

1. Describe how a swinging pendulum that slows with time illustrates the first law of thermodynamics.
2. When air is pumped into a bicycle tire, the air is compressed. Assuming that the volume is constant, express the change in internal energy in terms of q and w.
3. What is the relationship between enthalpy and internal energy for a reaction that occurs at constant pressure?
4. An intrepid scientist placed an unknown salt in a small amount of water. All the salt dissolved in the water, and the temperature of the solution dropped several degrees.

a. What is the sign of the enthalpy change for this reaction?
b. Assuming the heat capacity of the solution is the same as that of pure water, how would the scientist calculate the molar enthalpy change?
c. Propose an explanation for the decrease in temperature.

5. For years, chemists and physicists focused on enthalpy changes as a way to measure the spontaneity of a reaction. What arguments would you use to convince them not to use this method?
6. What is the relationship between enthalpy and internal energy for a reaction that occurs at constant volume?
7. The *enthalpy of combustion* (ΔH_{comb}) is defined thermodynamically as the enthalpy change for complete oxidation. The complete oxidation of hydrocarbons is represented by the following general equation: hydrocarbon + $O_2(g) \rightarrow CO_2(g) + H_2O(g)$. Enthalpies of combustion from reactions like this one can be measured experimentally with a high degree of precision. It has been found that the less stable the reactant, the more heat is evolved, so the more negative the value of ΔH_{comb}. In each pair of hydrocarbons, which member do you expect to have the greater (more negative) heat of combustion? Justify your answers.
   a. cyclopropane or cyclopentane
   b. butane or 2-methylpropane
   c. hexane or cyclohexane
8. Using a structural argument, explain why the *trans* isomer of 2-butene is more stable than the *cis* isomer. The enthalpies of formation of *cis*- and *trans*-2-butene are −7.1 kJ/mol and −11.4 kJ/mol, respectively.
9. Using structural arguments, explain why cyclopropane has a positive $\Delta H_f°$ (12.7 kJ/mol), whereas cyclopentane has a negative $\Delta H_f°$ (−18.4 kJ/mol). (Hint: consider bond angles.)

3. At constant pressure, $\Delta H = \Delta E + P\Delta V$.
4.
5.

Answers

1.
6.
7.
8.
9. With bond angles of 60°, cyclopropane is highly strained, causing it to be less stable than cyclopentane, which has nearly ideal tetrahedral geometry at each carbon atom.

Numerical Problems

1. A block of CO_2 weighing 15 g evaporates in a 5.0 L container at 25°C. How much work has been done if the gas is allowed to expand against an external pressure of 0.98 atm under isothermal conditions? The enthalpy of sublimation of CO_2 is 25.1 kJ/mol. What is the change in internal energy (kJ/mol) for the sublimation of CO_2 under these conditions?
2. Zinc and HCl react according to the following equation:
   $Zn(s) + 2HCl(aq) \rightarrow Zn^{2+}(aq) + 2Cl^{-}(aq) + H_2(g)$
   When 3.00 g of zinc metal is added to a dilute HCl solution at 1.00 atm and 25°C, and this reaction is allowed to go to completion at constant pressure, 6.99 kJ of heat must be removed to return the final solution to its original temperature. What are the values of *q* and *w*, and what is the change in internal energy?
3. Acetylene torches, used industrially to cut and weld metals, reach flame temperatures as high as 3000°C. The combustion reaction is as follows:
   $$2C_2H_2\,(g) + 5O_2\,(g) \rightarrow 4CO_2\,(g) + 2H_2O\,(l)\;\;\;\; \Delta H=-2599\;kJ$$
   Calculate the amount of work done against a pressure of 1.0 atm when 4.0 mol of acetylene are allowed to react with 10 mol of O_2 at 1.0 atm at 20°C. What is the change in internal energy for the reaction?
4. When iron dissolves in 1.00 M aqueous HCl, the products are $FeCl_2(aq)$ and hydrogen gas. Calculate the work done if 30 g of Fe react with excess hydrochloric acid in a closed vessel at 20°C. How much work is done if the reaction takes place in an open vessel with an external pressure of 1.0 atm?

Answer

1. −350 J; 8.2 kJ
2.
3.
4.

Contributors

- Anonymous

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Chapter 15.3: Enthalpy and Reactions

Learning Objectives

- To understand why enthalpy is an important state function.

Direction of Heat Flow

The reaction of powdered aluminum with iron(III) oxide, known as the thermite reaction, generates an enormous amount of heat—enough, in fact, to melt steel (see chapter opening image). The balanced chemical equation for the reaction is as follows:

$$2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + Al_2O_3(s)$$

We can also write this chemical equation as

$$2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + Al_2O_3(s) + heat$$

to indicate that heat is one of the products. Chemical equations in which heat is shown as either a reactant or a product are called *thermochemical equations*. In this reaction, the system consists of aluminum, iron, and oxygen atoms; everything else, including the container, makes up the surroundings. During the reaction, so much heat is produced that the iron liquefies. Eventually, the system cools; the iron solidifies as heat is transferred to the surroundings. A process in which heat (q) is transferred *from* a system *to* its surroundings is described as exothermicA process in which heat (q) is transferred *from* a system *to* its surroundings.. By convention, $q < 0$ for an exothermic reaction.

When you hold an ice cube in your hand, heat from the surroundings (including your hand) is transferred to the system (the ice), causing the ice to melt and your hand to become cold. We can describe this process by the following thermochemical equation:

$$heat + H_2O\,(s) \rightarrow H_2O\,(l)$$

When heat is transferred *to* a system *from* its surroundings, the process is endothermicA process in which heat q>0 is transferred *to* a system *from* its surroundings.. By convention, $q > 0$ for an endothermic reaction.

Enthalpy of Reaction

We have stated that the change in energy (ΔE) is equal to the sum of the heat produced and the work performed (Equation15.1.5). Work done by an expanding gas is called *pressure-volume work*, also called *PV work*. Consider, for example, a reaction that produces a gas, such as dissolving a piece of copper in concentrated nitric acid. The chemical equation for this reaction is as follows:

$$Cu\,(s) + 4HNO_3\,(aq) \rightarrow Cu(NO_3)_2\,(aq) + 2H_2O\,(l) + 2NO_3\,(g)$$

If the reaction is carried out in a closed system that is maintained at constant pressure by a movable piston, the piston will rise as nitrogen dioxide gas is formed (Figure 15.3.1). The system is performing work by lifting the piston against the downward force exerted by the atmosphere (i.e., *atmospheric pressure*). We find the amount of PV work done by multiplying the external pressure P by the change in volume caused by movement of the piston (ΔV). At a constant external pressure (here, atmospheric pressure)

$$w = -P\Delta V$$

The negative sign associated with PV work done indicates that the system loses energy. If the volume increases at constant pressure ($\Delta V > 0$), the work done by the system is negative, indicating that a system has lost energy by performing work on its surroundings. Conversely, if the volume decreases ($\Delta V < 0$), the work done by the system is positive, which means that the surroundings have performed work on the system, thereby increasing its energy.

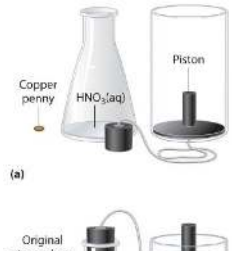
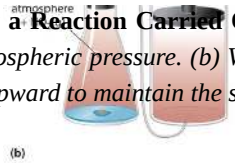


Figure 15.3.1 An Example of Work Performed by a Reaction Carried Out at Constant Pressure *(a) Initially, the system (a copper penny and concentrated nitric acid) is at atmospheric pressure. (b) When the penny is added to the nitric acid, the volume of NO_2 gas that is formed causes the piston to move upward to maintain the system at atmospheric pressure. In doing so, the system is performing work on its surroundings.*



The symbol E in Equation 15.1.5 represents the internal energyThe sum of the kinetic and potential energies of all of a system's component. Internal energy is a state function. of a system, which is the sum of the kinetic energy and potential energy of all its components. Additionally, $\Delta E = q + w$, where q is the heat produced by the system and w is the work performed by the system. It is the change in internal energy that produces heat plus work. Substituting Equation 8.1.5 we find that

$$\Delta E = q - P\Delta V$$

Thus, if a reaction were carried out in a constant volume system (a pressure cooker for example)

$$\Delta E = q_v$$

Where the subscipt v in q_v indicates that the process is carried out at constant volume. Thus, if the volume is held constant, the change in internal energy is equal to the heat flowing into or out of the system. However, we live in a constant pressure world, not a constant volume one. The atmospheric pressure at the surface of the earth where we live is roughly constant allowing for variation in barometric pressure due to weather or altitude.

To measure the energy changes that occur in chemical reactions, chemists usually use a related thermodynamic quantity called enthalpy (H)The sum of a system's internal energy E and the product of its pressure P and volume V (from the Greek *enthalpein*, meaning "to warm"). The enthalpy of a system is defined as the sum of its internal energy E plus the product of its pressure P and volume V:

$$H = E + PV$$

Because internal energy, pressure, and volume are all state functions, enthalpy is also a state function.

If a chemical change occurs at constant pressure (for a given P, $\Delta P = 0$), the change in enthalpy (ΔH)At constant pressure, the amount of heat transferred from the surroundings to the system or ΔH= q is

$$\Delta H = \Delta(E + PV) = \Delta E + \Delta PV = \Delta E + P\Delta V$$

Substituting $q + w$ for ΔE (Equation 15.1.5) and $-w$ for $P\Delta V$ (Equation 15.3.5), we obtain

$$\Delta H = \Delta E + P\Delta V = q_p + w - w = q_p$$

The subscript p is used here to emphasize that this equation is true only for a process that occurs at constant pressure. From Equation 15.3.10 we see that at constant pressure the change in enthalpy, ΔH of the system, defined as $H_{final} - H_{initial}$, is equal to the heat gained or lost.

$$\Delta H = H_{final} - H_{initial} = q_p$$

Just as with ΔE, because enthalpy is a state function, the magnitude of ΔH depends on only the initial and final states of the system, not on the path taken. The enthalpy change is the same even if the process does *not* occur at constant pressure. Most importantly, the change in enthalpy for a reaction can be determined by measuring the flow of heat into or out of the system. As we will see below, there are also cases where we want to know the amount of heat generated by a reaction, as for example for combustion of fuel. In that case knowing the molar change in enthalpy provides the information needed.

Finally, looking at Equation 15.3.9 shows that for reactions where the volume does not change, or better put does not change much, $\Delta H_{rxn} \sim \Delta E_{rxn}$. As a practical matter, this includes all reactions where all the products and reactants are either in the solid, liquid or aqueous phases. This is not generally true when there are gases on either side of the equation, a question which we will discuss in the chapter on gases.

Note the Pattern

To find ΔH, measure q_p.

When we study energy changes in chemical reactions, the most important quantity is usually the enthalpy of reaction (ΔH_{rxn})The change in enthalpy that occurs during a chemical reaction., the change in enthalpy that occurs during a reaction (such as the

dissolution of a piece of copper in nitric acid). If heat flows from a system to its surroundings, the enthalpy of the system decreases, so ΔH_{rxn} is negative. Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, so ΔH_{rxn} is positive. Thus $\Delta H_{rxn} < 0$ *for an exothermic reaction*, and $\Delta H_{rxn} > 0$ *for an endothermic reaction*. In chemical reactions, bond breaking requires an input of energy and is therefore an endothermic process, whereas bond making releases energy, which is an exothermic process. The sign conventions for heat flow and enthalpy changes are summarized in the following table:

Reaction Type	q	ΔH_{rxn}
exothermic	< 0	< 0 (heat flows from a system to its surroundings)
endothermic	> 0	> 0 (heat flows from the surroundings to a system)

If ΔH_{rxn} is negative, then the enthalpy of the products is less than the enthalpy of the reactants; that is, *an exothermic reaction is energetically downhill* (part (a) in Figure 15.3.2). Conversely, if ΔH_{rxn} is positive, then the enthalpy of the products is greater than the enthalpy of the reactants; thus, *an endothermic reaction is energetically uphill* (part (b) in Figure 15.3.2). Two important characteristics of enthalpy and changes in enthalpy are summarized in the following discussion.

Note the Pattern

Bond breaking requires an input of energy; bond making releases energy.

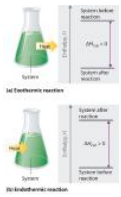


Figure 15.3.2 The Enthalpy of Reaction *Energy changes in chemical reactions are usually measured as changes in enthalpy. (a) If heat flows from a system to its surroundings, the enthalpy of the system decreases, ΔH_{rxn} is negative, and the reaction is exothermic; it is energetically downhill. (b) Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, ΔH_{rxn} is positive, and the reaction is endothermic; it is energetically uphill.*

- **Reversing a reaction or a process changes the sign of ΔH.** Ice *absorbs* heat when it melts (electrostatic interactions are broken), so liquid water must *release* heat when it freezes (electrostatic interactions are formed):

  $$heat + H_2O(s) \rightarrow H_2O(l) \quad \Delta H > 0$$

  $$H_2O(l) \rightarrow H_2O(s) + heat \quad \Delta H < 0$$

  In both cases, the *magnitude* of the enthalpy change is the same; only the *sign* is different.

- **Enthalpy is an extensive property (like mass).** The magnitude of ΔH for a reaction is proportional to the amounts of the substances that react. For example, a large fire produces more heat than a single match, even though the chemical reaction—the combustion of wood—is the same in both cases. For this reason, the enthalpy change for a reaction is usually given in kilojoules per mole of a particular reactant or product. Consider Equation 15.3.14, which describes the reaction of aluminum with iron(III) oxide (Fe_2O_3) at constant pressure. According to the reaction stoichiometry, 2 mol of Fe, 1 mol of Al_2O_3, and 851.5 kJ of heat are produced for every 2 mol of Al and 1 mol of Fe_2O_3 consumed:

  $$2Al\,(s) + Fe_2O_3\,(s) \rightarrow 2Fe\,(s) + Al_2O_3\,(s) + 815.5\ kJ$$

  Thus ΔH = −851.5 kJ/mol of Fe_2O_3. We can also describe ΔH for the reaction as −425.8 kJ/mol of Al: because 2 mol of Al are consumed in the balanced chemical equation, we divide −851.5 kJ by 2. When a value for ΔH, in kilojoules rather than kilojoules per mole, is written after the reaction, as in Equation 15.3.15, it is the value of ΔH corresponding to the reaction of the molar quantities of reactants as given in the balanced chemical equation:

  $$2Al\,(s) + Fe_2O_3\,(s) \rightarrow 2Fe\,(s) + Al_2O_3\,(s) \quad \Delta H_{rxn} = -851.5\ kJ$$

If 4 mol of Al and 2 mol of Fe_2O_3 react, the change in enthalpy is 2 × (−851.5 kJ) = −1703 kJ. We can summarize the relationship between the amount of each substance and the enthalpy change for this reaction as follows:

$$-\frac{851.5\ kJ}{2\ mol\ Al} = -\frac{425.8\ kJ}{1\ mol\ Al} = -\frac{1703\ kJ}{4\ mol\ Al}$$

The relationship between the magnitude of the enthalpy change and the mass of reactants is illustrated in Example 2.

Example 15.3.1

Certain parts of the world, such as southern California and Saudi Arabia, are short of freshwater for drinking. One possible solution to the problem is to tow icebergs from Antarctica and then melt them as needed. If ΔH is 6.01 kJ/mol for the reaction $H_2O(s) \rightarrow H_2O(l)$ at 0°C and constant pressure, how much energy would be required to melt a moderately large iceberg with a mass of 1.00 million metric tons (1.00×10^6 metric tons)? (A metric ton is 1000 kg.)

Given: energy per mole of ice and mass of iceberg

Asked for: energy required to melt iceberg

Strategy:

A Calculate the number of moles of ice contained in 1 million metric tons (1.00×10^6 metric tons) of ice.

B Calculate the energy needed to melt the ice by multiplying the number of moles of ice in the iceberg by the amount of energy required to melt 1 mol of ice.

Solution:

A Because enthalpy is an extensive property, the amount of energy required to melt ice depends on the amount of ice present. We are given ΔH for the process—that is, the amount of energy needed to melt 1 mol (or 18.015 g) of ice—so we need to calculate the number of moles of ice in the iceberg and multiply that number by ΔH (+6.01 kJ/mol):

$$\begin{aligned} moles\ H_2O &= 1.00 \times 10^6\ metric\ tons H_2O \left(\frac{1000\ \cancel{kg}}{1\ \cancel{metric\ ton}}\right)\left(\frac{1000\ \cancel{g}}{1\ \cancel{kg}}\right)\left(\frac{1\ mol\ H_2O}{18.015\ \cancel{g\ H_2O}}\right) \\ &= 5.55 \times 10^{10}\ mol H_2O \end{aligned}$$

B The energy needed to melt the iceberg is thus

$$\left(\frac{6.01\ kJ}{\cancel{mol\ H_2O}}\right)\left(5.55 \times 10^{10}\ \cancel{mol\ H_2O}\right) = 3.34 \times 10^{11}\ kJ$$

Because so much energy is needed to melt the iceberg, this plan would require a relatively inexpensive source of energy to be practical. To give you some idea of the scale of such an operation, the amounts of different energy sources equivalent to the amount of energy needed to melt the iceberg are shown in the table below.

Possible sources of the approximately 3.34×10^{11} kJ needed to melt a 1.00×10^6 metric ton iceberg
Combustion of 3.8×10^3 ft^3 of natural gas
Combustion of 68,000 barrels of oil
Combustion of 15,000 tons of coal
1.1×10^8 kilowatt-hours of electricity

Exercise

If 17.3 g of powdered aluminum are allowed to react with excess Fe_2O_3, how much heat is produced?

Answer: 273 kJ

Key Equations

definition of enthalpy

Equation 15.3.8: $H = E + PV$

pressure-volume work

Equation 15.3.5: $w = -P\Delta V$

enthalpy change at constant pressure

Equation 15.3.9: $\Delta H = \Delta E + P\Delta V$

Equation 15.3.10 $\Delta H = q_p$

Summary

In chemistry, the small part of the universe that we are studying is the **system**, and the rest of the universe is the **surroundings**. **Open systems** can exchange both matter and energy with their surroundings, **closed systems** can exchange energy but not matter with their surroundings, and **isolated systems** can exchange neither matter nor energy with their surroundings. A **state function** is a property of a system that depends on only its present **state**, not its history. A reaction or process in which heat is transferred from a system to its surroundings is **exothermic**. A reaction or process in which heat is transferred to a system from its surroundings is **endothermic**.

Enthalpy is a state function used to measure the heat transferred from a system to its surroundings or vice versa at constant pressure. Only the **change in enthalpy (ΔH)** can be measured. A negative ΔH means that heat flows from a system to its surroundings; a positive ΔH means that heat flows into a system from its surroundings. For a chemical reaction, the **enthalpy of reaction (ΔH_{rxn})** is the difference in enthalpy between products and reactants; the units of ΔH_{rxn} are kilojoules per mole. Reversing a chemical reaction reverses the sign of ΔH_{rxn}. The magnitude of ΔH_{rxn} also depends on the physical state of the reactants and the products because processes such as melting solids or vaporizing liquids are also accompanied by enthalpy changes: the **enthalpy of fusion (ΔH_{fus})** and the **enthalpy of vaporization (ΔH_{vap})**, respectively. The overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions, which is **Hess's law**. The **enthalpy of combustion (ΔH_{comb})** is the enthalpy change that occurs when a substance is burned in excess oxygen. The **enthalpy of formation (ΔH_f)** is the enthalpy change that accompanies the formation of a compound from its elements. **Standard enthalpies of formation** (ΔH^o_f) are determined under **standard conditions**: a pressure of 1 atm for gases and a concentration of 1 M for species in solution, with all pure substances present in their **standard states** (their most stable forms at 1 atm pressure and the temperature of the measurement). The standard heat of formation of any element in its most stable form is defined to be zero. The **standard enthalpy of reaction** (ΔH^o_{rxn}) can be calculated from the sum of the **standard enthalpies of formation** of the products (each multiplied by its stoichiometric coefficient) minus the sum of the standard enthalpies of formation of the reactants (each multiplied by its stoichiometric coefficient)—the "products minus reactants" rule. The **enthalpy of solution (ΔH_{soln})** is the heat released or absorbed when a specified amount of a solute dissolves in a certain quantity of solvent at constant pressure.

Key Takeaway

- Enthalpy is a state function whose change indicates the amount of heat transferred from a system to its surroundings or vice versa, at constant pressure.

Conceptual Problems

1. Heat implies the flow of energy from one object to another. Describe the energy flow in an

   a. exothermic reaction.

   b. endothermic reaction.

2. When a thermometer is suspended in an insulated thermos that contains a block of ice, the temperature recorded on the thermometer drops. Describe the direction of heat flow.

3. In each scenario, the system is defined as the mixture of chemical substances that undergoes a reaction. State whether each process is endothermic or exothermic.

   1. Water is added to sodium hydroxide pellets, and the flask becomes hot.
   2. The body metabolizes glucose, producing carbon dioxide and water.

3. Ammonium nitrate crystals are dissolved in water, causing the solution to become cool.

4. In each scenario, the system is defined as the mixture of chemical substances that undergoes a reaction. Determine whether each process is endothermic or exothermic.

    1. Concentrated acid is added to water in a flask, and the flask becomes warm.
    2. Water evaporates from your skin, causing you to shiver.
    3. A container of ammonium nitrate detonates.

5. Is Earth's environment an isolated system, an open system, or a closed system? Explain your answer.

6. Why is it impossible to measure the absolute magnitude of the enthalpy of an object or a compound?

7. Determine whether energy is consumed or released in each scenario. Explain your reasoning.

    1. A leaf falls from a tree.
    2. A motorboat maneuvers against a current.
    3. A child jumps rope.
    4. Dynamite detonates.
    5. A jogger sprints down a hill.

8. The chapter states that enthalpy is an extensive property. Why? Describe a situation that illustrates this fact.

9. The enthalpy of a system is affected by the physical states of the reactants and the products. Explain why.

10. Is the distance a person travels on a trip a state function? Why or why not?

11.

Contributors

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Chapter 15.4: Hess's Law

Learning Objectives

- To use Hess's law and thermochemical cycles to calculate enthalpy changes of chemical reactions.

Hess's Law

Because enthalpy is a state function, the enthalpy change for a reaction depends on *only* two things: (1) the masses of the reacting substances and (2) the physical states of the reactants and products. It does *not* depend on the path by which reactants are converted to products. If you climbed a mountain, for example, the altitude change would not depend on whether you climbed the entire way without stopping or you stopped many times to take a break. If you stopped often, the overall change in altitude would be the sum of the changes in altitude for each short stretch climbed. Similarly, when we add two or more balanced chemical equations to obtain a net chemical equation, *ΔH for the net reaction is the sum of the ΔH values for the individual reactions.* This principle is called Hess's lawThe enthalpy change ΔH for an overall reaction is the sum of the ΔH values for the individual reactions., after the Swiss-born Russian chemist Germain Hess (1802–1850), a pioneer in the study of thermochemistry. Hess's law allows us to calculate Δ*H* values for reactions that are difficult to carry out directly by adding together the known Δ*H* values for individual steps that give the overall reaction, even though the overall reaction may not actually occur via those steps.

We can illustrate Hess's law using the thermite reaction. The overall reaction shown in Equation 15.4.1 can be viewed as occurring in three distinct steps with known Δ*H* values. As shown in Figure 15.4.1, the first reaction produces 1 mol of solid aluminum oxide (Al_2O_3) and 2 mol of liquid iron at its melting point of 1758°C (part (a) in Equation 15.4.1); the enthalpy change for this reaction is −732.5 kJ/mol of Fe_2O_3. The second reaction is the conversion of 2 mol of liquid iron at 1758°C to 2 mol of solid iron at 1758°C (part (b) in Equation 15.4.1); the enthalpy change for this reaction is −13.8 kJ/mol of Fe (−27.6 kJ per 2 mol Fe). In the third reaction, 2 mol of solid iron at 1758°C is converted to 2 mol of solid iron at 25°C (part (c) in Equation 15.4.1); the enthalpy change for this reaction is −45.5 kJ/mol of Fe (−91.0 kJ per 2 mol Fe). As you can see in Figure 15.4.1, the overall reaction is given by the longest arrow (shown on the left), which is the sum of the three shorter arrows (shown on the right). Adding parts (a), (b), and (c) in Equation 15.4.1 gives the overall reaction, shown in part (d):

$$2Al\,(s,\ 25°C) + 2Fe_2O_3\,(s,\ 25°C) \rightarrow 2Fe\,(l,\ 1758°C) + 2Al\,(s,\ 1758°C) \quad \Delta H = -732.5\ kJ \quad (a)$$

$$2Fe\,(l,\ 1758°C) \rightarrow 2Fe\,(s,\ 1758°C) \quad \Delta H = -\ 27.6\ kJ \quad (b)$$

$$2Fe\,(s,\ 1758°C) + 2Al\,(s,\ 1758°C) \rightarrow 2Fe\,(l,\ 25°C) + 2Al\,(s,\ 25°C) \quad \Delta H = -\ 91.0\ kJ \quad (c)$$

$$2Al\,(s,\ 25°C) + 2Fe_2O_3\,(s,\ 25°C) \rightarrow 2Al\,(s,\ 25°C) + 2Fe_2O_3\,(s,\ 25°C) \quad \Delta H = -852.2\ kJ \quad (d)$$

By Hess's law, the enthalpy change for part (d) is the sum of the enthalpy changes for parts (a), (b), and (c). In essence, Hess's law enables us to calculate the enthalpy change for the sum of a series of reactions without having to draw a diagram like that in Figure 15.4.1.

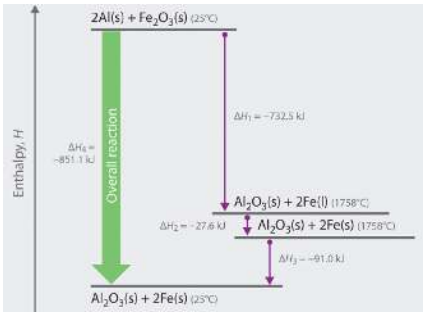


Figure 15.4.1 Energy Changes Accompanying the Thermite Reaction *Because enthalpy is a state function, the overall enthalpy change for the reaction of 2 mol of Al(s) with 1 mol of Fe_2O_3(s) is −851.1 kJ, whether the reaction occurs in a single step (ΔH_4, shown on the left) or in three hypothetical steps (shown on the right) that involve the successive formation of solid Al_2O_3 and liquid iron (ΔH_1), solid iron at 1758°C (ΔH_2), and solid iron at 25°C (ΔH_3). Thus $\Delta H_4 = \Delta H_1 + \Delta H_2 + \Delta H_3$, as stated by Hess's law.*

Comparing parts (a) and (d) in Equation 15.4.1 also illustrates an important point: *The magnitude of ΔH for a reaction depends on the physical states of the reactants and the products (gas, liquid, solid, or solution).* When the product is liquid iron at its melting point (part (a) in Equation 15.4.1), only 732.5 kJ of heat are released to the surroundings compared with 852 kJ when the product is

solid iron at 25°C (part (d) in Equation 15.4.1). The difference, 120 kJ, is the amount of energy that is released when 2 mol of liquid iron solidifies and cools to 25°C. It is important to specify the physical state of all reactants and products when writing a thermochemical equation.

When using Hess's law to calculate the value of ΔH for a reaction, follow this procedure:

1. Identify the equation whose ΔH value is unknown and write individual reactions with known ΔH values that, when added together, will give the desired equation.
2. Arrange the chemical equations so that the reaction of interest is the sum of the individual reactions.
3. If a reaction must be reversed, change the sign of ΔH for that reaction. Additionally, if a reaction must be multiplied by a factor to obtain the correct number of moles of a substance, multiply its ΔH value by that same factor.
4. Add together the individual reactions and their corresponding ΔH values to obtain the reaction of interest and the unknown ΔH.

We illustrate how to use this procedure in Example 3.

Example 15.4.1

When carbon is burned with limited amounts of oxygen gas (O_2), carbon monoxide (CO) is the main product:

$$(1)\ 2C(s) + O_2(g) \rightarrow 2CO(g) \quad \Delta H = -221.0\ kJ$$

When carbon is burned in excess O_2, carbon dioxide (CO_2) is produced:

$$(2)\ C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H = -393.5\ kJ$$

Use this information to calculate the enthalpy change per mole of CO for the reaction of CO with O_2 to give CO_2.

Given: two balanced chemical equations and their ΔH values

Asked for: enthalpy change for a third reaction

Strategy:

A After balancing the chemical equation for the overall reaction, write two equations whose ΔH values are known and that, when added together, give the equation for the overall reaction. (Reverse the direction of one or more of the equations as necessary, making sure to also reverse the sign of ΔH.)

B Multiply the equations by appropriate factors to ensure that they give the desired overall chemical equation when added together. To obtain the enthalpy change per mole of CO, write the resulting equations as a sum, along with the enthalpy change for each.

Solution:

A We begin by writing the balanced chemical equation for the reaction of interest:

$$(3)\ CO(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g) \quad \Delta H_{rxn} = ?$$

There are at least two ways to solve this problem using Hess's law and the data provided. The simplest is to write two equations that can be added together to give the desired equation and for which the enthalpy changes are known. Observing that CO, a reactant in Equation 3, is a product in Equation 1, we can reverse Equation (1) to give

$$2CO(g) \rightarrow 2C(s) + O_2(g) \quad \Delta H = +221.0\ kJ$$

Because we have reversed the direction of the reaction, the sign of ΔH is changed. We can use Equation 2 as written because its product, CO_2, is the product we want in Equation 3:

$$C(s) + O_2(g) \rightarrow CO_2(s) \quad \Delta H = -393.5\ kJ$$

B Adding these two equations together does not give the desired reaction, however, because the numbers of C(s) on the left and right sides do not cancel. According to our strategy, we can multiply the second equation by 2 to obtain 2 mol of C(s) as the reactant:

$$2C(s) + 2O_2(g) \rightarrow 2CO_2(s) \quad \Delta H = -787.0\ kJ$$

Writing the resulting equations as a sum, along with the enthalpy change for each, gives

$$2CO(g) \rightarrow \cancel{2C(s)} + \cancel{O_2(g)} \quad \Delta H = -\Delta H_1 = +221.0\ kJ$$
$$\cancel{2C(s)} + \cancel{2}O_2(g) \rightarrow 2CO_2(g) \quad \Delta H = -\Delta 2H_2 = -787.0\ kJ$$
$$2CO(g) + O_2(g) \rightarrow 2CO_2(g) \quad \Delta H = -566.0\ kJ$$

Note that the overall chemical equation and the enthalpy change for the reaction are both for the reaction of 2 mol of CO with O_2, and the problem asks for the amount *per mole of CO*. Consequently, we must divide both sides of the final equation *and the magnitude of ΔH* by 2:

$$CO(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g) \quad \Delta H = -283.0\ kJ$$

An alternative and equally valid way to solve this problem is to write the two given equations as occurring in steps. Note that we have multiplied the equations by the appropriate factors to allow us to cancel terms:

$$(A)\ 2C(s) + O_2(g) \rightarrow \cancel{2CO(g)} \quad \Delta H_A = \Delta H_1 = +221.0\ kJ$$
$$(B)\ \cancel{2CO(g)} + O_2(g) \rightarrow 2CO_2(g) \quad \Delta H_B = ?$$
$$(C)\ 2C(s) + 2O_2(g) \rightarrow 2CO_2(g) \quad \Delta H = 2\Delta H_2 = 2 \times (-393.5\ kJ) = -787.0\ kJ$$

The sum of reactions A and B is reaction C, which corresponds to the combustion of 2 mol of carbon to give CO_2. From Hess's law, $\Delta H_A + \Delta H_B = \Delta H_C$, and we are given ΔH for reactions A and C. Substituting the appropriate values gives

$$-221.0\ kJ + \Delta H_B = -787.0\ kJ$$
$$\Delta H_B = -566.0$$

This is again the enthalpy change for the conversion of 2 mol of CO to CO_2. The enthalpy change for the conversion of 1 mol of CO to CO_2 is therefore −566.0 ÷ 2 = −283.0 kJ/mol of CO, which is the same result we obtained earlier. As you can see, *there may be more than one correct way to solve a problem*.

Exercise

The reaction of acetylene (C_2H_2) with hydrogen (H_2) can produce either ethylene (C_2H_4) or ethane (C_2H_6):

$$C_2H_2(g) + H_2(g) \rightarrow C_2H_4(g) \quad \Delta H = -175.7\ kJ/mol\ C_2H_2$$
$$C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g) \quad \Delta H = -312.0\ kJ/mol\ C_2H_2$$

What is ΔH for the reaction of C_2H_4 with H_2 to form C_2H_6?

Answer: −136.3 kJ/mol of C_2H_4

Enthalpies of Reaction

Chapter 11 and Chapter 12 presented a wide variety of chemical reactions, and you learned how to write balanced chemical equations that include all the reactants and the products except heat. One way to report the heat absorbed or released would be to compile a massive set of reference tables that list the enthalpy changes for all possible chemical reactions, which would require an incredible amount of effort. Fortunately, Hess's law allows us to calculate the enthalpy change for virtually any conceivable chemical reaction using a relatively small set of tabulated data, such as the following:

- Enthalpy of combustion (ΔH_{comb})The change in enthalpy that occurs during a combustion reaction.: Enthalpy changes have been measured for the combustion of virtually any substance that will burn in oxygen; these values are usually reported as the enthalpy of combustion per mole of substance.
- Enthalpy of fusion (ΔH_{fus})The enthalpy change that acompanies the melting (fusion) of 1 mol of a substance.: The enthalpy change that accompanies the melting, or *fusion*, of 1 mol of a substance; these values have been measured for almost all the elements and for most simple compounds.
- Enthalpy of vaporization (ΔH_{vap})The enthalpy change that accompanies the vaporization of 1 mol of a substance.: The enthalpy change that accompanies the vaporization of 1 mol of a substance; these values have also been measured for nearly all the elements and for most volatile compounds.
- Enthalpy of solution (ΔH_{soln})The change in enthalpy that occurs when a specified amount of solute dissolves in a given quantity of solvent.: The enthalpy change when a specified amount of solute dissolves in a given quantity of solvent.

Table 15.4.1 Enthalpies of Vaporization and Fusion for Selected Substances at Their Boiling Points and Melting Points

Substance	ΔH_{vap} (kJ/mol)	ΔH_{fus} (kJ/mol)
argon (Ar)	6.3	1.3
methane (CH_4)	9.2	0.84
ethanol (CH_3CH_2OH)	39.3	7.6
benzene (C_6H_6)	31.0	10.9
water (H_2O)	40.7	6.0
mercury (Hg)	59.0	2.29
iron (Fe)	340	14

Note the Pattern

The sign convention is the same for all enthalpy changes: negative if heat is released by the system and positive if heat is absorbed by the system.

Summary

For a chemical reaction, the **enthalpy of reaction (ΔH_{rxn})** is the difference in enthalpy between products and reactants; the units of ΔH_{rxn} are kilojoules per mole. Reversing a chemical reaction reverses the sign of ΔH_{rxn}. The magnitude of ΔH_{rxn} also depends on the physical state of the reactants and the products because processes such as melting solids or vaporizing liquids are also accompanied by enthalpy changes: the **enthalpy of fusion (ΔH_{fus})** and the **enthalpy of vaporization (ΔH_{vap})**, respectively. The overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions, which is **Hess's law**. The **enthalpy of combustion (ΔH_{comb})** is the enthalpy change that occurs when a substance is burned in excess oxygen.

Key Takeaway

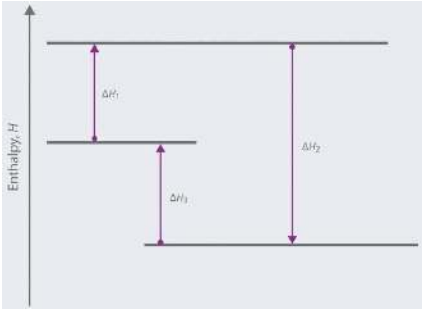
- Hess's law: The overall enthalpy change for a series of reactions is the sum of the enthalpy changes for the individual reactions:

Conceptual Problems

1. Based on the following energy diagram,

   a. write an equation showing how the value of ΔH_2 could be determined if the values of ΔH_1 and ΔH_3 are known.

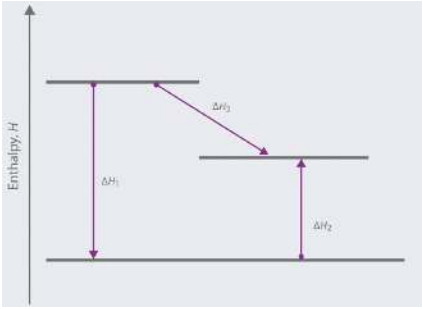
   b; identify each step as being exothermic or endothermic.



2. Based on the following energy diagram,

   a. write an equation showing how the value of ΔH_3 could be determined if the values of ΔH_1 and ΔH_2 are known.

   b. identify each step as being exothermic or endothermic.



3. Describe how Hess's law can be used to calculate the enthalpy change of a reaction that cannot be observed directly.
4. When you apply Hess's law, what enthalpy values do you need to account for each change in physical state?
    1. the melting of a solid
    2. the conversion of a gas to a liquid
    3. the solidification of a liquid
    4. the dissolution of a solid into water
5. In their elemental form, A_2 and B_2 exist as diatomic molecules. Given the following reactions, each with an associated $\Delta H°$, describe how you would calculate ΔH^o_f for the compound AB_2.

$$\begin{array}{lcll} 2AB & \rightarrow & A_2 + B_2 & \Delta H_1^o \\ 3AB & \rightarrow & AB_2 + A_2B & \Delta H_2^o \\ 2A_2B & \rightarrow & 2A_2 + B_2 & \Delta H_3^o \end{array}$$

Numerical Problems

1. Methanol is used as a fuel in Indianapolis 500 race cars. Use the following table to determine whether methanol or 2,2,4-trimethylpentane (isooctane) releases more energy per liter during combustion.

Fuel	$\Delta H^o_{combustion}$(kJ/mol)	Density (g/mL)
methanol	−726.1	0.791
2,2,4-trimethylpentane	−5461.4	0.692

2. a. Use the enthalpies of combustion given in the following table to determine which organic compound releases the greatest amount of energy per gram during combustion.

Fuel	$\Delta H^o_{combustion}$(kJ/mol)
methanol	−726.1
1-ethyl-2-methylbenzene	−5210.2
n-octane	−5470.5

    b. Calculate the standard enthalpy of formation of 1-ethyl-2-methylbenzene.
3. Given the enthalpies of combustion, which organic compound is the best fuel per gram?

Fuel	ΔH^o_f(kJ/mol)
ethanol	−1366.8
benzene	−3267.6
cyclooctane	−5434.7

Answers

1.

2.

a. To one decimal place

methanol: ΔH/g = −22.6 kJ

C_9H_{12}: ΔH/g = −43.3 kJ

octane: ΔH/g = −47.9 kJ

Octane provides the largest amount of heat per gram upon combustion.

b, $\Delta H_f(C_9H_{17})$ = −46.1 kJ/mol

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Chapter 15.5: Heats of Formation

Learning Objectives

- To understand Enthalpies of Formation and be able to use them to calculated Enthalpies of Reaction

Enthalpies of Formation

Chapter 11 and Chapter 12 presented a wide variety of chemical reactions, and you learned how to write balanced chemical equations that include all the reactants and the products except heat. One way to report the heat absorbed or released would be to compile a massive set of reference tables that list the enthalpy changes for all possible chemical reactions, which would require an incredible amount of effort. Fortunately, Hess's law allows us to calculate the enthalpy change for virtually any conceivable chemical reaction using a relatively small set of tabulated data starting from the elemental forms of each atom at 25 °C and 1 atm pressure.

- Enthalpy of formation (ΔH_f)The enthalpy change for the formation of 1 mol of a compound from its component elements.: The enthalpy change for the formation of 1 mol of a compound from its component elements, such as the formation of carbon dioxide from carbon and oxygen. The corresponding relationship is

  $$elements \rightarrow compound \quad \Delta H_{rxn} = \Delta H_f$$

  For example,

  $$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H_{rxn} = \Delta H_f[CO_2(g)]$$

  The sign convention for ΔH_f is the same as for any enthalpy change: $\Delta H_f < 0$ if heat is released when elements combine to form a compound and $\Delta H_f > 0$ if heat is absorbed.

Note the Pattern

The sign convention is the same for all enthalpy changes: negative if heat is released by the system and positive if heat is absorbed by the system.

Standard Enthalpies of Formation

The magnitude of ΔH for a reaction depends on the physical states of the reactants and the products (gas, liquid, solid, or solution), the pressure of any gases present, and the temperature at which the reaction is carried out. To avoid confusion caused by differences in reaction conditions and ensure uniformity of data, the scientific community has selected a specific set of conditions under which enthalpy changes are measured. These standard conditions serve as a reference point for measuring differences in enthalpy, much as sea level is the reference point for measuring the height of a mountain or for reporting the altitude of an airplane.

The standard conditionsThe conditions under which most thermochemical data are tabulated: 1 atm for all gases and a concentration of 1.0 M for all species in solution. for which most thermochemical data are tabulated are a *pressure* of 1 atmosphere (atm) for all gases and a *concentration* of 1 M for all species in solution (1 mol/L). In addition, each pure substance must be in its standard stateThe most stable form of a pure substance at a pressure of 1 atm at a specified temperature.. This is usually its most stable form at a pressure of 1 atm at a specified temperature. We assume a temperature of 25°C (298 K) for all enthalpy changes given in this text, unless otherwise indicated. Enthalpies of formation measured under these conditions are called standard enthalpies of formation (ΔH^o_f)The enthalpy change for the formation of 1 mol of a compound from its component elements when the component elements are each in their standard states. The standard enthalpy of formation of any element in its most stable form is zero by definition. (which is pronounced "delta H eff naught"). *The standard enthalpy of formation of any element in its standard state is zero by definition*. For example, although oxygen can exist as ozone (O_3), atomic oxygen (O), and molecular oxygen (O_2), O_2 is the most stable form at 1 atm pressure and 25°C. Similarly, hydrogen is H_2(g), not atomic hydrogen (H). Graphite and diamond are both forms of elemental carbon, but because graphite is more stable at 1 atm pressure and 25°C, the standard state of carbon is graphite (Figure 15.5.1). Therefore, O_2(g), H_2(g), and graphite have ΔH^o_f values of zero.



Figure 15.5.1 Elemental Carbon *Although graphite and diamond are both forms of elemental carbon, graphite is more stable at 1 atm pressure and 25°C than diamond is. Given enough time, diamond will revert to graphite under these conditions. Hence graphite is the standard state of carbon.*

The standard enthalpy of formation of glucose from the elements at 25°C is the enthalpy change for the following reaction:

$$6C\,(s, graphite) + 6H_2\,(g) + 3O_2\,(g) \rightarrow C_6H_{12}O_6\,(s) \quad \Delta H_f^o = -1273.3\ kJ$$

It is not possible to measure the value of ΔH^o_f for glucose, −1273.3 kJ/mol, by simply mixing appropriate amounts of graphite, O_2, and H_2 and measuring the heat evolved as glucose is formed; the reaction shown in Equation 15.5.2 does not occur at a measurable rate under any known conditions. Glucose is not unique; most compounds cannot be prepared by the chemical equations that define their standard enthalpies of formation. Instead, values of are obtained using Hess's law and standard enthalpy changes that have been measured for other reactions, such as combustion reactions. Values of ΔH^o_f for an extensive list of compounds are given in the Reference Tables. Note that ΔH^o_f values are always reported in kilojoules per mole of the substance of interest. Also notice in the Reference Tables that the standard enthalpy of formation of O_2(g) is zero because it is the most stable form of oxygen in its standard state.

Example 15.5.1

For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.

1. HCl(g)
2. $MgCO_3$(s)
3. $CH_3(CH_2)_{14}CO_2H$(s) (palmitic acid)

Given: compound

Asked for: balanced chemical equation for its formation from elements in standard states

Strategy:

Use the Reference Tables to identify the standard state for each element. Write a chemical equation that describes the formation of the compound from the elements in their standard states and then balance it so that 1 mol of product is made.

Solution:

To calculate the standard enthalpy of formation of a compound, we must start with the elements in their standard states. The standard state of an element can be identified in the Reference Tables by a ΔH^o_f value of 0 kJ/mol.

1. Hydrogen chloride contains one atom of hydrogen and one atom of chlorine. Because the standard states of elemental hydrogen and elemental chlorine are $H_2(g)$ and $Cl_2(g)$, respectively, the unbalanced chemical equation is

   $H_2(g) + Cl_2(g) \rightarrow HCl(g)$

   Fractional coefficients are required in this case because ΔH^o_f values are reported for *1 mol* of the product, HCl. Multiplying both $H_2(g)$ and $Cl_2(g)$ by 1/2 balances the equation:

   $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g)$\rightarrow HCl\left (g \right) \)
2. The standard states of the elements in this compound are Mg(s), C(s, graphite), and $O_2(g)$. The unbalanced chemical equation is thus

   $Mg(s) + C(s, graphite) + O_2(g) \rightarrow MgCO_3(s)$

   This equation can be balanced by inspection to give

   $Mg(g) + C(s, graphite) \frac{3}{2}O_2(g) \rightarrow MgCO_3(s)$
3. Palmitic acid, the major fat in meat and dairy products, contains hydrogen, carbon, and oxygen, so the unbalanced chemical equation for its formation from the elements in their standard states is as follows:

   $C(s, graphite) + H_2(g) + O_2(g) \rightarrow CH_3(CH_2)_{14}CO_2H(s)$

   There are 16 carbon atoms and 32 hydrogen atoms in 1 mol of palmitic acid, so the balanced chemical equation is

   $16C(s, graphite) + 16H_2(g) + O_2(g) \rightarrow CH_3(CH_2)_{14}CO_2H(s)$

Exercise

For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.

1. NaCl(s)
2. $H_2SO_4(l)$
3. $CH_3CO_2H(l)$ (acetic acid)

Answer:

1. $Na(g) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s)$
2. $H_2(g) + \frac{1}{8}S_8(s) + 2O_2(g) \rightarrow H_2SO_4(l)$
3. $2C(s) + O_2(g) + 2H_2(g) \rightarrow CH_3CO_2H(l)$

Standard Enthalpies of Reaction

Tabulated values of standard enthalpies of formation can be used to calculate enthalpy changes for *any* reaction involving substances whose ΔH_f^o values are known. The standard enthalpy of reaction (ΔH_{rxn})The enthalpy change that occurs when a reaction is carried out with all reactants and products in their standard state. is the enthalpy change that occurs when a reaction is carried out with all reactants and products in their standard states. Consider the general reaction

$$aA + bB \rightarrow cC + dD$$

where A, B, C, and D are chemical substances and *a*, *b*, *c*, and *d* are their stoichiometric coefficients. The magnitude of ΔH^o is the sum of the standard enthalpies of formation of the products, each multiplied by its appropriate coefficient, minus the sum of the standard enthalpies of formation of the reactants, also multiplied by their coefficients:

$$\Delta H^o_{rxn} = \underbrace{\left[c\Delta H^o_f(C) + d\Delta H^o_f(D)\right]}_{reactants} - \underbrace{\left[a\Delta H^o_f(A) + b\Delta H^o_f(B)\right]}_{products}$$

More generally, we can write

$$\Delta H^o_{rxn} = \sum m\Delta H^o_f(products) - \sum n\Delta H^o_f(reactants)$$

where the symbol Σ means "sum of" and *m* and *n* are the stoichiometric coefficients of each of the products and the reactants, respectively. "Products minus reactants" summations such as Equation 15.5.5 arise from the fact that enthalpy is a state function. Because many other thermochemical quantities are also state functions, "products minus reactants" summations are very common in chemistry; we will encounter many others in subsequent chapters.

Note the Pattern

Products minus reactants" summations are typical of state functions.

To demonstrate the use of tabulated ΔH^o values, we will use them to calculate ΔH_{rxn} for the combustion of glucose, the reaction that provides energy for your brain:

$$C_6H_{12}O_6(s) + O_2(g) \rightarrow CO_2(g) + 6H_2O(l)$$

Using Equation 15.5.5, we write

$$\Delta H^o_f = \left\{6\Delta H^o_f[CO_2(g)] + 6\Delta H^o_f[H_2O(g)]\right\} - \left\{6\Delta H^o_f[C_6H_{12}O_6(s)] + 6\Delta H^o_f[O_2(g)]\right\}$$

From the Reference Tables, the relevant ΔH^o_f values are $\Delta H^o_f[CO_2(g)]$ = -393.5 kJ/mol, $\Delta H^o_f[H_2O(l)]$ = -285.8 kJ/mol, and $\Delta H^o_f[C_6H_{12}O_6(s)]$ = -1273.3 kJ/mol. Because $O_2(g)$ is a pure element in its standard state, $\Delta H^o_f[O_2(g)]$ = 0 kJ/mol. Inserting these values into Equation 15.5.7 and changing the subscript to indicate that this is a combustion reaction, we obtain

$$\Delta H^o_{comb} = [6(-393.5\ kJ/mol) + 6(-285.8\ kJ/mol)] - [-1273.3 + 6(0\ kJ/mol)] = -2802.5\ kJ/mol$$

As illustrated in Figure 15.5.2 , we can use Equation 15.5.8 to calculate ΔH^o_f for glucose because enthalpy is a state function. The figure shows two pathways from reactants (middle left) to products (bottom). The more direct pathway is the downward green arrow labeled ΔH^o_{comb} The alternative hypothetical pathway consists of four separate reactions that convert the reactants *to the elements* in their standard states (upward purple arrow at left) and then convert the elements into the desired products (downward purple arrows at right). The reactions that convert the reactants to the elements are the reverse of the equations that define the ΔH^o_f values of the reactants. Consequently, the enthalpy changes are

$$\Delta H^o_1 = \Delta H^o_f[glucose(s)] = -1\ \cancel{mol\ glucose}\left(\frac{1273.3\ kJ}{1\ \cancel{mol\ glucose}}\right) = +1273.3\ kJ$$

$$\Delta H^o_2 = 6\Delta H^o_f[O_2(g)] = 6\ \cancel{mol\ O_2}\left(\frac{0\ kJ}{1\ \cancel{mol\ O_2}}\right) = 0\ kJ$$

(Recall that when we reverse a reaction, we must also reverse the sign of the accompanying enthalpy change.) The overall enthalpy change for conversion of the reactants (1 mol of glucose and 6 mol of O_2) to the elements is therefore +1273.3 kJ.

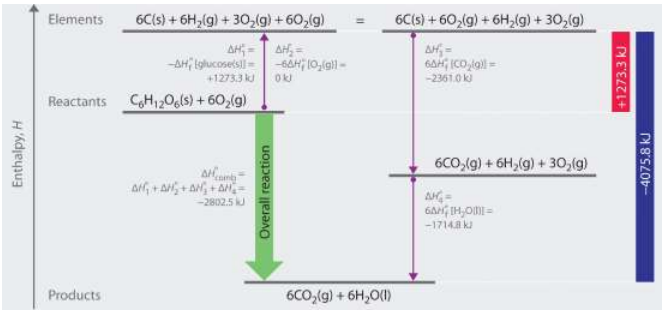


Figure 15.5.2 A Thermochemical Cycle for the Combustion of Glucose Two hypothetical pathways are shown from the reactants to the products. The green arrow labeled ΔH^o_{comb} indicates the combustion reaction. Alternatively, we could first convert the reactants to the elements via the reverse of the equations that define their standard enthalpies of formation (the upward arrow, labeled ΔH^o_1 and ΔH^o_2). Then we could convert the elements to the products via the equations used to define their standard

enthalpies of formation (the downward arrows, labeled ΔH^o_3 and ΔH^o_4). Because enthalpy is a state function, ΔH^o_{comb} is equal to the sum of the enthalpy changes $\Delta H^o_1 + \Delta H^o_2 + \Delta H^o_3 + \Delta H^o_4$.

The reactions that convert the elements to final products (downward purple arrows in Figure 15.5.2) are identical to those used to define the ΔH^o_f values of the products. Consequently, the enthalpy changes (from the Reference Tables) are

$$\Delta H^o_3 = \Delta H^o_f\left[CO_2\left(g\right)\right] = 6\ \cancel{mol\ CO_2}\left(\frac{393.5\ kJ}{1\ \cancel{mol\ CO_2}}\right) = -2361.0\ kJ$$

$$\Delta H^o_4 = 6\Delta H^o_f\left[H_2O\left(l\right)\right] = 6\ \cancel{mol\ H_2O}\left(\frac{-285.8\ kJ}{1\ \cancel{mol\ H_2O}}\right) = -1714.8\ kJ$$

The overall enthalpy change for the conversion of the elements to products (6 mol of carbon dioxide and 6 mol of liquid water) is therefore −4075.8 kJ. Because enthalpy is a state function, the difference in enthalpy between an initial state and a final state can be computed using *any* pathway that connects the two. Thus the enthalpy change for the combustion of glucose to carbon dioxide and water is the sum of the enthalpy changes for the conversion of glucose and oxygen to the elements (+1273.3 kJ) and for the conversion of the elements to carbon dioxide and water (−4075.8 kJ):

$$\Delta H^o_{comb} = +1273.3\ kJ + \left(-4075.8\ kJ\right) = -2802.5\ kJ$$

This is the same result we obtained using the "products minus reactants" rule and ΔH^o_f values. The two results must be the same because Equation 15.5.10 is just a more compact way of describing the thermochemical cycle shown in Figure 15.5.2.

Example 15.5.2

Long-chain fatty acids such as palmitic acid [$CH_3(CH_2)_{14}CO_2H$] are one of the two major sources of energy in our diet ($\Delta H^o f$ =−891.5 kJ/mol). Use the data in the Reference Table to calculate ΔH^o_{comb} for the combustion of palmitic acid. Based on the energy released in combustion *per gram*, which is the better fuel — glucose or palmitic acid?

Given: compound and $\Delta H^o f$ values

Asked for: ΔH^o_{comb} per mole and per gram

Strategy:

A After writing the balanced chemical equation for the reaction, use Equation 15.5.5 and the values from the Reference Table to calculate ΔH^o_{comb} the energy released by the combustion of 1 mol of palmitic acid.

B Divide this value by the molar mass of palmitic acid to find the energy released from the combustion of 1 g of palmitic acid. Compare this value with the value calculated in Equation 15.5.8 for the combustion of glucose to determine which is the better fuel.

Solution:

A To determine the energy released by the combustion of palmitic acid, we need to calculate its ΔH^o_f As always, the first requirement is a balanced chemical equation:

$$C_{16}H_{32}O_2(s) + 23O_2(g) \rightarrow 16CO_2(g) + 16H_2O(l)$$

Using Equation 15.5.5 ("products minus reactants") with ΔH^o_f values from the Reference Table (and omitting the physical states of the reactants and products to save space) gives

$$\Delta H^o_{comb} = \sum m\Delta H^o{}_f\left(products\right) - \sum n\Delta H^o{}_f\left(reactants\right)$$

$$= \left[16\left(-393.5\ kJ/mol\ CO_2\right) + 16\left(-285.8\ kJ/mol\ H_2O\right)\right]$$

$$-\left[-891.5\ kJ/mol\ C_{16}H_{32}O_2 + 23\left(0\ kJ/mol\ O_2\right)\right]$$

$$= -9977.3\ kJ/mol$$

This is the energy released by the combustion of 1 mol of palmitic acid.

B The energy released by the combustion of 1 g of palmitic acid is

$$\Delta H^o_{comb}\ per\ gram = \left(\frac{9977.3\ kJ}{\cancel{1\ mol}}\right)\left(\frac{\cancel{1\ mol}}{256.42\ g}\right) = -38.910\ kJ/g$$

As calculated in Equation 15.5.8, $\Delta H^{o}f$ of glucose is −2802.5 kJ/mol. The energy released by the combustion of 1 g of glucose is therefore

$$\Delta H^{o}_{comb} \text{ per gram} = \left(\frac{-2802.5\ kJ}{\cancel{1\ mol}}\right)\left(\frac{\cancel{1\ mol}}{180.16\ g}\right) = -15.556\ kJ/g$$

The combustion of fats such as palmitic acid releases more than twice as much energy per gram as the combustion of sugars such as glucose. This is one reason many people try to minimize the fat content in their diets to lose weight.

Exercise

Use the data in the Reference Tables to calculate ΔH^{o}_{rxn} for the *water–gas shift reaction*, which is used industrially on an enormous scale to obtain $H_2(g)$:

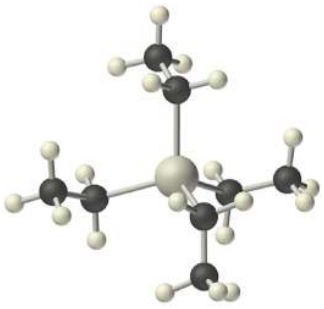
$$\underset{water-gas\ shift\ reaction}{CO\,(g) + H_2O\,(g) \rightarrow CO_2\,(g) + H_2\,(g)}$$

Answer: −41.2 kJ/mol

We can also measure the enthalpy change for another reaction, such as a combustion reaction, and then use it to calculate a compound's $\Delta H^{o}f$ which we cannot obtain otherwise. This procedure is illustrated in Example 3.

Example 15.5.3

Beginning in 1923, tetraethyllead [$(C_2H_5)_4Pb$] was used as an antiknock additive in gasoline in the United States. Its use was completely phased out in 1986 because of the health risks associated with chronic lead exposure. Tetraethyllead is a highly poisonous, colorless liquid that burns in air to give an orange flame with a green halo. The combustion products are $CO_2(g)$, $H_2O(l)$, and red PbO(s). What is the standard enthalpy of formation of tetraethyllead, given that $\Delta H^{o}f$ is −19.29 kJ/g for the combustion of tetraethyllead and $\Delta H^{o}f$ of red PbO(s) is −219.0 kJ/mol?



Tetraethyllead

Given: reactant, products, and ΔH^{o}_{comb} values

Asked for: ΔH^{o}_{f} of the reactants

Strategy:

A Write the balanced chemical equation for the combustion of tetraethyl lead. Then insert the appropriate quantities into Equation 5.27 to get the equation for ΔH^{o}_{f} of tetraethyl lead.

B Convert ΔH^{o}_{comb} per gram given in the problem to ΔH^{o}_{comb} per mole by multiplying ΔH^{o}_{comb} per gram by the molar mass of tetraethyllead.

C Use the Reference Table to obtain values of ΔH^{o}_{f} for the other reactants and products. Insert these values into the equation for ΔH^{o}_{f} of tetraethyl lead and solve the equation.

Solution:

A The balanced chemical equation for the combustion reaction is as follows:

$$2(C_2H_5)_4Pb(l) + 27O_2(g) \rightarrow 2PbO(s) + 16CO_2(g) + 20H_2O(l)$$

Using Equation 15.5.5 gives

$$\Delta H^o_{comb} = \left[2\Delta H^o_f\,(PbO) + 16\Delta H^o_f\,(CO_2) + 20\Delta H^o_f\,(H_2O)\right] - \left[2\Delta H^o_f\,((C_2H_5)_4\,Pb) + 27\Delta H^o_f\,(O_2)\right]$$

Solving for $\Delta H^o_f\,[(C_2H_5)4Pb]$ gives

$$\Delta H^o_f\,((C_2H_5)_4\,Pb) = \Delta H^o_f\,(PbO) + 8\Delta H^o_f\,(CO_2) + 10\Delta H^o_f\,(H_2O) - \tfrac{27}{2}\Delta H^o_f\,(O_2) - \tfrac{\Delta H^o_{comb}}{2}$$

The values of all terms other than $\Delta H^o_f\,[(C_2H_5)4Pb]$ are given in the Reference Table

B The magnitude of ΔH^o_{comb} is given in the problem in kilojoules per *gram* of tetraethyl lead. We must therefore multiply this value by the molar mass of tetraethyl lead (323.44 g/mol) to get ΔH^o_{comb} for 1 mol of tetraethyl lead:

$$\Delta H^o_{comb} = \left(\frac{-1929\ kJ}{\cancel{g}}\right)\left(\frac{323.44\ \cancel{g}}{mol}\right) = -6329\ kJ/mol$$

Because the balanced chemical equation contains 2 mol of tetraethyllead, ΔH^o_{rxn} is

$$\Delta H^o_{rxn} = 2\ \cancel{mol\ (C_2H5)_4\,Pb}\left(\frac{-6929\ kJ}{1\ \cancel{mol\ (C_2H5)_4\,Pb}}\right) = -12,480\ kJ$$

C Inserting the appropriate values into the equation for $\Delta H^o_f\,[(C_2H_5)4Pb]$ gives

$$\begin{aligned}\Delta H^o_f\,[(C_2H_4)_4\,Pb] &= [1\ mol\ PbO\ \times 219.0\ kJ/mol] + [8\ mol\ CO_2 \times (-393.5\ kJ/mol)] \\ &\quad + [10\ mol\ H_2O \times (-285.8\ kJ/mol)] + [-27/2\ mol\ O_2) \times 0\ kJ/mol\ O_2] \\ &\quad [12,480.2\ kJ/mol\ \ (C_2H_5)_4\,Pb] \\ &= -219.0\ kJ - 3148\ kJ - 2858kJ - 0kJ + 6240\ kJ = 15kJ/mol\end{aligned}$$

Exercise

Ammonium sulfate $[(NH_4)_2SO_4]$ is used as a fire retardant and wood preservative; it is prepared industrially by the highly exothermic reaction of gaseous ammonia with sulfuric acid:

$2NH_3(g) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(s)$

The value of ΔH^o_{rxn} is −2805 kJ/g H_2SO_4. Use the data in Appendix A to calculate the standard enthalpy of formation of ammonium sulfate (in kilojoules per mole).

Answer: −1181 kJ/mol

Key Equations

relationship between ΔH^o_{rxn} and ΔH^o_f

Equation 15.5.5: $\Delta H^o_{rxn} = \Sigma\Delta H^o_f(\text{products}) - \Delta H^o_f(\text{reactants})$

Summary

The **enthalpy of formation (ΔH_f)** is the enthalpy change that accompanies the formation of a compound from its elements. **Standard enthalpies of formation** (ΔH^o_f) are determined under **standard conditions**: a pressure of 1 atm for gases and a concentration of 1 M for species in solution, with all pure substances present in their **standard states** (their most stable forms at 1 atm pressure and the temperature of the measurement). The standard heat of formation of any element in its most stable form is defined to be zero. The **standard enthalpy of reaction** (ΔH^o_{rxn}) can be calculated from the sum of the **standard enthalpies of formation** of the products (each multiplied by its stoichiometric coefficient) minus the sum of the standard enthalpies of formation of the reactants (each multiplied by its stoichiometric coefficient)—the "products minus reactants" rule. The **enthalpy of solution (ΔH_{soln})** is the heat released or absorbed when a specified amount of a solute dissolves in a certain quantity of solvent at constant pressure.

Key Takeaways

- The standard state for measuring and reporting enthalpies of formation or reaction is 25 °C and 1 atm.
- The elemental form of each atom is that with the lowest enthalpy in the standard state.
- The standard state heat of formation for the elemental form of each atom is zero.

Conceptual Problems

1. Describe how Hess's law can be used to calculate the enthalpy change of a reaction that cannot be observed directly.
2. When you apply Hess's law, what enthalpy values do you need to account for each change in physical state?
3. What is the difference between ΔH^o_f and ΔH_f?
4. How can ΔH^o_f of a compound be determined if the compound cannot be prepared by the reactions used to define its standard enthalpy of formation?
5. For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.

   a. HBr

   b. CH_3OH

   c. $NaHCO_3$
6. Describe the distinction between ΔH_{soln} and ΔH_f.
7. The following table lists ΔH^o_{soln} values for some ionic compounds. If 1 mol of each solute is dissolved in 500 mL of water, rank the resulting solutions from warmest to coldest.

Compound	ΔH^o_{soln}(kJ/mol)
KOH	−57.61
$LiNO_3$	−2.51
$KMnO_4$	43.56
$NaC_2H_3O_2$	−17.32

Numerical Problems

1. Using "Appendix A, calculate ΔH^o_{rxn} for each chemical reaction.

   a. $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$

   b. $CaCO_3(s, \text{calcite}) \rightarrow CaO(s) + CO_2(g)$

   c. $AgNO_3(s) + NaCl(s) \rightarrow AgCl(s) + NaNO_3(s)$
2. Using "Appendix A, determine ΔH^o_{rxn} for each chemical reaction.

   a. $2Na(s) + Pb(NO_3)_2(s) \rightarrow 2NaNO_3(s) + Pb(s)$

   b. $Na_2CO_3(s) + H_2SO_4(l) \rightarrow Na_2SO_4(s) + CO_2(g) + H_2O(l)$

   c. $2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$
3. Calculate ΔH^o_{rxn} for each chemical equation. If necessary, balance the chemical equations.

   a. $Fe(s) + CuCl_2(s) \rightarrow FeCl_2(s) + Cu(s)$

   b. $(NH_4)_2SO_4(s) + Ca(OH)_2(s) \rightarrow CaSO_4(s) + NH_3(g) + H_2O(l)$

   c. $Pb(s) + PbO_2(s) + H_2SO_4(l) \rightarrow PbSO_4(s) + H_2O(l)$
4. Calculate ΔH^o_{rxn} for each reaction. If necessary, balance the chemical equations.

   a. $4HBr(g) + O_2(g) \rightarrow 2H_2O(l) + 2Br_2(l)$

   b. $2KBr(s) + H_2SO_4(l) \rightarrow K_2SO_4(s) + 2HBr(g)$

   c. $4Zn(s) + 9HNO_3(l) \rightarrow 4Zn(NO_3)_2(s) + NH_3(g) + 3H_2O(l)$

5. Use the data in "Appendix A to calculate ΔH^o_f for the reaction Sn(s, white) + $4HNO_3(l) \rightarrow SnO_2(s) + 4NO_2(g) + 2H_2O(l)$.
6. Use the data in "Appendix A to calculate ΔH^o_f for the reaction $P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(l)$.
7. How much heat is released or required in the reaction of 0.50 mol of HBr(g) with 1.0 mol of chlorine gas to produce bromine gas?
8. How much energy is released or consumed if 10.0 g of N_2O_5 is completely decomposed to produce gaseous nitrogen dioxide and oxygen?
9. In the mid-1700s, a method was devised for preparing chlorine gas from the following reaction:

   $NaCl(s) + H_2SO_4(l) + MnO_2(s) \rightarrow Na_2SO_4(s) + MnCl_2(s) + H_2O(l) + Cl_2(g)$

   Calculate ΔH^o_{rxn} for this reaction. Is the reaction exothermic or endothermic?
10. Would you expect heat to be evolved during each reaction?
    1. solid sodium oxide with gaseous sulfur dioxide to give solid sodium sulfite
    2. solid aluminum chloride reacting with water to give solid aluminum oxide and hydrogen chloride gas
11. How much heat is released in preparing an aqueous solution containing 6.3 g of calcium chloride, an aqueous solution containing 2.9 g of potassium carbonate, and then when the two solutions are mixed together to produce potassium chloride and calcium carbonate?
12.

Answers

1. a. −1203 kJ/mol O_2

   b. 179.2 kJ

   c. −59.3 kJ
2.
3.
4.
5. −174.1 kJ/mol
6.
7. −20.3 kJ
8.
9. −34.3 kJ/mol Cl_2; exothermic
10.
11. ΔH = −2.86 kJ $CaCl_2$: −4.6 kJ; K_2CO_3, −0.65 kJ; mixing, −0.28 kJ

Contributors

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Chapter 15.6: Enthalpies of Solution

Learning Objectives

- To understand Enthalpies of Solution and be able to use them to calculate the Heat absorbed or emitted when making solutions.

Enthalpies of Solution and Dilution

Physical changes, such as melting or vaporization, and chemical reactions, in which one substance is converted to another, are accompanied by changes in enthalpy. Two other kinds of changes that are accompanied by changes in enthalpy are the dissolution of solids and the dilution of concentrated solutions.

The dissolution of a solid can be described as follows:

$$solute\,(s) + solvent\,(l) \rightarrow soulution\,(l)$$

The values of ΔH_{soln} for some common substances are given in Table 15.6.1 . The sign and the magnitude of ΔH_{soln} depend on specific attractive and repulsive interactions between the solute and the solvent; these factors were discussed in Chapter 12. When substances dissolve, the process can be either exothermic ($\Delta H_{soln} < 0$) or endothermic ($\Delta H_{soln} > 0$), as you can see from the data in Table 15.6.1.

Table 15.6.1 Enthalpies of Solution at 25°C of Selected Ionic Compounds in Water (in kJ/mol)

	Anion				
Cation	Fluoride	Chloride	Bromide	Iodide	Hydroxide
lithium	4.7	−37.0	−48.8	−63.3	−23.6
sodium	0.9	3.9	−0.6	−7.5	−44.5
potassium	−17.7	17.2	19.9	20.3	−57.6
ammonium	−1.2	14.8	16.8	13.7	—
silver	−22.5	65.5	84.4	112.2	—
magnesium	−17.7	−160.0	−185.6	−213.2	2.3
calcium	11.5	−81.3	−103.1	−119.7	−16.7
	Nitrate	Acetate	Carbonate	Sulfate	
lithium	−2.5	—	−18.2	−29.8	
sodium	20.5	−17.3	−26.7	2.4	
potassium	34.9	−15.3	−30.9	23.8	
ammonium	25.7	−2.4	—	6.6	
silver	22.6	—	22.6	17.8	
magnesium	−90.9	—	−25.3	−91.2	
calcium	−19.2	—	−13.1	−18.0	

Substances with large positive or negative enthalpies of solution have commercial applications as instant cold or hot packs. Single-use versions of these products are based on the dissolution of either calcium chloride ($CaCl_2$, ΔH_{soln} = −81.3 kJ/mol) or ammonium nitrate (NH_4NO_3, ΔH_{soln} = +25.7 kJ/mol). Both types consist of a plastic bag that contains about 100 mL of water plus a dry chemical (40 g of $CaCl_2$ or 30 g of NH_4NO_3) in a separate plastic pouch. When the pack is twisted or struck sharply, the inner plastic bag of water ruptures, and the salt dissolves in the water. If the salt is $CaCl_2$, heat is released to produce a solution with a temperature of about 90°C; hence the product is an “instant hot compress.” If the salt is NH_4NO_3, heat is absorbed when it dissolves, and the temperature drops to about 0° for an “instant cold pack.”

A similar product based on the *precipitation* of sodium acetate, not its dissolution, is marketed as a reusable hand warmer (Figure 15.6.1). At high temperatures, sodium acetate forms a highly concentrated aqueous solution. With cooling, an unstable *supersaturated* solution containing excess solute is formed. When the pack is agitated, sodium acetate trihydrate [$CH_3CO_2Na{\cdot}3H_2O$] crystallizes, and heat is evolved:

$$Na^+(aq) + CH_3CO_2^-(aq) + H_2O(l) \rightarrow CH_3CO_2Na \cdot \bullet H_2O(s) \qquad \Delta H = -\Delta H_{soln} = -19.7\ kJ/mol$$

A bag of concentrated sodium acetate solution can be carried until heat is needed, at which time vigorous agitation induces crystallization and heat is released. The pack can be reused after it is immersed in hot water until the sodium acetate redissolves.



Figure 15.6.2 An Instant Hot Pack Based on the Crystallization of Sodium Acetate *The hot pack is at room temperature prior to agitation (left). Because the sodium acetate is in solution, you can see the metal disc inside the pack. After the hot pack has been agitated, the sodium acetate crystallizes (right) to release heat. Because of the mass of white sodium acetate that has crystallized, the metal disc is no longer visible.*

The amount of heat released or absorbed when a substance is dissolved is not a constant; it depends on the final concentration of the solute. The ΔH_{soln} values given previously and in Table 15.6.1 for example, were obtained by measuring the enthalpy changes at various concentrations and extrapolating the data to infinite dilution.

Because ΔH_{soln} depends on the concentration of the solute, diluting a solution can produce a change in enthalpy. If the initial dissolution process is exothermic ($\Delta H < 0$), then the dilution process is also exothermic. This phenomenon is particularly relevant for strong acids and bases, which are often sold or stored as concentrated aqueous solutions. If water is added to a concentrated solution of sulfuric acid (which is 98% H_2SO_4 and 2% H_2O) or sodium hydroxide, the heat released by the large negative ΔH can cause the solution to boil. Dangerous spattering of strong acid or base can be avoided if the concentrated acid or base is slowly added to water, so that the heat liberated is largely dissipated by the water. Thus you should **never add water to a strong acid or base**; a useful way to avoid the danger is to remember: *Add water to acid and get blasted!*

Summary

The **enthalpy of solution (ΔH_{soln})** is the heat released or absorbed when a specified amount of a solute dissolves in a certain quantity of solvent at constant pressure.

Key Takeaway

- Enthalpy is a state function whose change indicates the amount of heat transferred from a system to its surroundings or vice versa, at constant pressure.

Conceptual Problems

1. Describe the distinction between ΔH_{soln} and ΔH_f.
2. Does adding water to concentrated acid result in an endothermic or an exothermic process?
3. The following table lists ΔH^o_{soln} values for some ionic compounds. If 1 mol of each solute is dissolved in 500 mL of water, rank the resulting solutions from warmest to coldest.

Compound	ΔH^o_{soln}(kJ/mol)
KOH	−57.61
$LiNO_3$	−2.51
$KMnO_4$	43.56
$NaC_2H_3O_2$	−17.32

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Chapter 15.7: Fossil Fuels

Learning Objectives

- To use thermochemical concepts to discuss environmental issues.

Our contemporary society requires the constant expenditure of huge amounts of energy to heat our homes, provide telephone and cable service, transport us from one location to another, provide light when it is dark outside, and run the machinery that manufactures material goods. The United States alone consumes almost 10^6 kJ per person per day, which is about 100 times the normal required energy content of the human diet. This figure is about 30% of the world's total energy usage, although only about 5% of the total population of the world lives in the United States.

In contrast, the average energy consumption elsewhere in the world is about 10^5 kJ per person per day, although actual values vary widely depending on a country's level of industrialization. In this section, we describe various sources of fossil fuel energy and their impact on the environment.

Driven by environmental concerns about climate change and pollution, the world is undergoing a transformation from fossil fuels to renewable resources such as solar, and wind. The role that hydro and nuclear energy will play is uncertain and especially in the later case a policy rather than a scientific issue.

Fossil Fuels

According to the law of conservation of energy, energy can never actually be "consumed"; it can only be changed from one form to another.

Fossil fuels, coal, oil and natural gas are the result of anaerobic decay of dead plants and animals laid down hundreds of millions of years ago, most of which took place well before the dinosaurs strode the earth. Fossil fuels slowly formed as further geological layers compressed and heated the dead organic matter. The energy content of fossil fuels results from the transformation of sunlight into vegetation and the chemical transformation brought about by anaerobic cooking at high pressures and temperatures over geological times.

Figure 15.7.1 represents a plant for generating electricity using oil or coal where the fuel is burned in a boiler, superheating steam which then powers a turbine for electrical generation. Oil derived fuels are seldom used in large power plants but diesel is used commonly in small electrical generators either in remote locations or as back up for when electrical distribution systems fail. Natural gas fueled power plants burn the fuel directly in the turbine which is similar to a jet engine. Coal power plants can convert ~40% of the energy released from combustion to electricity. In comparison, nuclear power plants can be more than 50% efficient and gas turbines can approach 60% mostly due to higher operating temperatures. Co-generation, using the plant to produce not only electricity but also heat for industrial or other purposes can raise overall efficiency by 10 - 15 % or so.

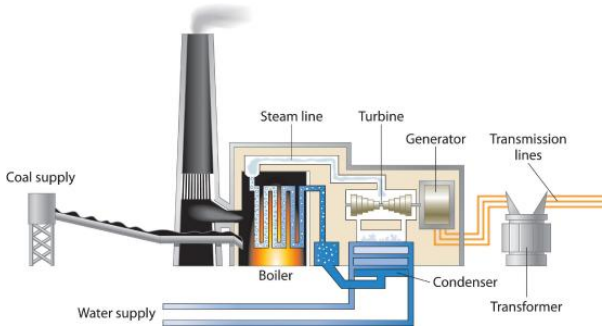


Figure 15.7.1 Electricity from Coal *A coal-powered electric power plant uses the combustion of coal to produce steam, which drives a turbine to produce electricity.*

The total expenditure of energy in the world each year is about 3×10^{21} kJ. Today, more than 80% of this energy is provided by the combustion of fossil fuels: oil, coal, and natural gas (The sources of the energy consumed in the United States in 2009 are shown in Figure 15.7.2.) but as Table 15.7.1 from the Wikipedia shows, energy usage is a complex issue. Petroleum dominates as a source of energy for transportation because gasoline is easy to transport, but is very little used for electrical generation, whereas 91% of coal is used for electrical generation. The other major use of coal is as a reducing agent for metal refining from ores. The former is called thermal coal, the latter metallurgical coal.

Table 15.7.1: Energy useage in the United States for 2008

Supply Sources	Percent of Source	Demand Sectors	Percent of Sector
Petroleum 37.1%	71% Transportation 23% Industrial 5% Residential and Commercial 1% Electric Power	Transportation 27.8%	95% Petroleum 2% Natural Gas 3% Renewable Energy
Natural Gas 23.8%	3% Transportation 34% Industrial 34% Residential and Commercial 29% Electric Power	Industrial 20.6%	42% Petroleum 40% Natural Gas 9% Coal 10% Renewable Energy
Coal 22.5%	8% Industrial <1% Residential and Commercial 91% Electric Power	Residential and Commercial 10.8%	16% Petroleum 76% Natural Gas 1% Coal 1% Renewable Energy
Renewable Energy 7.3%	11% Transportation 28% Industrial 10% Residential and Commercial 51% Electric Power	Electric Power 40.1%	1% Petroleum 17% Natural Gas 51% Coal 9% Renewable Energy 21% Nuclear Electric Power
Nuclear Electric Power 8.5%	100% Electric Power		

Coal

Coal was primarily laid down from the large swamp forests of the Carboniferous Period. Coal deposits are found today where those forests were Coal is a complex solid material derived primarily from plants that died and were buried hundreds of millions of years ago and were subsequently subjected to high temperatures and pressures. Because plants contain large amounts of *cellulose*, derived from linked glucose units, the structure of coal is more complex than that of petroleum (Figure 15.7.3). In particular, coal contains a large number of oxygen atoms that link parts of the structure together, in addition to the basic framework of carbon–carbon bonds. It is impossible to draw a single structure for coal; however, because of the prevalence of rings of carbon atoms (due to the original high cellulose content), coal is more similar to an aromatic hydrocarbon than an aliphatic one.

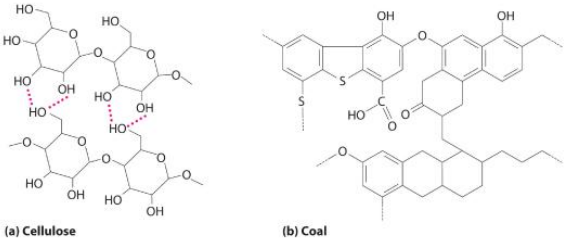
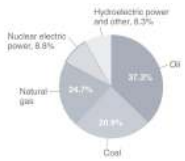


Figure 15.7.2 *Energy Consumption in the United States by Source, 2009*



More than 80% of the total energy expended is provided by the combustion of fossil fuels, such as oil, coal, and natural gas.

Figure 15.7.3 ***The Structures of Cellulose and Coal*** *(a) Cellulose consists of long chains of cyclic glucose molecules linked by hydrogen bonds. (b) When cellulose is subjected to high pressures and temperatures for long periods of time, water is eliminated, and bonds are formed between the rings, eventually producing coal. This drawing shows some of the common structural features of coal; note the presence of many different kinds of ring structures.*

There are four distinct classes of coal (Table 15.7.2); their hydrogen and oxygen contents depend on the length of time the coal has been buried and the pressures and temperatures to which it has been subjected. Lignite, with a hydrogen:carbon ratio of about 1.0 and a high oxygen content, has the lowest ΔH_{comb}. Lignite is extensively mined in Germany and Poland. Anthracite, in contrast, with a hydrogen:carbon ratio of about 0.5 and the lowest oxygen content, has the highest ΔH_{comb} and is the highest grade of coal. Anthracite is the first choice for metallurgical refining. The most abundant form in the Western United States in anthracite while that in the Eastern United States is bituminous coal, which has a high sulfur content because of the presence of small particles of pyrite (FeS_2). Combustion of coal releases the sulfur in FeS_2 as SO_2, which is a major contributor to acid rain. Table 15.7.3 compares the ΔH_{comb} per gram of oil, natural gas, and coal with those of selected organic compounds.

Table 15.7.2 Properties of Different Types of Coal

Type	% Carbon	Hydrogen:Carbon Mole Ratio	% Oxygen	% Sulfur	Heat Content	US Deposits
anthracite	92	0.5	3	1	high	Pennsylvania, New York
bituminous	80	0.6	8	5	medium	Appalachia, Midwest, Utah
subbituminous	77	0.9	16	1	medium	Rocky Mountains
lignite	71	1.0	23	1	low	Montana

Table 15.7.3 Enthalpies of Combustion of Common Fuels and Selected Organic Compounds

Fuel	ΔH_{comb} (kJ/g)
dry wood	−15
peat	−20.8
bituminous coal	−28.3
charcoal	−35
kerosene	−37
C_6H_6 (benzene)	−41.8
crude oil	−43
natural gas	−50
C_2H_2 (acetylene)	−50.0
CH_4 (methane)	−55.5
gasoline	−84
hydrogen	−143

Peat, a precursor to coal, is the partially decayed remains of plants that grow in the swampy areas of the Carboniferous Period. It is removed from the ground in the form of soggy bricks of mud that will not burn until they have been dried. Even though peat is a smoky, poor-burning fuel that gives off relatively little heat, humans have burned it since ancient times (Figure 15.7.4). If a peat bog were buried under many layers of sediment for a few million years, the peat would eventually be compressed and heated enough to become lignite, the lowest grade of coal; given enough time and heat, lignite would eventually become anthracite, a much better fuel.

Converting Coal to Gaseous and Liquid Fuels

As a solid, coal is much more difficult to mine and ship than petroleum (a liquid) or natural gas. Consequently, more than 75% of the coal produced each year is simply burned in power plants to produce electricity. Methods to convert coal to gaseous fuels (*coal gasification*) or liquid fuels (*coal liquefaction*) exist, but are not particularly economical unless the prices of oil and natural gas are high. With the development of fracking and the subsequent fall in oil and natural gas prices interest in these processes has fallen however they have played an important role in the past. In the most common approach to coal gasification, coal reacts with steam to produce a mixture of CO and H_2 known as *synthesis gas*, or *syngas*:Because coal is 70%–90% carbon by mass, it is approximated as C in Equation 15.7.1



Figure 15.7.4 A Peat Bog
Peat is a smoky fuel that burns poorly and produces little heat, but it has been used as a fuel since ancient times.

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g) \quad \Delta H = 131\ kJ$$

Converting coal to syngas removes any sulfur present and produces a clean-burning mixture of gases. Syngas or town gas was used for cooking until the 1960s when natural gas pipelines were built. Because syngas contains carbon monoxide (CO) it is poisonous, which accounts for scenes in old movies where people were killed by sticking their heads into an oven and allowing the gas to flow.

Syngas is can also used as a reactant to produce methane and methanol. A promising approach is to convert coal directly to methane through a series of reactions:

$$\begin{array}{ll} 2C(s) + 2H_2O(g) \rightarrow \cancel{2CO(g)} + \cancel{2H_2(g)} & \Delta H_1 = 262\ kJ \\ \cancel{CO(g)} + \cancel{H_2O(g)} \rightarrow CO_2(g) + \cancel{H_2(g)} & \Delta H_2 = -41\ kJ \\ \cancel{CO(g)} + \cancel{3H_2(g)} \rightarrow CH_4(g) + \cancel{H_2O(g)} & \Delta H_3 = -206\ kJ \\ \hline 2C(s) + 2H_2O(g) \rightarrow CH_4(g) + CO_2(g) & \Delta H_3 = 15\ kJ \end{array}$$

Techniques available for converting coal to liquid fuels are not economically competitive with the production of liquid fuels from petroleum. Current approaches to coal liquefaction use a catalyst to break the complex network structure of coal into more manageable fragments. The products are then treated with hydrogen (from syngas or other sources) under high pressure to produce a liquid more like petroleum. Subsequent distillation, cracking, and reforming can be used to create products similar to those obtained from petroleum.

Petroleum

The petroleum that is pumped out of the ground is a complex mixture of several thousand organic compounds including straight-chain alkanes, cycloalkanes, alkenes, and aromatic hydrocarbons with four to several hundred carbon atoms. The identities and relative abundances of the components vary depending on the source. So Texas crude oil is somewhat different from Saudi Arabian crude oil. In fact, the analysis of petroleum from different deposits can produce a “fingerprint” of each, which is useful in tracking down the sources of spilled crude oil. For example, Texas crude oil is “sweet,” meaning that it contains a small amount of sulfur-containing molecules, whereas Saudi Arabian crude oil is “sour,” meaning that it contains a relatively large amount of sulfur-containing molecules.

Gasoline

Petroleum is converted to useful products such as gasoline in three steps: distillation, cracking, and reforming. Recall that distillation separates compounds on the basis of their relative volatility, which is usually inversely proportional to their boiling points. Part (a) in Figure 15.7.5 shows a cutaway drawing of a column used in the petroleum industry for separating the

components of crude oil. The petroleum is heated to approximately 400°C (750°F), at which temperature it has become a mixture of liquid and vapor. This mixture, called the feedstock, is introduced into the refining tower. The most volatile components (those with the lowest boiling points) condense at the top of the column where it is cooler, while the less volatile components condense nearer the bottom. Some materials are so nonvolatile that they collect at the bottom without evaporating at all. Thus the composition of the liquid condensing at each level is different. These different fractions, each of which usually consists of a mixture of compounds with similar numbers of carbon atoms, are drawn off separately. Part (b) in Figure 15.7.5 shows the typical fractions collected at refineries, the number of carbon atoms they contain, their boiling points, and their ultimate uses. These products range from gases used in natural and bottled gas to liquids used in fuels and lubricants to gummy solids used as tar on roads and roofs.

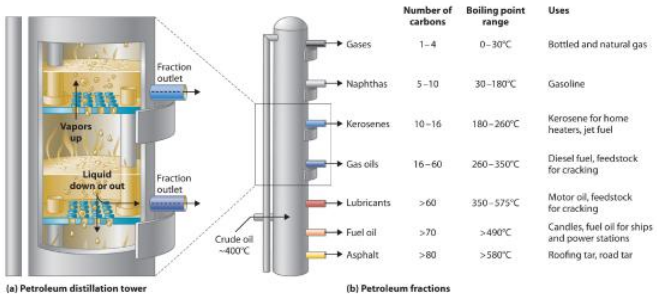


Figure 15.7.5: **The Distillation of Petroleum.** *(a) This is a diagram of a distillation column used for separating petroleum fractions. (b) Petroleum fractions condense at different temperatures, depending on the number of carbon atoms in the molecules, and are drawn off from the column. The most volatile components (those with the lowest boiling points) condense at the top of the column, and the least volatile (those with the highest boiling points) condense at the bottom.*

The economics of petroleum refining are complex. For example, the market demand for kerosene and lubricants is much lower than the demand for gasoline, yet all three fractions are obtained from the distillation column in comparable amounts. Furthermore, most gasolines and jet fuels are blends with very carefully controlled compositions that cannot vary as their original feedstocks did. To make petroleum refining more profitable, the less volatile, lower-value fractions must be converted to more volatile, higher-value mixtures that have carefully controlled formulas. The first process used to accomplish this transformation is cracking, in which the larger and heavier hydrocarbons in the kerosene and higher-boiling-point fractions are heated to temperatures as high as 900°C. High-temperature reactions cause the carbon–carbon bonds to break, which converts the compounds to lighter molecules similar to those in the gasoline fraction. Thus in cracking, a straight-chain alkane with a number of carbon atoms corresponding to the kerosene fraction is converted to a mixture of hydrocarbons with a number of carbon atoms corresponding to the lighter gasoline fraction. The second process used to increase the amount of valuable products is called reforming; it is the chemical conversion of straight-chain alkanes to either branched-chain alkanes or mixtures of aromatic hydrocarbons. Metal catalysts such as platinum are used to drive the necessary chemical reactions. The mixtures of products obtained from cracking and reforming are separated by fractional distillation.

Octane Ratings

The quality of a fuel is indicated by its octane rating, which is a measure of its ability to burn in a combustion engine without knocking or pinging. Knocking and pinging signal premature combustion (Figure 15.8.6), which can be caused either by an engine malfunction or by a fuel that burns too fast. In either case, the gasoline-air mixture detonates at the wrong point in the engine cycle, which reduces the power output and can damage valves, pistons, bearings, and other engine components. The various gasoline formulations are designed to provide the mix of hydrocarbons least likely to cause knocking or pinging in a given type of engine performing at a particular level.

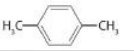
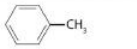
Name	Condensed Structural Formula	Octane Rating	Name	Condensed Structural Formula	Octane Rating
n-heptane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	0	*o*-xylene		107
n-hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	25	ethanol	CH_3CH_2OH	108
n-pentane	$CH_3CH_2CH_2CH_2CH_3$	62	*t*-butyl alcohol	$(CH_3)_3COH$	113
isooctane	$(CH_3)_3CCH_2CH(CH_3)_2$	100	*p*-xylene		116
benzene		106	methyl *t*-butyl ether	$H_3COC(CH_3)_3$	116
methanol	CH_3OH	107	toluene		118

***Figure 15.76**: The Burning of Gasoline in an Internal Combustion Engine. (a) Normally, fuel is ignited by the spark plug, and combustion spreads uniformly outward. (b) Gasoline with an octane rating that is too low for the engine can ignite prematurely, resulting in uneven burning that causes knocking and pinging.*

The octane scale was established in 1927 using a standard test engine and two pure compounds: n-heptane and isooctane (2,2,4-trimethylpentane). n-Heptane, which causes a great deal of knocking on combustion, was assigned an octane rating of 0, whereas isooctane, a very smooth-burning fuel, was assigned an octane rating of 100. Chemists assign octane ratings to different blends of gasoline by burning a sample of each in a test engine and comparing the observed knocking with the amount of knocking caused by specific mixtures of n-heptane and isooctane. For example, the octane rating of a blend of 89% isooctane and 11% n-heptane is simply the average of the octane ratings of the components weighted by the relative amounts of each in the blend. Converting percentages to decimals, we obtain the octane rating of the mixture:

$$0.89(100) + 0.11(0) = 89 \tag{4.7.1}$$

A gasoline that performs at the same level as a blend of 89% isooctane and 11% n-heptane is assigned an octane rating of 89; this represents an intermediate grade of gasoline. Regular gasoline typically has an octane rating of 87; premium has a rating of 93 or higher.

As shown in Figure 4.7.3, many compounds that are now available have octane ratings greater than 100, which means they are better fuels than pure isooctane. In addition, antiknock agents, also called octane enhancers, have been developed. One of the most widely used for many years was tetraethyllead $[(C_2H_5)_4Pb]$, which at approximately 3 g/gal gives a 10–15-point increase in octane rating. Since 1975, however, lead compounds have been phased out as gasoline additives because they are highly toxic.

Other enhancers, such as methyl t-butyl ether (MTBE), have been developed to take their place that combine a high octane rating with minimal corrosion to engine and fuel system parts. Unfortunately, when gasoline containing MTBE leaks from underground storage tanks, the result has been contamination of the groundwater in some locations, resulting in limitations or outright bans on the use of MTBE in certain areas. As a result, the use of alternative octane enhancers such as ethanol, which can be obtained from renewable resources such as corn, sugar cane, and, eventually, corn stalks and grasses, is increasing.

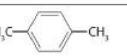
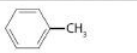
Name	Condensed Structural Formula	Octane Rating	Name	Condensed Structural Formula	Octane Rating
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n-hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	25	ethanol	CH_3CH_2OH	108
n-pentane	$CH_3CH_2CH_2CH_2CH_3$	62	*t*-butyl alcohol	$(CH_3)_3COH$	113
isooctane	$(CH_3)_3CCH_2CH(CH_3)_2$	100	*p*-xylene		116
benzene		106	methyl *t*-butyl ether	$H_3COC(CH_3)_3$	116
methanol	CH_3OH	107	toluene		118

***Figure 15.7.6**: The Octane Ratings of Some Hydrocarbons and Common Additives*

Natural Gas

Natural gas is a (mostly) combustible gas found underground. While primarily composed of methane (70-90%) the gas from each well has a different composition and the value of the other components affects the value of the gas. The gas from wells that are rich in methane is called dry and wells that have a considerable amount of higher hydrocarbons produce wet gas. The higher hydrocarbons have value above that of methane so stripping them out is important. Some wells are sour because their gas has hydrogen sulfide which must be removed before the gas can be used for heating or generating electricity.

Finally, a few wells in Texas and nearby Oklahoma have a relatively high amount of helium (0.3 - 2.7%). The Helium Act of 1925 established a national helium reserve at Cliffside near Amarillo TX. Political pressure and costs pushed laws to privatize the reserve, but other policy considerations including the need for helium for scientific research has slowed the process.

Table 15.8.4: Composition of Natural Gas

Gas	Molecular Formula	Composition
Methane	CH_4	70-95%
Ethane	C_2H_6	0-20%
Carbon Dioxide	CO_2	0-8%
Nitrogen	N_2	0-5%
Hydrogen Sulfide	H_2S	0-5%
Propane	C_3H_8	Traces
Butane	C_4H_{10}	Traces
Rare Gases	He (also Ne)	0-3% (only in Texas)

The purification of natural gas is a complex process with many steps as each of the impurities is stripped out

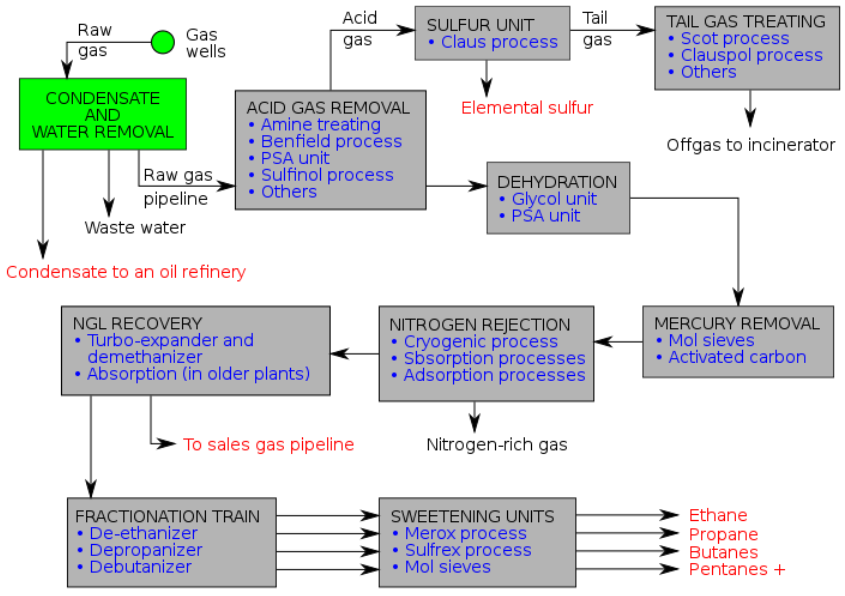


Figure 15.7.7: Purification of natural gas: *Prospective Chemical Engineers can find details about each process by searching the net. The flow chart is from the Wikipedia*

Gas turbine power plants to generate electricity are coming increasingly into use as fracking and other advanced drilling technologies have driven the cost of natural gas down and the supply up. While on a continental scale natural gas is transported by pipelines, natural gas can be cooled and compressed to be transported as liquified natural gas. Gas turbine power plants are small and quickly built. They can be rapidly spun up to meet peak demand. More detailed information can be found at the Department of Energy Fossil Fuel web site

The Carbon Cycle and the Greenhouse Effect

Since 1850 the burning of fossil fuels has increased the concentration of carbon dioxide in the atmosphere from 280 to just over 400 ppmV. A continued increase in the CO_2 burden in the atmosphere will have serious negative effects and this requires shifting our entire energy producing economy from fossil fuels to non-carbon sources such as hydro, solar, wind and nuclear. These include sea level rise that will threaten low lying cities including but not limited to Miami Beach and Norfolk in the US, even a meter or more coupled with storm surge and high tides can cause massive damage as was seen during Hurricane Sandy. Increased carbon dioxide in the atmosphere has already measurably decreased the pH of the oceans. Sea life is adapted to a narrow range of pH.

Higher global temperatures of 2 or 3 C may not seem much, but one should keep in mind that the average global temperature during the ice ages was only ~6 C lower than it is today. During the Eemian interglacial the average temperature was only a few degrees higher than the present and the sea level was 6-9 m higher. Finally, humans are mammals who maintain a core temperature within a few degrees of 37.0 C. In hot weather we do so by evaporation of sweat however there are limits to this and by 2100 there is a significant probability even in the US that at least a few days a year will reach this limit by 2100. Given that most people on earth do not have access to air conditioning, parts of the planet may become uninhabitable. Indeed a worst case and a serious problem that merits attention.

Given the constraints of this text it is difficult to provide the level of detail needed to understand why this is so. A good source for those interested in learning more is David Archer's Global Warming, Understanding the Forecast and An Introduction to Modern Climate Change by Andrew Dessler

There are a few basic facts that anyone starting to learn about the issue need to know. First, that the Earth gains energy from the Sun, and that it must radiate the energy at the same rate. If more energy is absorbed than radiated the Earth will warm up, if less energy is absorbed than radiated it will cool. As discussed in Section 15.1 solar radiation follows a 5500 K blackbody distribution while radiation from the surface of the earth is also black body but at ~290K. This is shown schematically in Figure 15.8.8

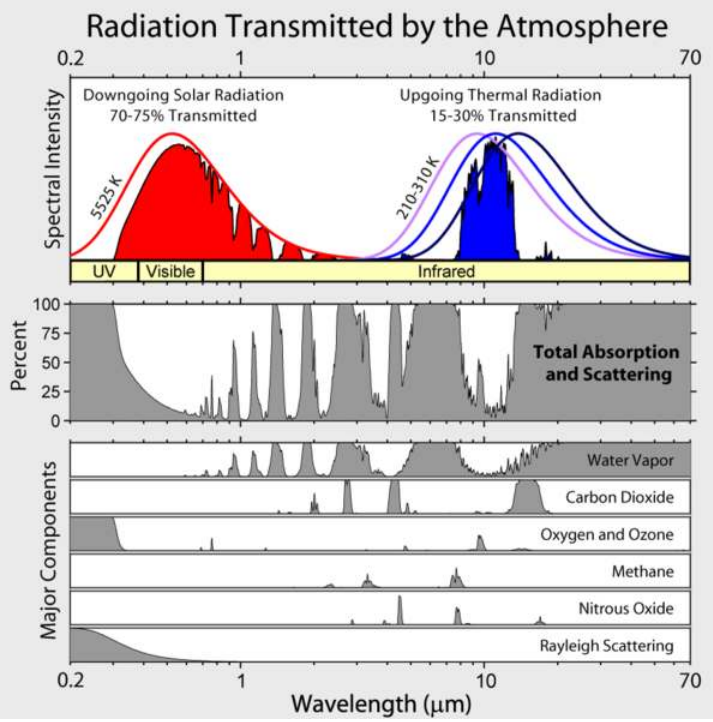


Figure 15.7.8: Origin of the greenhouse effect. *The top box show the intensity of solar radiation at the top of the Earth's atmosphere to the left and the infrared emission from the atmosphere to the left. The next shows the net absorption in the atmosphere across the spectrum. The bottom show the absorption by different atmospheric species at their current concentrations. Figure from the Wikipedia*

The atmosphere cools with altitude up to about 15 km where it starts warming again because of absorption of UV radiation by ozone in the stratosphere. The transition between the troposphere and the stratosphere is called the tropopause and is the coldest part of the atmosphere.

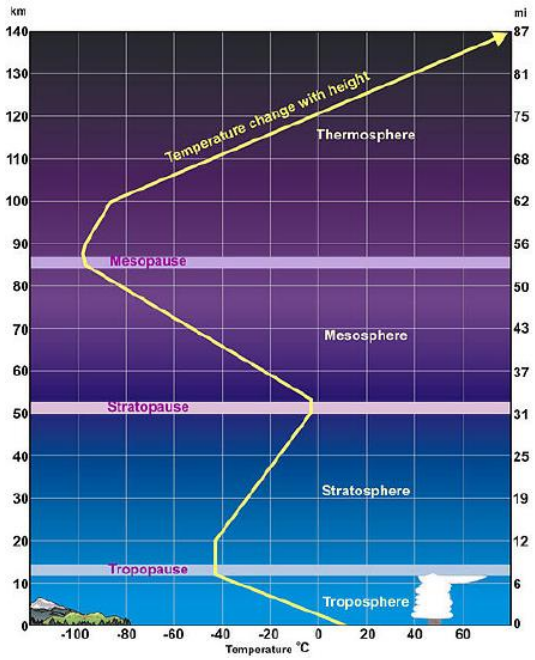


Figure 15.7.9 *The thermal structure of the atmosphere. The troposphere is the lowest level,extending from the the surface to the tropopause which is at 12-15 km altitude, more in the tropics and less less at the poles. The troposphere is the section of the atmosphere relevant to the greenhouse effect. The ozone layer is found in the stratosphere and one observes the aurora borealis or northern lights in the mesosphere Taken from Wikimedia*

Figure 15.7.10 shows the IR emission spectrum observed looking down on the earth from a high altitude balloon

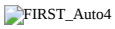


Figure 15.7.10: High resolution far infrared emission spectrum of the atmosphere looking down from a high altitude balloon at 35 km. *The strong band between 600 and 700 cm^{-1} is associated with CO_2, the sharp band at ~ 1100 cm^{-1} is associated with ozone and the feature near 1300 cm^{-1} is due to methane. The sharp lines (the hair) are due to water vapor. Spectrum is from the Federal Earth Observation Portal and was taken by an instrument operated by NASA/Langeley Research Center*

The dotted lines in Figure 15.8.9 are blackbody curves. The IR window shown schematically in blue in Figure 15.8.8 is the region between the ozone and the carbon dioxide band, where the emission from the hot, 320 K ground follows the blackbody curve with a few sharp water vapor absorption lines. At those wavelengths, in the IR window, the emission comes directly from the surface. The CO_2 band extends down to about a 220 K blackbody curve. What this means is that radiation from CO_2 only escapes to space from the level in the troposphere where that is the temperature. The rate of emission is proportional to T^4 so the rate of emission from higher, therefore colder levels, is slower. Radiation in this area of the spectrum from the surface is blocked and only the greatly reduced emission from the upper troposphere escapes to space. The same is true for the ozone and methane bands as well as the water lines.

The net effect is that the surface must warm in order to maintain the balance between incoming solar radiation and the outgoing emission. There is a simple calculation which models the atmosphere as a one dimensional problem and calculates what the

temperature of the surface would be if there were no greenhouse gases. The result is 255 K, rather cold. In fact if one attempts a more complex calculation the effective temperature without greenhouse gases would be even colder.

What happens if we increase the carbon dioxide in the atmosphere? The altitude at which the atmosphere can emit radiation to space will rise because of increased absorption by the CO_2. Since in the troposphere the temperature decreases with altitude, the rate of emission from a higher level must decrease. Again, in order to maintain the balance between incoming solar radiation and the outgoing emission the surface will have to warm even more, thus the term global warming. The change is not linear with increasing CO_2 but logarithmic. But, of course it is not so simple, because increasing the surface temperature will increase the water vapor pressure in the atmosphere, which will increase the temperature further.

We also have to understand the flow of carbon between the atmosphere, the biosphere, the upper oceans and the deep. Observations to date show that natural emissions of CO_2 from these reservoirs are in balance with absorption, while only about half of fossil fuel emissions remain in the atmosphere, the rest being absorbed by the upper ocean and the biosphere. The three upper reservoirs equilibrate in a decade or less, but flow into the deep ocean requires roughly a thousand years.

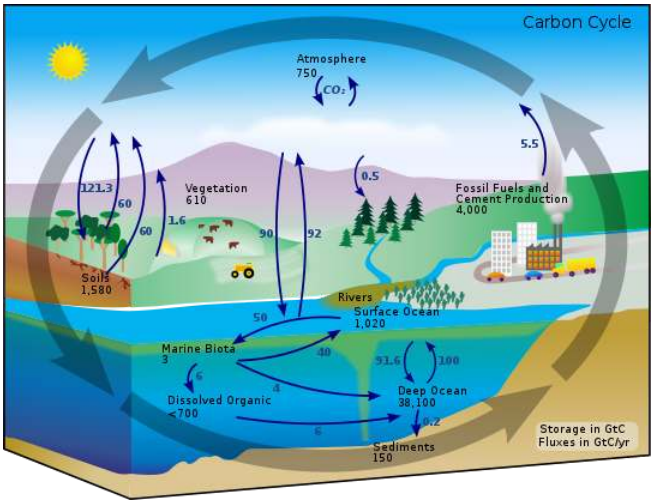


Figure 15.7.11: The carbon cycle. *Figure from the Wikipedia*

There is no doubt that atmospheric CO_2 levels are increasing, and the major reason for this increase is the combustion of fossil fuels. An extremely conservative statement of the situation today can be found in the 2014 Synthesis Report from the IPCC, a consensus between scientists and policymakers. The report starkly states that

> Cumulative emissions of CO_2 largely determine global mean surface warming by the late 21st century and beyond.

and concludes that

> Continued emission of greenhouse gases will cause further warming and long-lasting changes in all components of the climate system, increasing the likelihood of severe, pervasive and irreversible impacts for people and ecosystems. Limiting climate change would require substantial and sustained reductions in greenhouse gas emissions which, together with adaptation, can limit climate change risks.

The situation is serious, but we can work together to limit and even reverse damage while maintaining our standard of living in the developed world while helping the developing world to a better future. However, the issues are complex and we can only touch on some of the basics here.

Summary

More than 80% of the energy used by modern society (about 3×10^{17} kJ/yr) is from the combustion of fossil fuels. Because of their availability, ease of transport, and facile conversion to convenient fuels, natural gas and petroleum are currently the preferred fuels. Coal is primarily used for electricity generation. The combustion of fossil fuels releases large amounts of CO_2 that upset the balance of the **carbon cycle** and result in a steady increase in atmospheric CO_2 levels. Because CO_2 is a

greenhouse gas, which absorbs heat before it can be radiated from Earth into space, CO_2 in the atmosphere results in increased surface temperatures (the **greenhouse effect**).

Key Takeaway

- Thermochemical concepts can be used to calculate the efficiency of various forms of fuel, which can then be applied to environmental issues.

Conceptual Problems

1. What is meant by the term *greenhouse gases*? List three greenhouse gases that have been implicated in global warming.
2. Name three factors that determine the rate of planetary CO_2 uptake.
3. The structure of coal is quite different from the structure of gasoline. How do their structural differences affect their enthalpies of combustion? Explain your answer.

Numerical Problems

1. One of the side reactions that occurs during the burning of fossil fuels is
   $4FeS_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(s) + 8SO_2(g)$
   a. How many kilojoules of energy are released during the combustion of 10 lb of FeS_2?
   b. How many pounds of SO_2 are released into the atmosphere?
   c. Discuss the potential environmental impacts of this combustion reaction.
2. How many kilograms of CO_2 are released during the combustion of 16 gal of gasoline? Assume that gasoline is pure isooctane with a density of 0.6919 g/mL. If this combustion was used to heat 4.5×10^3 L of water from an initial temperature of 11.0°C, what would be the final temperature of the water assuming 42% efficiency in the energy transfer?
3. A 60 W light bulb is burned for 6 hours. If we assume an efficiency of 38% in the conversion of energy from oil to electricity, how much oil must be consumed to supply the electrical energy needed to light the bulb? (1 W = 1 J/s)
4. How many liters of cyclohexane must be burned to release as much energy as burning 10.0 lb of pine logs? The density of cyclohexane is 0.7785 g/mL, and its $\Delta H_{comb} = -46.6$ kJ/g.

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Chapter 15.8: Calorimetry

Learning Objectives

- To use calorimetric data to calculate enthalpy changes.

Thermal energy itself cannot be measured easily, but the temperature change caused by the flow of thermal energy between objects or substances can be measured. CalorimetryA set of techniques used to measure enthalpy changes in chemical (reactions) and physical changes (melting for example) processes. describes a set of techniques employed to measure enthalpy changes in chemical (reactions) and physical(melting for example) processes using devices called *calorimeters*.

To have any meaning, the quantity that is actually measured in a calorimetric experiment, the change in the temperature of the device, must be related to the heat evolved or consumed in a chemical reaction. We begin this section by explaining how the flow of thermal energy affects the temperature of an object.

Heat Capacity

We have seen that the temperature of an object changes when it absorbs or loses thermal energy. The *magnitude* of the temperature change depends on both the *amount* of thermal energy transferred (q) and the *heat capacity* of the object. Its heat capacity (C)J/^{o}C. The amount of energy needed to raise the temperature of an object 1°C. The units of heat capacity are joules per degree Celsius is the amount of energy needed to raise the temperature of the object exactly 1°C; the units of C are joules per degree Celsius (J/°C).

Note that a degree Celsius is exactly the same as a Kelvin, so the heat capacities can be expresses equally well, and perhaps a bit more correctly in SI, as joules per Kelvin, J/K

The change in temperature (ΔT) is

$$\Delta T = \frac{q}{C}$$

where q is the amount of heat (in joules), C is the heat capacity (in joules per degree Celsius), and ΔT is $T_{\text{final}} - T_{\text{initial}}$ (in degrees Celsius). Note that ΔT is *always* written as the final temperature minus the initial temperature.

Since Kelvin and degrees Celcius are exactly the same the DIFFERENCE $\Delta T = T_{\text{final}} - T_{\text{initial}}$ is the same whether one uses Kelving (K) or Celcius (°C) for BOTH T_{final} and T_{initial} , but make sure not to mix these two temperature units.

The value of C is intrinsically a positive number because it is defined as energy necessary to RAISE the temperature, but ΔT and q can be either positive or negative, and they both must have the *same* sign. If ΔT and q are positive, then *heat flows from the surroundings into an object*. If ΔT and q are negative, then *heat flows from an object into its surroundings*.

The heat capacity of an object depends on both its *mass* and its *composition*. For example, doubling the mass of an object doubles its heat capacity. Consequently, the amount of substance must be indicated when the heat capacity of the substance is reported. The molar heat capacity (C_p)The amount of energy needed to increase the temperature of 1 mol of a substance by 1°C. The units of

$$C_p \; J/mol \cdot ^o C \qquad \textbf{(Chapter 15.8.1)}$$

is the amount of energy needed to increase the temperature of 1 mol of a substance by 1°C; the units of C_p are thus J/(mol·°C).The subscript p indicates that the value was measured at constant pressure. The specific heat (C_s)The amount of energy needed to increase the temperature of 1 g of a substance by 1°C. The units of

$$C_s \; J/g \cdot ^o C \qquad \textbf{(Chapter 15.8.2)}$$

is the amount of energy needed to increase the temperature of 1 g of a substance by 1°C; its units are thus J/(g·°C). We can relate the quantity of a substance, the amount of heat transferred, its heat capacity, and the temperature change in two ways:

$$q = nC_p\Delta T$$

$$q = mC_s\Delta T$$

The specific heats of some common substances are given in Table 15.8.1 Note that the specific heat values of most solids are less than 1 J/(g·°C), whereas those of most liquids are about 2 J/(g·°C). Water in its solid and liquid states is an exception. The heat capacity of ice is twice as high as that of most solids; the heat capacity of liquid water, 4.184 J/(g·°C), is one of the highest known.

Table 15.8.1 Specific Heats of Selected Substances at 25°C

Compound	Specific Heat [J/(g·°C)]
$H_2O(l)$	4.184
$H_2O(g)$	2.062
CH_3OH (methanol)	2.531
CH_3CH_2OH (ethanol)	2.438
n-C_6H_{14} (*n*-hexane)	2.270
C_6H_6 (benzene)	1.745
C(s) (graphite)	0.709
C(s) (diamond)	0.509
Al(s)	0.897
Fe(s)	0.449
Cu(s)	0.385
Au(s)	0.129
Hg(l)	0.140
NaCl(s)	0.864
MgO(s)	0.921
SiO_2(s) (quartz)	0.742
$CaCO_3$(s) (calcite)	0.915

The high specific heat of liquid water has important implications for life on Earth. A given mass of water releases more than five times as much heat for a 1°C temperature change as does the same mass of limestone or granite. Consequently, coastal regions of our planet tend to have less variable climates than regions in the center of a continent. After absorbing large amounts of thermal energy from the sun in summer, the water slowly releases the energy during the winter, thus keeping coastal areas warmer than otherwise would be expected (Figure 15.8.1). Water's capacity to absorb large amounts of energy without undergoing a large increase in temperature also explains why swimming pools and waterbeds are usually heated. Heat must be applied to raise the temperature of the water to a comfortable level for swimming or sleeping and to maintain that level as heat is exchanged with the surroundings. Moreover, because the human body is about 70% water by mass, a great deal of energy is required to change its temperature by even 1°C. Consequently, the mechanism for maintaining our body temperature at about 37°C does not have to be as finely tuned as would be necessary if our bodies were primarily composed of a substance with a lower specific heat.

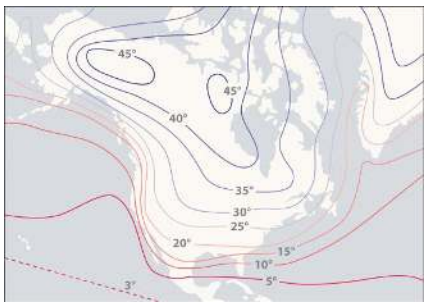


Figure 15.8.1 The High Specific Heat of Liquid Water Has Major Effects on Climate *Regions that are near very large bodies of water, such as oceans or lakes, tend to have smaller temperature differences between summer and winter months than regions in*

the center of a continent. The contours on this map show the difference between January and July monthly mean surface temperatures (in degrees Celsius).

Example 15.8.1

A home solar energy storage unit uses 400 L of water for storing thermal energy. On a sunny day, the initial temperature of the water is 22.0°C. During the course of the day, the temperature of the water rises to 38.0°C as it circulates through the water wall. How much energy has been stored in the water? (The density of water at 22.0°C is 0.998 g/mL.)



Passive solar system. *During the day (a), sunlight is absorbed by water circulating in the water wall. At night (b), heat stored in the water wall continues to warm the air inside the house.*

Given: volume and density of water and initial and final temperatures

Asked for: amount of energy stored

Strategy:

A Use the density of water at 22.0°C to obtain the mass of water (m) that corresponds to 400 L of water. Then compute ΔT for the water.

B Determine the amount of heat absorbed by substituting values for m, C_s, and ΔT into Equation 15.8.3

Solution:

A The mass of water is

$$mass\ of\ H_2O = 400\ \cancel{L}\left(\frac{1000\ \cancel{mL}}{1\ \cancel{L}}\right)\left(\frac{0.998\ g}{1\ \cancel{mL}}\right) \qquad \text{(Chapter 15.8.3)}$$
$$= 3.99 \times 10^5 g\ H_2O$$

The temperature change (ΔT) is 38.0°C − 22.0°C = +16.0°C.

B From Table 15.8.1, the specific heat of water is 4.184 J/(g·°C). From Equation 15.8.3 the heat absorbed by the water is thus

$$q = mC_s\Delta T = \left(3.99X10^5\ \cancel{g}\right)\left(\frac{4.184\ J}{\cancel{g}\cdot\cancel{^\circ C}}\right)\left(16.0\ \cancel{^\circ C}\right) \qquad \text{(Chapter 15.8.4)}$$
$$= 2.67 \times 10^7 J = 2.67 \times 10^4 kJ$$

Both q and ΔT are positive, consistent with the fact that the water has absorbed energy.

Exercise

Some solar energy devices used in homes circulate air over a bed of rocks that absorb thermal energy from the sun. If a house uses a solar heating system that contains 2500 kg of sandstone rocks, what amount of energy is stored if the temperature of the rocks increases from 20.0°C to 34.5°C during the day? Assume that the specific heat of sandstone is the same as that of quartz (SiO_2) in Table 15.8.1.

Answer: 2.7×10^4 kJ (Even though the mass of sandstone is more than six times the mass of the water in Example 7, the amount of thermal energy stored is the same to two significant figures.)

When two objects at different temperatures are placed in contact, heat flows from the warmer object to the cooler one until the temperature of both objects is the same. The law of conservation of energy says that the total energy cannot change during this process:

$$q_{cold} + q_{hot} = 0$$

The equation implies that the amount of heat that flows *from* a warmer object is the same as the amount of heat that flows *into* a cooler object. Because the direction of heat flow is opposite for the two objects, the sign of the heat flow values must be opposite:

$$q_{cold} = -q_{hot}$$

Thus heat is conserved in any such process, consistent with the law of conservation of energy.

Note the Pattern

Substituting for q from Equation 15.8.3 gives

$$[mC_s\Delta T]_{hot} + [mC_s\Delta T]_{hot} = 0$$

which can be rearranged to give

$$[mC_s\Delta T]_{hot} = -[mC_s\Delta T]_{hot}$$

When two objects initially at different temperatures are placed in contact, we can use Equation 15.8.7 to calculate the final temperature if we know the chemical composition and mass of the objects.

Example 15.8.2

If a 30.0 g piece of copper pipe at 80.0°C is placed in 100.0 g of water at 27.0°C, what is the final temperature? Assume that no heat is transferred to the surroundings.

Given: mass and initial temperature of two objects

Asked for: final temperature

Strategy:

Using Equation 15.8.7 and writing ΔT as $T_{\text{final}} - T_{\text{initial}}$ for both the copper and the water, substitute the appropriate values of m, C_s, and T_{initial} into the equation and solve for T_{final}.

Solution:

We can adapt Equation 15.8.7 to solve this problem, remembering that ΔT is defined as $T_{\text{final}} - T_{\text{initial}}$:

$$[mC_s(T_{final} - T_{initial})]_{Cu} + [mC_s(T_{final} - T_{initial})]_{H_2O} = 0 \quad \text{(Chapter 15.8.5)}$$

Substituting the data provided in the problem and Table 15.8.1 gives

$$[(30\ g)(0.385\ J)(T_{final} - T_{initial})]_{Cu} + [mC_s(T_{final} - T_{initial})]_{H_2O} = 0 \quad \text{(Chapter 15.8.6)}$$

$$T_{final}\,(11.6\ J/°C) - 924\ J + T_{final}\,(418.4\ J/°C) - 11,300\ J \quad \text{(Chapter 15.8.7)}$$

$$T_{final}\,(430\ J/\,(g \cdot °\ C)) = -12,224\ J \quad \text{(Chapter 15.8.8)}$$

$$T_{final} = -28.4\ °C \quad \text{(Chapter 15.8.9)}$$

Exercise (a)

If a 14.0 g chunk of gold at 20.0°C is dropped into 25.0 g of water at 80.0°C, what is the final temperature if no heat is transferred to the surroundings?

Answer: 80.0°C

Exercise (b)

A 28.0 g chunk of aluminum is dropped into 100.0 g of water with an initial temperature of 20.0°C. If the final temperature of the water is 24.0°C, what was the initial temperature of the aluminum? (Assume that no heat is transferred to the surroundings.)

Answer: 90.6°C

Measuring Heat Flow

In Example 15.8.1, radiant energy from the sun was used to raise the temperature of water. A calorimetric experiment uses essentially the same procedure, except that the thermal energy change accompanying a chemical reaction is responsible for the change in temperature that takes place in a calorimeter. If the reaction releases heat ($q_{rxn} < 0$), then heat is absorbed by the calorimeter ($q_{calorimeter} > 0$) and its temperature increases. Conversely, if the reaction absorbs heat ($q_{rxn} > 0$), then heat is transferred from the calorimeter to the system ($q_{calorimeter} < 0$) and the temperature of the calorimeter decreases. In both cases, *the amount of heat absorbed or released by the calorimeter is equal in magnitude and opposite in sign to the amount of heat produced or consumed by the reaction*. The heat capacity of the calorimeter or of the reaction mixture may be used to calculate the amount of heat released or absorbed by the chemical reaction. The amount of heat released or absorbed per gram or mole of reactant can then be calculated from the mass of the reactants.

Constant-Pressure Calorimetry

Because ΔH is defined as the heat flow at constant pressure, measurements made using a constant-pressure calorimeterA device used to measure enthalpy changes in chemical processes at constant pressure. give ΔH values directly. This device is particularly well suited to studying reactions carried out in solution at a constant atmospheric pressure. A "student" version, called a *coffee-cup calorimeter* (Figure 15.8.2), is often encountered in general chemistry laboratories. Commercial calorimeters operate on the same principle, but they can be used with smaller volumes of solution, have better thermal insulation, and can detect a change in temperature as small as several millionths of a degree (10^{-6}°C). Because the heat released or absorbed at constant pressure is equal to ΔH, the relationship between heat and ΔH_{rxn} is

$$\Delta H_{rxn} = q_{rxn} = -q_{calorimater} = -mC_s\Delta T \tag{15.8.8}$$

The use of a constant-pressure calorimeter is illustrated in Example 3.

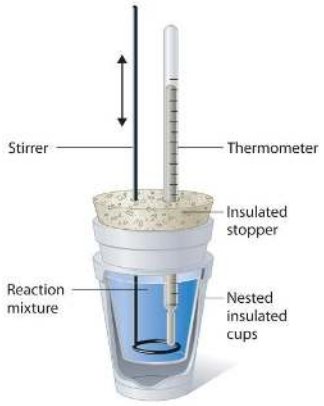


Figure 15.8.2 A Coffee-Cup Calorimeter *This simplified version of a constant-pressure calorimeter consists of two Styrofoam cups nested and sealed with an insulated stopper to thermally isolate the system (the solution being studied) from the surroundings (the air and the laboratory bench). Two holes in the stopper allow the use of a thermometer to measure the temperature and a stirrer to mix the reactants.*

Example 15.8.3

When 5.03 g of solid potassium hydroxide are dissolved in 100.0 mL of distilled water in a coffee-cup calorimeter, the temperature of the liquid increases from 23.0°C to 34.7°C. The density of water in this temperature range averages 0.9969 g/cm^3. What is ΔH_{soln} (in kilojoules per mole)? Assume that the calorimeter absorbs a negligible amount of heat and, because of the large volume of water, the specific heat of the solution is the same as the specific heat of pure water.

Given: mass of substance, volume of solvent, and initial and final temperatures

Asked for: ΔH_{soln}

Strategy:

A Calculate the mass of the solution from its volume and density and calculate the temperature change of the solution.

B Find the heat flow that accompanies the dissolution reaction by substituting the appropriate values into Equation 15.8.8.

C Use the molar mass of KOH to calculate ΔH_{soln}.

Solution:

A To calculate ΔH_{soln}, we must first determine the amount of heat released in the calorimetry experiment. The mass of the solution is

$$(100.0\ mL\ H2O)\left(0.9969\ g/\cancel{mL}\right) + 5.03\ g\ KOH = 104.72\ g$$

The temperature change is (34.7°C − 23.0°C) = +11.7°C.

B Because the solution is not very concentrated (approximately 0.9 M), we assume that the specific heat of the solution is the same as that of water. The heat flow that accompanies dissolution is thus

$$q_{calorimater} = mC_s\Delta T = \left(104.72\ \cancel{g}\right)\left(\frac{4.184\ J}{\cancel{g}\cdot\cancel{^\circ C}}\right)(11.7\ ^\circ C) = 5130\ J = 5.13\ lJ$$

The temperature of the solution increased because heat was absorbed by the solution ($q > 0$). Where did this heat come from? It was released by KOH dissolving in water. From Equation 15.8, we see that

$$\Delta H_{rxn} = -q_{calorimeter} = -5.13\ \text{kJ}$$

This experiment tells us that dissolving 5.03 g of KOH in water is accompanied by the *release* of 5.13 kJ of energy. Because the temperature of the solution increased, the dissolution of KOH in water must be exothermic.

C The last step is to use the molar mass of KOH to calculate ΔH_{soln}—the heat released when dissolving 1 mol of KOH:

$$\Delta H_{soln} = \left(\frac{5.13\ kJ}{5.03\ \cancel{g}}\right)\left(\frac{56.11\ \cancel{g}}{1\ mol}\right) = -57.2\ kJ/mol \qquad \text{(Chapter 15.8.10)}$$

Exercise

A coffee-cup calorimeter contains 50.0 mL of distilled water at 22.7°C. Solid ammonium bromide (3.14 g) is added and the solution is stirred, giving a final temperature of 20.3°C. Using the same assumptions as in Example 9, find ΔH_{soln} for NH_4Br (in kilojoules per mole).

Answer: 16.6 kJ/mol

Constant-Volume Calorimetry

Constant-pressure calorimeters are not very well suited for studying reactions in which one or more of the reactants is a gas, such as a combustion reaction. The enthalpy changes that accompany combustion reactions are therefore measured using a constant-volume calorimeter, such as the bomb calorimeter (A device used to measure energy changes in chemical processes. shown schematically in Figure 15.8.3). The reactant is placed in a steel cup inside a steel vessel with a fixed volume (the “bomb”). The bomb is then sealed, filled with excess oxygen gas, and placed inside an insulated container that holds a known amount of water. Because combustion reactions are exothermic, the temperature of the bath and the calorimeter increases during combustion. If the heat capacity of the bomb and the mass of water are known, the heat released can be calculated.

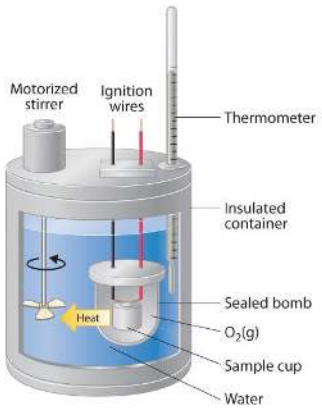


Figure 15.8.3 A Bomb Calorimeter *After the temperature of the water in the insulated container has reached a constant value, the combustion reaction is initiated by passing an electric current through a wire embedded in the sample. Because this calorimeter operates at constant volume, the heat released is not precisely the same as the enthalpy change for the reaction.*

Because the volume of the system (the inside of the bomb) is fixed, the combustion reaction occurs under conditions in which the volume, but not the pressure, is constant. As we noted in Chapter 9.2 the heat released by a reaction carried out at constant volume is identical to the change in *internal energy* (ΔE) rather than the enthalpy change (ΔH); ΔE is related to ΔH by an expression that depends on the change in the number of moles of gas during the reaction. The difference between the heat flow measured at constant volume and the enthalpy change is usually quite small, however (on the order of a few percent). Assuming that $\Delta E < \Delta H$, the relationship between the measured temperature change and ΔH_{comb} is given in Equation 15.8.9 , where C_{bomb} is the total heat capacity of the steel bomb and the water surrounding it:

$$\Delta H_{comb} < q_{comb} = q_{calorimater} = C_{bomb}\Delta T \tag{15.8.9}$$

To measure the heat capacity of the calorimeter, we first burn a carefully weighed mass of a standard compound whose enthalpy of combustion is accurately known. Benzoic acid ($C_6H_5CO_2H$) is often used for this purpose because it is a crystalline solid that can be obtained in high purity. The combustion of benzoic acid in a bomb calorimeter releases 26.38 kJ of heat per gram (i.e., its ΔH_{comb} = −26.38 kJ/g). This value and the measured increase in temperature of the calorimeter can be used in Equation 15.8.9 to determine C_{bomb}. The use of a bomb calorimeter to measure the ΔH_{comb} of a substance is illustrated in Example 10.

Example 15.8.4

The combustion of 0.579 g of benzoic acid in a bomb calorimeter caused a 2.08°C increase in the temperature of the calorimeter. The chamber was then emptied and recharged with 1.732 g of glucose and excess oxygen. Ignition of the glucose resulted in a temperature increase of 3.64°C. What is the ΔH_{comb} of glucose?



Given: mass and ΔT for combustion of standard and sample

Asked for: ΔH_{comb} of glucose

Strategy:

A Calculate the value of q_{rxn} for benzoic acid by multiplying the mass of benzoic acid by its ΔH_{comb}. Then determine the heat capacity of the calorimeter (C_{bomb}) from q_{comb} and ΔT.

B Calculate the amount of heat released during the combustion of glucose by multiplying the heat capacity of the bomb by the temperature change. Determine the ΔH_{comb} of glucose by multiplying the amount of heat released per gram by the molar mass of glucose.

Solution:

The first step is to use Equation 15.8.9 and the information obtained from the combustion of benzoic acid to calculate C_{bomb}. We are given ΔT, and we can calculate q_{comb} from the mass of benzoic acid:

$$qcomb = \left(0.579\ \cancel{g}\right)\left(-26.38\ kJ/\cancel{g}\right) = -15.3\ kJ \tag{Chapter 15.8.11}$$

From Equation 15.8.9,

$$-Cbomb = \frac{q_{comb}}{\Delta T} = \frac{-15.3\ kJ}{2.08\ ^oC} = -7.34\ kJ/^oC \tag{Chapter 15.8.12}$$

B According to the strategy, we can now use the heat capacity of the bomb to calculate the amount of heat released during the combustion of glucose:

$$q_{comb} = -C_{bomb}\Delta T = (-7.34\ kJ/^oC)\,(3.64\ ^oC) = -26.7\ kJ \tag{Chapter 15.8.13}$$

Because the combustion of 1.732 g of glucose released 26.7 kJ of energy, the ΔH_{comb} of glucose is

$$\Delta H_{comb} = \left(\frac{-26.7\ kJ}{1.732\ \cancel{g}}\right)\left(\frac{180.16\ \cancel{g}}{mol}\right) = -2780\ kJ/mol \tag{Chapter 15.8.14}$$
$$= 2.78 \times 10^3\ kJ/mol$$

This result is in good agreement (< 1% error) with the value of ΔH_{comb} = −2803 kJ/mol that calculated using enthalpies of formation.

Exercise

When 2.123 g of benzoic acid is ignited in a bomb calorimeter, a temperature increase of 4.75°C is observed. When 1.932 g of methylhydrazine (CH_3NHNH_2) is ignited in the same calorimeter, the temperature increase is 4.64°C. Calculate the ΔH_{comb} of methylhydrazine, the fuel used in the maneuvering jets of the US space shuttle.



Methylhydrazine

Answer: −1.30 × 10^3 kJ/mol

Key Equations

relationship of quantity of a substance, heat capacity, heat flow, and temperature change

Equation 15.8.2: $q = nC_p\Delta T$

Equation 15.8.3: $q = mC_s\Delta T$

constant-pressure calorimetry

Equation 15.8.8: $\Delta H_{rxn} = q_{rxn} = -q_{calorimeter} = -mC_s\Delta T$

constant-volume calorimetry

Equation 15.8.9: $\Delta H_{comb} < q_{comb} = -q_{calorimeter} = -C_{bomb}\Delta T$

Summary

Calorimetry is the set of techniques used to measure enthalpy changes during chemical processes. It uses devices called *calorimeters*, which measure the change in temperature when a chemical reaction is carried out. The magnitude of the temperature change depends on the amount of heat released or absorbed and on the heat capacity of the system. The **heat capacity (*C*)** of an object is the amount of energy needed to raise its temperature by 1°C; its units are joules per degree Celsius. The **specific heat (C_s)** of a substance is the amount of energy needed to raise the temperature of 1 g of the substance by 1°C, and the **molar heat capacity (C_p)** is the amount of energy needed to raise the temperature of 1 mol of a substance by 1°C. Liquid water has one of the highest

specific heats known. Heat flow measurements can be made with either a **constant-pressure calorimeter**, which gives ΔH values directly, or a **bomb calorimeter**, which operates at constant volume and is particularly useful for measuring enthalpies of combustion.

Key Takeaway

- Calorimetry measures enthalpy changes during chemical processes, where the magnitude of the temperature change depends on the amount of heat released or absorbed and on the heat capacity of the system.

Conceptual Problems

1. Can an object have a negative heat capacity? Why or why not?
2. What two factors determine the heat capacity of an object? Does the specific heat also depend on these two factors? Explain your answer.
3. Explain why regions along seacoasts have a more moderate climate than inland regions do.
4. Although soapstone is more expensive than brick, soapstone is frequently the building material of choice for fireplaces, particularly in northern climates with harsh winters. Propose an explanation for this.

Numerical Problems

1. Using Equation 15.8.2 and Equation 15.8.3, derive a mathematical relationship between C_s and C_p.
2. Complete the following table for 28.0 g of each element at an initial temperature of 22.0°C.

Element	q (J)	C_p [J/(mol·K)]	Final T (°C)
nickel	137	26.07	
silicon		19.789	3.0
zinc	603		77.5
mercury	137		57

3. Using Table 15.8.1, how much heat is needed to raise the temperature of a 2.5 g piece of copper wire from 20°C to 80°C? How much heat is needed to increase the temperature of an equivalent mass of aluminum by the same amount? If you were using one of these metals to channel heat away from electrical components, which metal would you use? Once heated, which metal will cool faster? Give the specific heat for each metal.
4. Gold has a molar heat capacity of 25.418 J/(mol·K), and silver has a molar heat capacity of 23.350 J/(mol·K).
    1. If you put silver and gold spoons of equal mass into a cup of hot liquid and wait until the temperature of the liquid is constant, which spoon will take longer to cool down when removed from the hot liquid?
    2. If 8.00 g spoons of each metal at 20.0°C are placed in an insulated mug with 50.0 g of water at 97.0°C, what will be the final temperature of the water after the system has equilibrated? (Assume that no heat is transferred to the surroundings.)
5. In an exothermic reaction, how much heat would need to be evolved to raise the temperature of 150 mL of water 7.5°C? Explain how this process illustrates the law of conservation of energy.
6. How much heat must be evolved by a reaction to raise the temperature of 8.0 oz of water 5.0°C? What mass of lithium iodide would need to be dissolved in this volume of water to produce this temperature change?
7. A solution is made by dissolving 3.35 g of an unknown salt in 150 mL of water, and the temperature of the water rises 3.0°C. The addition of a silver nitrate solution results in a precipitate. Assuming that the heat capacity of the solution is the same as that of pure water, use the information in Table 9.5.1 and solubility rules to identify the salt.
8. Using the data in Table 9.8.2, calculate the change in temperature of a calorimeter with a heat capacity of 1.78 kJ/°C when 3.0 g of charcoal is burned in the calorimeter. If the calorimeter is in a 2 L bath of water at an initial temperature of 21.5°C, what will

be the final temperature of the water after the combustion reaction (assuming no heat is lost to the surroundings)?

9. A 3.00 g sample of TNT (trinitrotoluene, $C_7H_5N_3O_6$) is placed in a bomb calorimeter with a heat capacity of 1.93 kJ/°C; the ΔH_{comb} of TNT is −3403.5 kJ/mol. If the initial temperature of the calorimeter is 19.8°C, what will be the final temperature of the calorimeter after the combustion reaction (assuming no heat is lost to the surroundings)? What is the ΔH_f of TNT?

Answers

1. $C_p = C_s \times$ (molar mass)
2.
3. For Cu: q = 58 J; For Al: q = 130 J; Even though the values of the molar heat capacities are very similar for the two metals, the specific heat of Cu is only about half as large as that of Al, due to the greater molar mass of Cu versus Al: C_s = 0.385 and 0.897 *J*/(g·K) for Cu and Al, respectively. Thus loss of one joule of heat will cause almost twice as large a decrease in temperature of Cu versus Al.
4.
5. 4.7 kJ
6.
7. ΔH_{soln} = −0.56 kJ/g; based on reaction with $AgNO_3$, salt contains halide; dividing ΔH_{soln} values in Table 5.2 by molar mass of salts gives lithium bromide as best match, with −0.56 kJ/g.
8.
9. T_{final} = 43.1°C; the combustion reaction is

$$4C_7H_5N_3O_{6(s)} + 21O_{2(g)} \rightarrow 28CO_{2(g)} + 10H_2O_{(g)} + 6N_{2(g)} \quad \text{(Chapter 15.8.15)}$$

with

$$\Delta^\circ_f H(TNT) = -65.5\ kJ/mol \quad \text{(Chapter 15.8.16)}$$

Contributors

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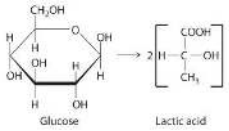
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Application Problems

1. Palm trees grow on the coast of southern England even though the latitude is the same as that of Winnipeg, Canada. What is a plausible explanation for this phenomenon? (Hint: the Gulf Stream current is a factor.)

2. During intense exercise, your body cannot provide enough oxygen to allow the complete combustion of glucose to carbon dioxide. Under these conditions, an alternative means of obtaining energy from glucose is used in which glucose ($C_6H_{12}O_6$) is converted to lactic acid ($C_3H_5O_3H$). The equation for this reaction is as follows:

   $C_6H_{12}O_6 \rightarrow 2C_3H_5O_3H$

   1. Calculate the energy yield for this reaction per mole of glucose.
   2. How does this energy yield compare with that obtained per mole of glucose for the combustion reaction?
   3. Muscles become sore after intense exercise. Propose a chemical explanation for this.

3. ♦ During the late spring, icebergs in the North Atlantic pose a hazard to shipping. To avoid them, ships travel routes that are about 30% longer. Many attempts have been made to destroy icebergs, including using explosives, torpedoes, and bombs. How much heat must be generated to melt 15% of a 1.9×10^8 kg iceberg? How many kilograms of TNT (trinitrotoluene, $C_7H_5N_3O_6$) would be needed to provide enough energy to melt the ice? (The ΔH for explosive decomposition of TNT is −1035.8 kJ/mol.)

4. ♦ During smelting, naturally occurring metal oxides are reduced by carbon at high temperature. For copper(II) oxide, this process includes the following series of chemical equations:

   $CuO(s) + C(s) \rightarrow Cu(l) + CO(g)$ $2C(s) + O_2(g) \rightarrow 2CO(g)$ $CuO(l) + CO(g) \rightarrow Cu(s) + CO_2(g)$

   The final products are CO_2 and Cu. The discovery of this process led to the increasing use of ores as sources of metals in ancient cultures. In fact, between 3000 BC and 2000 BC, the smelting of copper was well established, and beads made from copper are some of the earliest known metal artifacts.

   1. Write a balanced chemical equation for the overall reaction of CuO, C, and O_2 to give *only* CO_2 and Cu.
   2. Using Hess's law and the data in the Reference Tables, calculate ΔH_{rxn} for the smelting of CuO ore to give Cu and CO_2.
   3. Assuming complete reaction, how much heat was released if 23 g of Cu metal was produced from its ore?

5. ♦ The earliest known Egyptian artifacts made from tin metal date back to approximately 1400 BC. If the smelting process for SnO_2 occurs via the reaction sequence

   $SnO_2(s) + 2C(s) \rightarrow Sn(s) + 2CO(g)$ $SnO_2(s) + 2CO(g) \rightarrow Sn(s) + 2CO_2(g)$

   what is ΔH_{rxn} for the conversion of SnO_2 to Sn (s, white) by this smelting process? How much heat was released or required if 28 g of Sn metal was produced from its ore, assuming complete reaction?

6. ♦ An average American consumes approximately 10^6 kJ of energy per day. The average life expectancy of an American is 77.9 years.

   1. How much coal would need to be burned to provide enough energy to meet a person's energy demands if the efficiency of energy production from coal is 38%?
   2. If the coal contains 0.6% by mass FeS_2, how many kilograms of sulfuric acid are produced during the time in part (a)?

7. Several theories propose that life on Earth evolved in the absence of oxygen. One theory is that primitive organisms used fermentation processes, in which sugars are decomposed in an oxygen-free environment, to obtain energy. Many kinds of fermentation processes are possible, including the conversion of glucose to lactic acid (a), to CO_2 and ethanol (b), and to ethanol and acetic acid (c):

1. $C_6H_{12}O_6(s) \rightarrow 2C_3H_6O_3(s)$
2. $C_6H_{12}O_6(s) \rightarrow 2C_2H_5OH(l) + 2CO_2(g)$
3. $C_6H_{12}O_6(s) + H_2O(l) \rightarrow C_2H_5OH(l) + CH_3CO_2H(l) + 2H_2(g) + 2CO_2(g)$

Reaction (a) occurs in rapidly exercising muscle cells, reaction (b) occurs in yeast, and reaction (c) occurs in intestinal bacteria. Using the Reference Tables, calculate which reaction gives the greatest energy yield (most negative ΔH^o_{rxn}) per mole of glucose.

8. A 70 kg person expends 85 Cal/h watching television. If the person eats 8 cups of popcorn that contains 55 Cal per cup, how many kilojoules of energy from the popcorn will have been burned during a 2 h movie? After the movie, the person goes outside to play tennis and burns approximately 500 Cal/h. How long will that person have to play tennis to work off all the residual energy from the popcorn?
9. ♦ Photosynthesis in higher plants is a complex process in which glucose is synthesized from atmospheric carbon dioxide and water in a sequence of reactions that uses light as an energy source. The overall reaction is as follows:

$$6CO_2\,(g) + 6H_2O\,(l) \rightarrow 6C_6H_{12}O_6\,(s) + 6O_2\,(g) \qquad \text{(Chapter 15.9.1)}$$

Glucose may then be used to produce the complex carbohydrates, such as cellulose, that constitute plant tissues.

1. Is the reaction endothermic or exothermic?
2. How many grams of glucose are produced per kilogram of carbon dioxide?
3. A 2.5 lb sweet potato is approximately 73% water by mass. If the remaining mass is made up of carbohydrates derived from glucose, how much carbon dioxide was needed to grow this sweet potato?
4. How many kilojoules of energy are stored in the potato?
5. Which releases more energy—digestion of the potato or combustion of the potato?

10. Proteins contain approximately 4 Cal/g, carbohydrates approximately 4 Cal/g, and fat approximately 9 Cal/g. How many kilojoules of energy are available from the consumption of one serving (8 oz) of each food in the table? (Data are shown per serving.)

Food	Protein (g)	Fat (g)	Carbohydrates (g)
sour cream	7	48	10
banana	2	1	35
cheeseburger	60	31	40
green peas	8	1	21

11. When you eat a bowl of cereal with 500 g of milk, how many Calories must your body burn to warm the milk from 4°C to a normal body temperature of 37°C? (Assume milk has the same specific heat as water.) How many Calories are burned warming the same amount of milk in a 32°C bowl of oatmeal from 32°C to normal body temperature? In some countries that experience starvation conditions, it has been found that infants don't starve even though the milk from their mothers doesn't contain the number of Calories thought necessary to sustain them. Propose an explanation for this.
12. Approximately 810 kJ of energy is needed to evaporate water from the leaves of a 9.2 m tree in one day. What mass of water is evaporated from the tree?

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CHAPTER OVERVIEW

Chapter 16: Entropy and Free Energy

- Chapter 16.1: The Second Law of Thermodynamics
- Chapter 16.2: Entropy Changes and the Third Law of Thermodynamics
- Chapter 16.3: Free Energy
- Chapter 16.4: Spontaneity and Equilibrium
- Chapter 16.5: Comparing Thermodynamics and Kinetics
- Chapter 16.6: End of Chapter Material

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Chapter 16.1: The Second Law of Thermodynamics

Learning Objectives

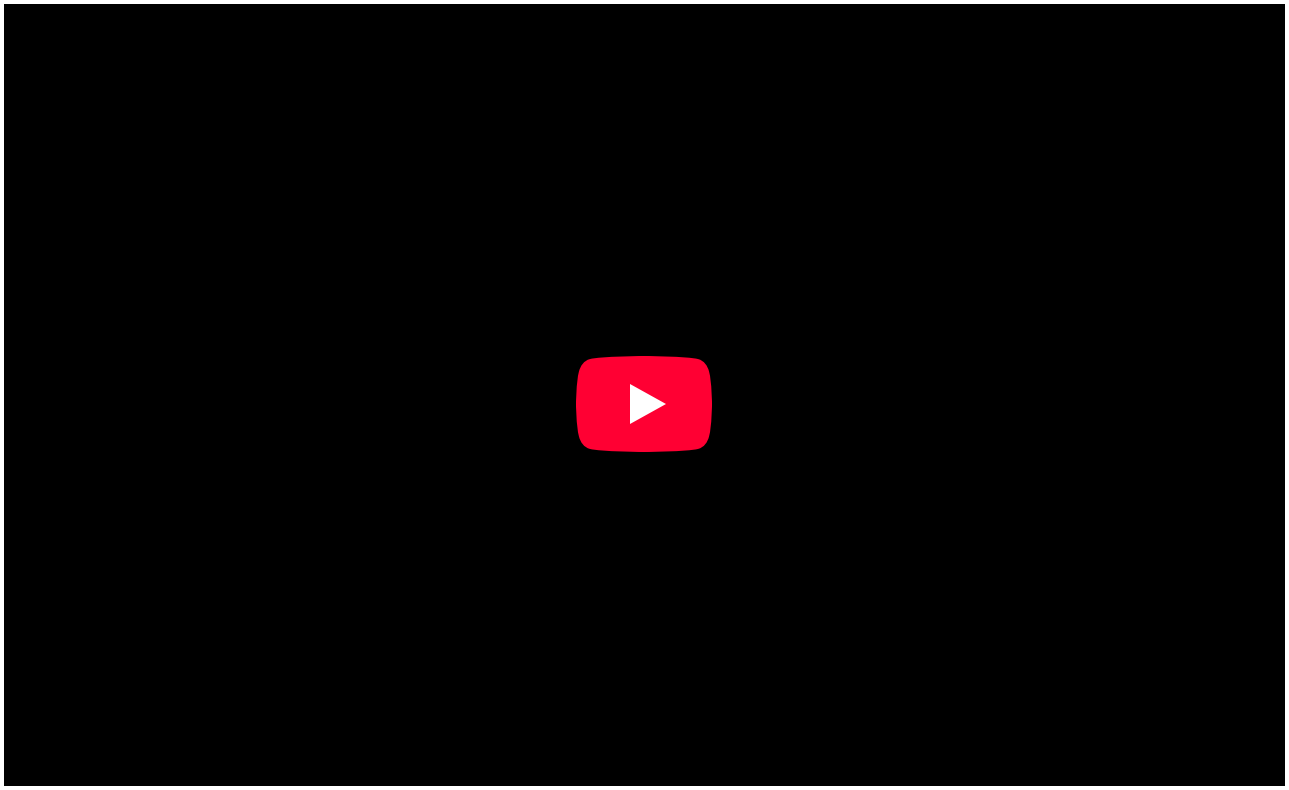
- To understand the relationship between internal energy and entropy.

The first law of thermodynamics governs changes in the state function we have called internal energy (E). According to Section 15.3 , changes in the internal energy (ΔE) are closely related to changes in the enthalpy (ΔH), which is a measure of the heat flow between a system and its surroundings at constant pressure. You also learned in Chapter 15 that the enthalpy change for a chemical reaction can be calculated using tabulated values of enthalpies of formation. This information, however, does not tell us whether a particular process or reaction will occur spontaneously.

Let's consider a familiar example of spontaneous change. If a hot frying pan that has just been removed from the stove is allowed to come into contact with a cooler object, such as cold water in a sink, heat will flow from the hotter object to the cooler one, in this case usually releasing steam. Eventually both objects will reach the same temperature, at a value between the initial temperatures of the two objects. This transfer of heat from a hot object to a cooler one obeys the first law of thermodynamics: energy is conserved.

Now consider the same process in reverse. Suppose that a hot frying pan in a sink of cold water were to become hotter while the water became cooler. As long as the same amount of thermal energy was gained by the frying pan and lost by the water, the first law of thermodynamics would be satisfied. Yet we all know that such a process cannot occur: heat always flows from a hot object to a cold one, never in the reverse direction. That is, *by itself* the magnitude of the heat flow associated with a process does not predict whether the process will occur spontaneously.

For many years, chemists and physicists tried to identify a single measurable quantity that would enable them to predict whether a particular process or reaction would occur spontaneously. Initially, many of them focused on enthalpy changes and hypothesized that an exothermic process would always be spontaneous. But although it is true that many, if not most, spontaneous processes are exothermic, there are also many spontaneous processes that are *not* exothermic. For example, at a pressure of 1 atm, ice melts spontaneously at temperatures greater than 0°C, yet this is an endothermic process because heat is absorbed. Similarly, many salts (such as NH_4NO_3, NaCl, and KBr) dissolve spontaneously in water even though they absorb heat from the surroundings as they dissolve (i.e., $\Delta H_{soln} > 0$). Reactions can also be both spontaneous and highly endothermic, like the reaction of barium hydroxide with ammonium thiocyanate shown in Figure 16.1.1



Endothermic Reaction *The reaction of barium hydroxide with ammonium thiocyanate is spontaneous but highly endothermic. Water, one product of the reaction, quickly freezes into slush. When water is placed on a block of wood under the flask, the highly endothermic reaction that takes place in the flask freezes water that has been placed under the beaker, so the flask becomes frozen to the wood.*

Thus enthalpy is not the only factor that determines whether a process is spontaneous. For example, after a cube of sugar has dissolved in a glass of water so that the sucrose molecules are uniformly dispersed in a dilute solution, they never spontaneously come back together in solution to form a sugar cube. Moreover, the molecules of a gas remain evenly distributed throughout the entire volume of a glass bulb and never spontaneously assemble in only one portion of the available volume. To help explain why these phenomena proceed spontaneously in only one direction requires an additional state function called entropy (S), a thermodynamic property of all substances that is proportional to their degree of disorder.

Entropy

Chemical and physical changes in a system may be accompanied by either an increase or a decrease in the disorder of the system, corresponding to an increase in entropy ($\Delta S > 0$) or a decrease in entropy ($\Delta S < 0$), respectively. As with any other state function, the change in entropy is defined as the difference between the entropies of the final and initial states: $\Delta S = S_f - S_i$.

When a gas expands into a vacuum, its entropy increases because the increased volume allows for greater atomic or molecular disorder. The greater the number of atoms or molecules in the gas, the greater the disorder. The magnitude of the entropy of a system depends on the number of microscopic states, or *microstates*, associated with it (in this case, the number of atoms or molecules); that is, the greater the number of microstates, the greater the entropy.

We can illustrate the concepts of microstates and entropy using a deck of playing cards, as shown in Figure 16.1.2. In any new deck, the 52 cards are arranged by four suits, with each suit arranged in descending order. If the cards are shuffled, however, there are approximately 10^{68} different ways they might be arranged, which corresponds to 10^{68} different microscopic states. The entropy of an ordered new deck of cards is therefore low, whereas the entropy of a randomly shuffled deck is high. Card games assign a higher value to a hand that has a low degree of disorder. In games such as five-card poker, only 4 of the 2,598,960 different possible hands, or microstates, contain the highly ordered and valued arrangement of cards called a royal flush, almost 1.1 million hands contain one pair, and more than 1.3 million hands are completely disordered and therefore have no value. Because the last two arrangements are far more probable than the first, the value of a poker hand is inversely proportional to its entropy. For example, a new, unshuffled deck of cards has only a single arrangement, so there is only one microstate. In contrast, a randomly shuffled deck can have any one of approximately 10^{68} different arrangements, which correspond to 10^{68} different microstates.

We can see how to calculate these kinds of probabilities for a chemical system by considering the possible arrangements of a sample of four gas molecules in a two-bulb container (Figure 16.1.2). There are five possible arrangements: all four molecules in the left bulb (I); three molecules in the left bulb and one in the right bulb (II); two molecules in each bulb (III); one molecule in the left bulb and three molecules in the right bulb (IV); and four molecules in the right bulb (V). If we assign a different color to each molecule to keep track of it for this discussion (remember, however, that in reality the molecules are indistinguishable from one another), we can see that there are 16 different ways the four molecules can be distributed in the bulbs, each corresponding to a particular microstate. As shown in Figure 16.1.2, arrangement I is associated with a single microstate, as is arrangement V, so each arrangement has a probability of 1/16. Arrangements II and IV each have a probability of 4/16 because each can exist in four microstates. Similarly, six different microstates can occur as arrangement III, making the probability of this arrangement 6/16. Thus the arrangement that we would expect to encounter, with half the gas molecules in each bulb, is the *most probable* arrangement. The others are not impossible but simply less likely.

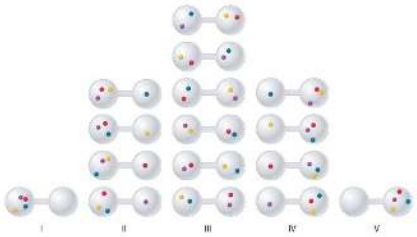


Figure 16.1.2 The Possible Microstates for a Sample of Four Gas Molecules in Two Bulbs of Equal Volume*There are 16 different ways to distribute four gas molecules between the bulbs, with each distribution corresponding to a particular microstate. Arrangements I and V each produce a single microstate with a probability of 1/16. This particular arrangement is relatviely improbable so likely not observed. Arrangements II and IV each produce four microstates, with a probability of 4/16. Arrangement III, with half the gas molecules in each bulb, has a probability of 6/16. It is the one encompassing the most microstates, so it is the most probable.*

Instead of four molecules of gas, let's now consider 1 L of an ideal gas at standard temperature and pressure (STP), which contains 2.69×10^{22} molecules (6.022×10^{23} molecules/22.4 L). If we allow the sample of gas to expand into a second 1 L container, the probability of finding all 2.69×10^{22} molecules in one container and none in the other at any given time is extremely small, approximately 2.69×10^{22} The probability of such an occurrence is effectively zero. Although nothing prevents the molecules in the gas sample from occupying only one of the two bulbs, that particular arrangement is so improbable that it is never actually observed. The probability of arrangements with essentially equal numbers of molecules in each bulb is quite high, however, because there are *many* equivalent microstates in which the molecules are distributed equally. Hence a macroscopic sample of a gas occupies all of the space available to it, simply because this is the most probable arrangement.

A disordered system has a greater number of possible microstates than does an ordered system, so it has a higher entropy. This is most clearly seen in the entropy changes that accompany phase transitions, such as solid to liquid or liquid to gas. As you know from Chapter 7, Chapter 8, and Chapter 9, a crystalline solid is composed of an ordered array of molecules, ions, or atoms that occupy fixed positions in a lattice, whereas the molecules in a liquid are free to move and tumble within the volume of the liquid; molecules in a gas have even more freedom to move than those in a liquid. Each degree of motion increases the number of available microstates, resulting in a higher entropy. Thus the entropy of a system must increase during melting ($\Delta S_{fus} > 0$). Similarly, when a liquid is converted to a vapor, the greater freedom of motion of the molecules in the gas phase means that $\Delta S_{vap} > 0$. Conversely, the reverse processes (condensing a vapor to form a liquid or freezing a liquid to form a solid) must be accompanied by a decrease in the entropy of the system: $\Delta S < 0$.

Note the Pattern

Entropy (S) is a thermodynamic property of all substances that is proportional to their degree of disorder. The greater the number of possible microstates for a system, the greater the disorder and the higher the entropy.

Experiments show that the magnitude of ΔS_{vap} is 80–90 J/(mol·K) for a wide variety of liquids with different boiling points. However, liquids that have highly ordered structures due to hydrogen bonding or other intermolecular interactions tend to have significantly higher values of ΔS_{vap}. For instance, ΔS_{vap} for water is 102 J/(mol·K). Another process that is accompanied by entropy changes is the formation of a solution. As illustrated in Figure 16.1.3, the formation of a liquid solution from a crystalline solid (the solute) and a liquid solvent is expected to result in an increase in the number of available microstates of the system and hence its entropy. Indeed, dissolving a substance such as NaCl in water disrupts both the ordered crystal lattice of NaCl and the ordered hydrogen-bonded structure of water, leading to an increase in the entropy of the system. At the same time, however, each dissolved Na^+ ion becomes hydrated by an ordered arrangement of at least six water molecules, and the Cl^- ions also cause the water to adopt a particular local structure. Both of these effects *increase* the order of the system, leading to a *decrease* in entropy. The overall entropy change for the formation of a solution therefore depends on the relative magnitudes of these opposing factors. In the case

of an NaCl solution, disruption of the crystalline NaCl structure and the hydrogen-bonded interactions in water is quantitatively more important, so $\Delta S_{soln} > 0$.

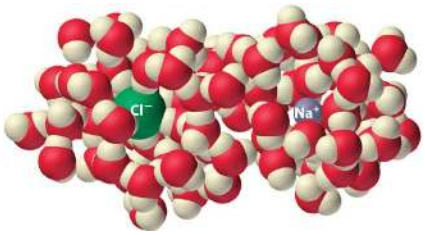


Figure 16.1.3 The Effect of Solution Formation on Entropy *Dissolving NaCl in water results in an increase in the entropy of the system. Each hydrated ion, however, forms an ordered arrangement with water molecules, which decreases the entropy of the system. The magnitude of the increase is greater than the magnitude of the decrease, so the overall entropy change for the formation of an NaCl solution is positive.*

Example 16.1.1

Predict which substance in each pair has the higher entropy and justify your answer.

1. 1 mol of $NH_3(g)$ or 1 mol of He(g), both at 25°C
2. 1 mol of Pb(s) at 25°C or 1 mol of Pb(l) at 800°C

Given: amounts of substances and temperature

Asked for: higher entropy

Strategy:

From the number of atoms present and the phase of each substance, predict which has the greater number of available microstates and hence the higher entropy.

Solution:

1. Both substances are gases at 25°C, but one consists of He atoms and the other consists of NH_3 molecules. With four atoms instead of one, the NH_3 molecules have more motions available, leading to a greater number of microstates. Hence we predict that the NH_3 sample will have the higher entropy.
2. The nature of the atomic species is the same in both cases, but the phase is different: one sample is a solid, and one is a liquid. Based on the greater freedom of motion available to atoms in a liquid, we predict that the liquid sample will have the higher entropy.

Exercise

Predict which substance in each pair has the higher entropy and justify your answer.

1. 1 mol of He(g) at 10 K and 1 atm pressure or 1 mol of He(g) at 250°C and 0.2 atm
2. a mixture of 3 mol of $H_2(g)$ and 1 mol of $N_2(g)$ at 25°C and 1 atm or a sample of 2 mol of $NH_3(g)$ at 25°C and 1 atm

Answer:

1. 1 mol of He(g) at 250°C and 0.2 atm (higher temperature and lower pressure indicate greater volume and more microstates)
2. a mixture of 3 mol of $H_2(g)$ and 1 mol of $N_2(g)$ at 25°C and 1 atm (more molecules of gas are present)

Reversible and Irreversible Changes

Changes in entropy (ΔS), together with changes in enthalpy (ΔH), enable us to predict in which direction a chemical or physical change will occur spontaneously. Before discussing how to do so, however, we must understand the difference between a reversible process and an irreversible one. In a reversible process, every intermediate state between the extremes is an equilibrium state, regardless of the direction of the change. In contrast, an irreversible process is one in which the intermediate states are not equilibrium states, so change occurs spontaneously in only one direction. As a result, *a reversible process can change direction at any time, whereas an irreversible process cannot*. When a gas expands reversibly against an external pressure such as a piston, for example, the expansion can be reversed at any time by reversing the motion of the piston; once the gas is compressed, it can be allowed to expand again, and the process can continue indefinitely. In contrast, the expansion of a gas into a vacuum ($P_{ext} = 0$) is irreversible because the external pressure is measurably less than the internal pressure of the gas. No equilibrium states exist, and the gas expands irreversibly. When gas escapes from a microscopic hole in a balloon into a vacuum, for example, the process is irreversible; the direction of airflow cannot change.

Because work done during the expansion of a gas depends on the opposing external pressure ($w = P_{ext}\Delta V$), *work done in a reversible process is always equal to or greater than work done in a corresponding irreversible process*: $w_{rev} \geq w_{irrev}$. Whether a process is reversible or irreversible, $\Delta E = q + w$. Because E is a state function, the magnitude of ΔE does *not* depend on reversibility and is independent of the path taken. So

$$\Delta E = q_{rev} + w_{rev} = q_{irrev} + w_{irrev}$$

Note the Pattern

Work done in a reversible process is always equal to or greater than work done in a corresponding irreversible process: $w_{rev} \geq w_{irrev}$.

In other words, ΔE for a process is the same whether that process is carried out in a reversible manner or an irreversible one. We now return to our earlier definition of entropy, using the magnitude of the heat flow for a reversible process (q_{rev}) to define entropy quantitatively.

The Relationship between Internal Energy and Entropy

Because the quantity of heat transferred (q_{rev}) is directly proportional to the absolute temperature of an object (T) ($q_{rev} \propto T$), the hotter the object, the greater the amount of heat transferred. Moreover, adding heat to a system increases the kinetic energy of the component atoms and molecules and hence their disorder ($\Delta S \propto q_{rev}$). Combining these relationships for any reversible process,

$$q_{rev} = T\Delta S \;\; and \;\; \Delta S = \frac{q_{rev}}{T}$$

Because the numerator (q_{rev}) is expressed in units of energy (joules), the units of ΔS are joules/kelvin (J/K). Recognizing that the work done in a reversible process at constant pressure is $w_{rev} = -P\Delta V$, we can express Equation 16.1.1 as follows:

$$\Delta E = q_{rev} + w_{rev} = T\Delta S - P\Delta V$$

Thus the change in the internal energy of the system is related to the change in entropy, the absolute temperature, and the PV work done.

To illustrate the use of Equation 16.1.2 and Equation 16.1.3, we consider two reversible processes before turning to an irreversible process. When a sample of an ideal gas is allowed to expand reversibly at constant temperature, heat must be added to the gas during expansion to keep its T constant (Figure 16.1.4). The internal energy of the gas does not change because the temperature of the gas does not change; that is, $\Delta E = 0$ and $q_{rev} = -w_{rev}$. During expansion, $\Delta V > 0$, so the gas performs work on its surroundings: $w_{rev} = -P\Delta V < 0$. According to Equation 16.1.3, this means that q_{rev} must increase during expansion; that is, the gas must absorb heat from the surroundings during expansion, and the surroundings must give up that same amount of heat. The entropy change of the system is therefore $\Delta S_{sys} = +q_{rev}/T$, and the entropy change of the surroundings is $\Delta S_{surr} = -q_{rev}/T$. The corresponding change in entropy of the universe is then as follows:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = \frac{q_{rev}}{T} + \left(-\frac{q_{rev}}{T}\right) = 0$$

Thus no change in ΔS_{univ} has occurred.

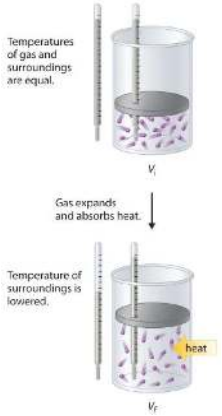


Figure 16.1.4 Expansion of Gas at Constant Temperature *In the initial state (top), the temperatures of a gas and the surroundings are the same. During the reversible expansion of the gas, heat must be added to the gas to maintain a constant temperature. Thus the internal energy of the gas does not change, but work is performed on the surroundings. In the final state (bottom), the temperature of the surroundings is lower because the gas has absorbed heat from the surroundings during expansion.*

Now consider the reversible melting of a sample of ice at 0°C and 1 atm. The enthalpy of fusion of ice is 6.01 kJ/mol, which means that 6.01 kJ of heat are absorbed reversibly from the surroundings when 1 mol of ice melts at 0°C, as illustrated in Figure 16.1.5. The surroundings constitute a sample of low-density carbon foam that is thermally conductive, and the system is the ice cube that has been placed on it. The direction of heat flow along the resulting temperature gradient is indicated with an arrow. From Equation 16.1.2, we see that the entropy of fusion of ice can be written as follows:

$$\Delta S_{fus} = \frac{q_{rev}}{T} = \frac{\Delta H_{fus}}{T}$$



Figure 16.1.5 Thermograms Showing That Heat Is Absorbed from the Surroundings When Ice Melts at 0°C *By convention, a thermogram shows cold regions in blue, warm regions in red, and thermally intermediate regions in green. When an ice cube (the system, dark blue) is placed on the corner of a square sample of low-density carbon foam with very high thermal conductivity, the temperature of the foam is lowered (going from red to green). As the ice melts, a temperature gradient appears, ranging from warm to very cold. An arrow indicates the direction of heat flow from the surroundings (red and green) to the ice cube. The amount of heat lost by the surroundings is the same as the amount gained by the ice, so the entropy of the universe does not change.*

In this case, ΔS_{fus} = (6.01 kJ/mol)/(273 K) = 22.0 J/(mol·K) = ΔS_{sys}. The amount of heat lost by the surroundings is the same as the amount gained by the ice, so $\Delta S_{surr} = q_{rev}/T$ = −(6.01 kJ/mol)/(273 K) = −22.0 J/(mol·K). Once again, we see that the entropy of the universe does not change:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 22.0\ J/(mol \cdot K) - 22.0\ J/(mol \cdot K) = 0$$

In these two examples of reversible processes, the entropy of the universe is unchanged. This is true of all reversible processes and constitutes part of the second law of thermodynamics: *the entropy of the universe remains constant in a reversible process, whereas the entropy of the universe increases in an irreversible (spontaneous) process*.

Note the Pattern

The entropy of the universe increases during a spontaneous process.

As an example of an irreversible process, consider the entropy changes that accompany the spontaneous and irreversible transfer of heat from a hot object to a cold one, as occurs when lava spewed from a volcano flows into cold ocean water. The cold substance, the water, gains heat ($q > 0$), so the change in the entropy of the water can be written as $\Delta S_{cold} = q/T_{cold}$. Similarly, the hot substance, the lava, loses heat ($q < 0$), so its entropy change can be written as $\Delta S_{hot} = -q/T_{hot}$, where T_{cold} and T_{hot} are the temperatures of the cold and hot substances, respectively. The total entropy change of the universe accompanying this process is therefore

$$\Delta S_{univ} = \Delta S_{cold} + \Delta S_{hot} = \frac{q}{T_{cold}} + \left(-\frac{q}{T_{hot}}\right)$$

The numerators on the right side of Equation 16.1.6 are the same in magnitude but opposite in sign. Whether ΔS_{univ} is positive or negative depends on the relative magnitudes of the denominators. By definition, $T_{hot} > T_{cold}$, so $-q/T_{hot}$ must be less than q/T_{cold}, and ΔS_{univ} must be positive. As predicted by the second law of thermodynamics, the entropy of the universe increases during this irreversible process. Any process for which ΔS_{univ} is positive is, by definition, a spontaneous one that will occur as written. Conversely, any process for which ΔS_{univ} approaches zero will not occur spontaneously as written but will occur spontaneously in the reverse direction. We see, therefore, that heat is spontaneously transferred from a hot substance, the lava, to a cold substance, the ocean water. In fact, if the lava is hot enough (e.g., if it is molten), so much heat can be transferred that the water is converted to steam (Figure 16..3.6).



Figure 16.1.6 Spontaneous Transfer of Heat from a Hot Substance to a Cold Substance *When molten lava flows into cold ocean water, so much heat is spontaneously transferred to the water that steam is produced.*

Example 6

Tin has two allotropes with different structures. Gray tin (α-tin) has a structure similar to that of diamond, whereas white tin (β-tin) is denser, with a unit cell structure that is based on a rectangular prism. At temperatures greater than 13.2°C, white tin is the more stable phase, but below that temperature, it slowly converts reversibly to the less dense, powdery gray phase. This phenomenon plagued Napoleon's army during his ill-fated invasion of Russia in 1812: the buttons on his

soldiers' uniforms were made of tin and disintegrated during the Russian winter, adversely affecting the soldiers' health (and morale). The conversion of white tin to gray tin is exothermic, with $\Delta H = -2.1$ kJ/mol at 13.2°C.

1. What is ΔS for this process?
2. Which is the more highly ordered form of tin—white or gray?

Given: ΔH and temperature

Asked for: ΔS and relative degree of order

Strategy:

Use Equation 16.1.2 to calculate the change in entropy for the reversible phase transition. From the calculated value of ΔS, predict which allotrope has the more highly ordered structure.

Solution:

1. We know from Equation 16.1.2 that the entropy change for any reversible process is the heat transferred (in joules) divided by the temperature at which the process occurs. Because the conversion occurs at constant pressure, and ΔH and ΔE are essentially equal for reactions that involve only solids, we can calculate the change in entropy for the reversible phase transition where $q_{rev} = \Delta H$. Substituting the given values for ΔH and temperature in kelvins (in this case, T = 13.2°C = 286.4 K),

$$\Delta S = \frac{q_{rev}}{T} = \frac{\left(-2.1\ \cancel{kJ}/mol\right)\left(1000\ J/\cancel{kJ}\right)}{286.4\ K} = -7.3\ J/(mol \cdot K)$$

2. The fact that $\Delta S < 0$ means that entropy decreases when white tin is converted to gray tin. Thus gray tin must be the more highly ordered structure.

Exercise

Elemental sulfur exists in two forms: an orthorhombic form (S_α), which is stable below 95.3°C, and a monoclinic form (S_β), which is stable above 95.3°C. The conversion of orthorhombic sulfur to monoclinic sulfur is endothermic, with ΔH = 0.401 kJ/mol at 1 atm.

1. What is ΔS for this process?
2. Which is the more highly ordered form of sulfur—S_α or S_β?

Answer:

1. 1.09 J/(mol·K)
2. S_α

Summary

A measure of the disorder of a system is its **entropy (*S*)**, a state function whose value increases with an increase in the number of available microstates. A **reversible process** is one for which all intermediate states between extremes are equilibrium states; it can change direction at any time. In contrast, an **irreversible process** occurs in one direction only. The change in entropy of the system or the surroundings is the quantity of heat transferred divided by the temperature. The **second law of thermodynamics** states that in a reversible process, the entropy of the universe is constant, whereas in an irreversible process, such as the transfer of heat from a hot object to a cold object, the entropy of the universe increases.

Key Takeaways

- For a given system, the greater the number of microstates, the higher the entropy.

- During a spontaneous process, the entropy of the universe increases.

Key Equation

Entropy change

Equation 16.1.2: $\Delta S = \frac{q_{rev}}{T}$ </math>

Conceptual Problems

1. A Russian space vehicle developed a leak, which resulted in an internal pressure drop from 1 atm to 0.85 atm. Is this an example of a reversible expansion? Has work been done?
2. Which member of each pair do you expect to have a higher entropy? Why?
   a. solid phenol or liquid phenol
   b. 1-butanol or butane
   c. cyclohexane or cyclohexanol
   d. 1 mol of N_2 mixed with 2 mol of O_2 or 2 mol of NO_2
   e. 1 mol of O_2 or 1 mol of O_3
   f. 1 mol of propane at 1 atm or 1 mol of propane at 2 atm
3. Determine whether each process is reversible or irreversible.
   a. ice melting at 0°C
   b. salt crystallizing from a saline solution
   c. evaporation of a liquid in equilibrium with its vapor in a sealed flask
   d. a neutralization reaction
4. Determine whether each process is reversible or irreversible.
   a. cooking spaghetti
   b. the reaction between sodium metal and water
   c. oxygen uptake by hemoglobin
   d. evaporation of water at its boiling point
5. Explain why increasing the temperature of a gas increases its entropy. What effect does this have on the internal energy of the gas?
6. For a series of related compounds, does ΔS_{vap} increase or decrease with an increase in the strength of intermolecular interactions in the liquid state? Why?
7. Is the change in the enthalpy of reaction or the change in entropy of reaction more sensitive to changes in temperature? Explain your reasoning.
8. Solid potassium chloride has a highly ordered lattice structure. Do you expect ΔS_{soln} to be greater or less than zero? Why? What opposing factors must be considered in making your prediction?
9. Aniline ($C_6H_5NH_2$) is an oily liquid at 25°C that darkens on exposure to air and light. It is used in dying fabrics and in staining wood black. One gram of aniline dissolves in 28.6 mL of water, but aniline is completely miscible with ethanol. Do you expect ΔS_{soln} in H_2O to be greater than, less than, or equal to ΔS_{soln} in CH_3CH_2OH? Why?

Answers

1. No, it is irreversible; no work is done because the external pressure is effectively zero.
2.
3. a. reversible
   b. irreversible
   c. reversible
   d. irreversible
4.

5.
6.
7.
8.
9. Water has a highly ordered, hydrogen-bonded structure that must reorganize to accommodate hydrophobic solutes like aniline. In contrast, we expect that aniline will be able to disperse randomly throughout ethanol, which has a significantly less ordered structure. We therefore predict that ΔS_{soln} in ethanol will be more positive than ΔS_{soln} in water.

Numerical Problems

1. Liquid nitrogen, which has a boiling point of −195.79°C, is used as a coolant and as a preservative for biological tissues. Is the entropy of nitrogen higher or lower at −200°C than at −190°C? Explain your answer. Liquid nitrogen freezes to a white solid at −210.00°C, with an enthalpy of fusion of 0.71 kJ/mol. What is its entropy of fusion? Is freezing biological tissue in liquid nitrogen an example of a reversible process or an irreversible process?
2. Using the second law of thermodynamics, explain why heat flows from a hot body to a cold body but not from a cold body to a hot body.
3. One test of the spontaneity of a reaction is whether the entropy of the universe increases: $\Delta S_{univ} > 0$. Using an entropic argument, show that the following reaction is spontaneous at 25°C:
   $4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$
   Why does the entropy of the universe increase in this reaction even though gaseous molecules, which have a high entropy, are consumed?
4. Calculate the missing data in the following table.

Compound	ΔH_{fus} (kJ/mol)	ΔS_{fus} [J/(mol·K)]	Melting Point (°C)
acetic acid	11.7		16.6
CH_3CN	8.2	35.9	
CH_4	0.94		−182.5
CH_3OH		18.2	−97.7
formic acid	12.7	45.1	

   Based on this table, can you conclude that entropy is related to the nature of functional groups? Explain your reasoning.
5. Calculate the missing data in the following table.

Compound	ΔH_{vap} (kJ/mol)	ΔS_{vap} [J/(mol·K)]	Boiling Point (°C)
hexanoic acid	71.1		105.7
hexane	28.9	85.5	
formic acid		60.7	100.8
1-hexanol	44.5		157.5

   The text states that the magnitude of ΔS_{vap} tends to be similar for a wide variety of compounds. Based on the values in the table, do you agree?

Contributors

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An Endothermic Reaction from the University of Washington, Department of Chemistry on YouTube

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Chapter 16.2: Entropy Changes and the Third Law of Thermodynamics

Learning Objectives

- To use thermodynamic cycles to calculate changes in entropy.

The atoms, molecules, or ions that compose a chemical system can undergo several types of molecular motion, including translation, rotation, and vibration (Figure 16.2.1). The greater the molecular motion of a system, the greater the number of possible microstates and the higher the entropy. A perfectly ordered system with only a single microstate available to it would have an entropy of zero. The only system that meets this criterion is a perfect crystal at a temperature of absolute zero (0 K), in which each component atom, molecule, or ion is fixed in place within a crystal lattice and exhibits no motion. Such a state of perfect order (or, conversely, zero disorder) corresponds to zero entropy. In practice, absolute zero is an ideal temperature that is unobtainable, and a perfect single crystal is also an ideal that cannot be achieved. Nonetheless, the combination of these two ideals constitutes the basis for the third law of thermodynamics: *the entropy of any perfectly ordered, crystalline substance at absolute zero is zero*.

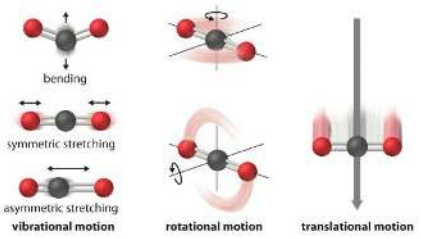


Figure 16.2.1 Molecular Motions*Vibrational, rotational, and translational motions of a carbon dioxide molecule are illustrated here. Only a perfectly ordered, crystalline substance at absolute zero would exhibit no molecular motion and have zero entropy. In practice, this is an unattainable ideal.*

The third law of thermodynamics has two important consequences: it defines the *sign* of the entropy of any substance at temperatures above absolute zero as positive, and it provides a fixed reference point that allows us to measure the *absolute entropy* of any substance at any temperature.In practice, chemists determine the absolute entropy of a substance by measuring the molar heat capacity (C_p) as a function of temperature and then plotting the quantity C_p/T versus T. The *area* under the curve between 0 K and any temperature T is the absolute entropy of the substance at T. In contrast, other thermodynamic properties, such as internal energy and enthalpy, can be evaluated in only *relative* terms, not absolute terms. In this section, we examine two different ways to calculate ΔS for a reaction or a physical change. The first, based on the definition of absolute entropy provided by the third law of thermodynamics, uses tabulated values of absolute entropies of substances. The second, based on the fact that entropy is a state function, uses a thermodynamic cycle similar to those we first encountered in Chapter 9.

Calculating ΔS from Standard Molar Entropy Values

One way of calculating ΔS for a reaction is to use tabulated values of the standard molar entropy ($S°$), which is the entropy of 1 mol of a substance at a standard temperature of 298 K; the units of $S°$ are J/(mol·K). Unlike enthalpy or internal energy, it is possible to obtain absolute entropy values by measuring the entropy change that occurs between the reference point of 0 K [corresponding to S = 0 J/(mol·K)] and 298 K.

As shown in Table 16.2.1 , for substances with approximately the same molar mass and number of atoms, $S°$ values fall in the order $S°$(gas) > $S°$(liquid) > $S°$(solid). For instance, $S°$ for liquid water is 70.0 J/(mol·K), whereas $S°$ for water vapor is 188.8 J/(mol·K). Likewise, $S°$ is 260.7 J/(mol·K) for gaseous I_2 and 116.1 J/(mol·K) for solid I_2. This order makes qualitative sense based on the kinds and extents of motion available to atoms and molecules in the three phases. The correlation between physical state and absolute entropy is illustrated in Figure 16.2.2, which is a generalized plot of the entropy of a substance versus temperature.

Table 16.2.1 Standard Molar Entropy Values of Selected Substances at 25°C

Substance	$S°$ [J/(mol·K)]
Gases	
He	126.2
H_2	130.7
Ne	146.3
Ar	154.8
Kr	164.1
Xe	169.7
H_2O	188.8
N_2	191.6
O_2	205.2
CO_2	213.8
I_2	260.7
Liquids	
H_2O	70.0
CH_3OH	126.8
Br_2	152.2
CH_3CH_2OH	160.7
C_6H_6	173.4
CH_3COCl	200.8
C_6H_{12} (cyclohexane)	204.4
C_8H_{18} (isooctane)	329.3
Solids	
C (diamond)	2.4
C (graphite)	5.7
LiF	35.7
SiO_2 (quartz)	41.5
Ca	41.6
Na	51.3
MgF_2	57.2
K	64.7
NaCl	72.1
KCl	82.6

Substance	$S°$ [J/(mol·K)]
I_2	116.1

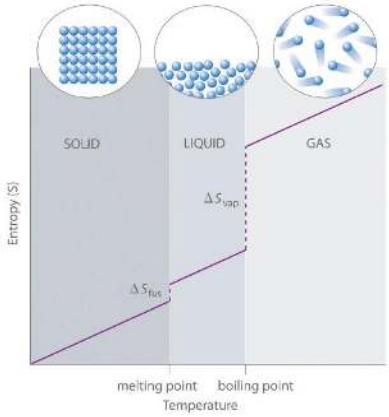


Figure 16.2.2 A Generalized Plot of Entropy versus Temperature for a Single Substance *Absolute entropy increases steadily with increasing temperature until the melting point is reached, where it jumps suddenly as the substance undergoes a phase change from a highly ordered solid to a disordered liquid (ΔS_{fus}). The entropy again increases steadily with increasing temperature until the boiling point is reached, where it jumps suddenly as the liquid undergoes a phase change to a highly disordered gas (ΔS_{vap}).*

A closer examination of Table 16.2.1 also reveals that substances with similar molecular structures tend to have similar $S°$ values. Among crystalline materials, those with the lowest entropies tend to be rigid crystals composed of small atoms linked by strong, highly directional bonds, such as diamond [$S° = 2.4$ J/(mol·K)]. In contrast, graphite, the softer, less rigid allotrope of carbon, has a higher $S°$ [5.7 J/(mol·K)] due to more disorder in the crystal. Soft crystalline substances and those with larger atoms tend to have higher entropies because of increased molecular motion and disorder. Similarly, the absolute entropy of a substance tends to increase with increasing molecular complexity because the number of available microstates increases with molecular complexity. For example, compare the $S°$ values for $CH_3OH(l)$ and $CH_3CH_2OH(l)$. Finally, substances with strong hydrogen bonds have lower values of $S°$, which reflects a more ordered structure.

To calculate $\Delta S°$ for a chemical reaction from standard molar entropies, we use the familiar "products minus reactants" rule, in which the absolute entropy of each reactant and product is multiplied by its stoichiometric coefficient in the balanced chemical equation. Example 7 illustrates this procedure for the combustion of the liquid hydrocarbon isooctane (C_8H_{18}; 2,2,4-trimethylpentane).

Example 16.2.1

Use the data in Table 16.2.1 to calculate $\Delta S°$ for the reaction of liquid isooctane with $O_2(g)$ to give $CO_2(g)$ and $H_2O(g)$ at 298 K.

Given: standard molar entropies, reactants, and products

Asked for: $\Delta S°$

Strategy:

Write the balanced chemical equation for the reaction and identify the appropriate quantities in Table 16.2.1. Subtract the sum of the absolute entropies of the reactants from the sum of the absolute entropies of the products, each multiplied by their appropriate stoichiometric coefficients, to obtain $\Delta S°$ for the reaction.

Solution:

The balanced chemical equation for the complete combustion of isooctane (C_8H_{18}) is as follows:

$$C_8H18\,(l) + \frac{25}{2}O_2\,(g) \rightarrow 8CO_2\,(g) + 9H_2O\,(g)$$

We calculate $\Delta S°$ for the reaction using the "products minus reactants" rule, where m and n are the stoichiometric coefficients of each product and each reactant:

$$\Delta S_{rxn} = \sum mS_o\,(products) - \sum nS_o\,(reactants)$$

$$= [8S_o\,(CO_2) + 9S_o\,(H_2O)] - \left[S_o\,(C_8H_{18}) + \frac{25}{2}S_o\,(O_2)\right]$$

$$= \left\{\left[8\ \cancel{mol}\ CO_2 \times 213.8\ J/\left(\cancel{mol}\cdot K\right)\right] + \left[9\ \cancel{mol}\ H_2O \times 188.8\ J/\left(\cancel{mol}\cdot K\right)\right]\right\}$$
$$-\left\{\left[1\ \cancel{mol}\ C_8H_{18} \times 329.3\ J/\left(\cancel{mol}\cdot K\right)\right] + \left[\frac{25}{2}\ \cancel{mol}\ O_2 \times 205.2\ J/\left(\cancel{mol}\cdot K\right)\right]\right\}$$

\(=515.3 J/K \

$\Delta S°$ is positive, as expected for a combustion reaction in which one large hydrocarbon molecule is converted to many molecules of gaseous products.

Exercise

Use the data in Table 16.2.1 to calculate $\Delta S°$ for the reaction of H_2(g) with liquid benzene (C_6H_6) to give cyclohexane (C_6H_{12}).

Answer: −361.1 J/K

Note the Pattern

Entropy increases with softer, less rigid solids, solids that contain larger atoms, and solids with complex molecular structures.

Note the Pattern

$\Delta S°$ for a reaction can be calculated from absolute entropy values using the same "products minus reactants" rule used to calculate $\Delta H°$.

Calculating ΔS from Thermodynamic Cycles

We can also calculate a change in entropy using a thermodynamic cycle. As you learned, the molar heat capacity (C_p) is the amount of heat needed to raise the temperature of 1 mol of a substance by 1°C at constant pressure. Similarly, C_v is the amount of heat needed to raise the temperature of 1 mol of a substance by 1°C at constant volume. The increase in entropy with increasing temperature in Figure 16.2.2 is approximately proportional to the heat capacity of the substance.

Recall that the entropy change (ΔS) is related to heat flow (q_{rev}) by $\Delta S = q_{rev}/T$. Because $q_{rev} = nC_p\Delta T$ at constant pressure or $nC_v\Delta T$ at constant volume, where n is the number of moles of substance present, the change in entropy for a substance whose temperature changes from T_1 to T_2 is as follows:

$$dS = \frac{q_{rev}}{T} = nC_p\frac{dT}{T_P}$$

Integrating both sides of the equation from T_1 to T_2.

$$\Delta S = nC_p\,ln\frac{T_2}{T_1}\quad (constant\ pressure)$$

Similarly,

$$\Delta S = nC_v \, ln\frac{T_2}{T_1} \quad (constant\ volume)$$

Thus we can use a combination of heat capacity measurements (Equation 16.2.1 or Equation 16.2.2) and experimentally measured values of enthalpies of fusion or vaporization if a phase change is involved to calculate the entropy change corresponding to a change in the temperature of a sample.

We can use a thermodynamic cycle to calculate the entropy change when the phase change for a substance such as sulfur cannot be measured directly. As noted in the exercise in Example 6, elemental sulfur exists in two forms (part (a) in Figure 16.2.3): an orthorhombic form with a highly ordered structure (S_α) and a less-ordered monoclinic form (S_β). The orthorhombic (α) form is more stable at room temperature but undergoes a phase transition to the monoclinic (β) form at temperatures greater than 95.3°C (368.5 K). The transition from S_α to S_β can be described by the thermodynamic cycle shown in part (b) in Figure 16.2.3, in which liquid sulfur is an intermediate. The change in entropy that accompanies the conversion of liquid sulfur to S_β ($-\Delta S_{fus(\beta)} = \Delta S_3$ in the cycle) cannot be measured directly. Because entropy is a state function, however, ΔS_3 can be calculated from the overall entropy change (ΔS_t) for the S_α–S_β transition, which equals the sum of the ΔS values for the steps in the thermodynamic cycle, using Equation 16.2.2 and tabulated thermodynamic parameters (the heat capacities of S_α and S_β, $\Delta H_{fus(\alpha)}$, and the melting point of S_α.)

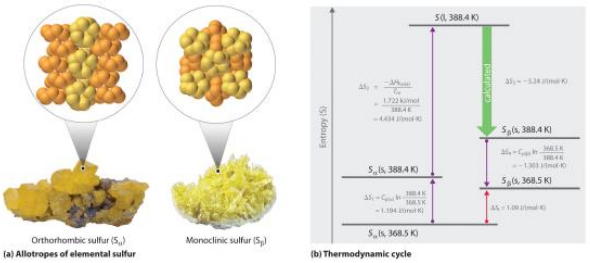


Figure 16.2.3 Two Forms of Elemental Sulfur and a Thermodynamic Cycle Showing the Transition from One to the Other *(a) Orthorhombic sulfur (S_α) has a highly ordered structure in which the S_8 rings are stacked in a "crankshaft" arrangement. Monoclinic sulfur (S_β) is also composed of S_8 rings but has a less-ordered structure. (b) At 368.5 K, S_α undergoes a phase transition to S_β. Although ΔS_3 cannot be measured directly, it can be calculated using the values shown in this thermodynamic cycle.*

If we know the melting point of S_α (T_m = 115.2°C = 388.4 K) and ΔS_t for the overall phase transition [calculated to be 1.09 J/(mol·K) in the exercise in Example 6], we can calculate ΔS_3 from the values given in part (b) in Figure 16.2.3 where $C_{p(\alpha)}$ = 22.70 J/mol·K and $C_{p(\beta)}$ = 24.77 J/mol·K (subscripts on ΔS refer to steps in the cycle):

$$\Delta S_t = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4$$

$$1.09\ J/(mol \cdot K) = C_{p(\alpha)}\, ln\frac{T_2}{T_1} + \frac{\Delta H_{fus}}{T_m} + \Delta S_3 + C_{p(\beta)}\, ln\frac{T_4}{T_3}$$

|(=22.70\; J/\left (mol\cdot K \right)ln\dfrac{388.4}{368.5}+\dfrac{1.722\;\cancel{kJ}/mol}{388.4\;K}\times 1000\; J/\cancel{kJ} + \Delta S_{3}+24.77\; J/\left (mol\cdot K \right)ln\dfrac{368.5}{388.4}\)

$$[1.194\ J/(mol \cdot K)] + [4.434\ J/(mol \cdot K)] + \Delta S_3 + [-1.303\ J/(mol \cdot K)]$$

Solving for ΔS_3 gives a value of −3.24 J/(mol·K). As expected for the conversion of a less ordered state (a liquid) to a more ordered one (a crystal), ΔS_3 is negative.

Summary

The **third law of thermodynamics** states that the entropy of any perfectly ordered, crystalline substance at absolute zero is zero. At temperatures greater than absolute zero, entropy has a positive value, which allows us to measure the *absolute entropy* of a substance. Measurements of the heat capacity of a substance and the enthalpies of fusion or vaporization can be used to calculate the changes in entropy that accompany a physical change. The entropy of 1 mol of a substance at a standard

temperature of 298 K is its **standard molar entropy (*S*°)**. We can use the "products minus reactants" rule to calculate the standard entropy change (Δ*S*°) for a reaction using tabulated values of *S*° for the reactants and the products.

Key Takeaway

- Entropy changes can be calculated using the "products minus reactants" rule or from a combination of heat capacity measurements and measured values of enthalpies of fusion or vaporization.

Key Equations

Temperature dependence of entropy at constant pressure

Equation 16.2.2: $\Delta S = nC_p \ln\frac{T_2}{T_1}$

Temperature dependence of entropy at constant volume

Equation 16.2.3: $\Delta S = nC_v \ln\frac{T_2}{T_1}$

Conceptual Problems

1. Crystalline $MgCl_2$ has $S°$ = 89.63 J/(mol·K), whereas aqueous $MgCl_2$ has $S°$ = −25.1 J/(mol·K). Is this consistent with the third law of thermodynamics? Explain your answer.
2. Why is it possible to measure absolute entropies but not absolute enthalpies?
3. How many microstates are available to a system at absolute zero? How many are available to a substance in its liquid state?
4. Substance A has a higher heat capacity than substance B. Do you expect the absolute entropy of substance A to be less than, similar to, or greater than that of substance B? Why? As the two substances are heated, for which substance do you predict the entropy to increase more rapidly?
5. Phase transitions must be considered when calculating entropy changes. Why?

Numerical Problems

1. What is the final temperature of water when 5.20 g of ice at 0.0°C are added to 250 mL of water in an insulated thermos at 30.0°C? The value of ΔH_{fus} for water is 6.01 kJ/mol, and the heat capacity of liquid water is 75.3 J/(mol·°C). What is the entropy change for this process?
2. Calculate the change in both enthalpy and entropy when a 3.0 g block of ice melts at 0.0°C [$\Delta H_{fus}(H_2O)$ = 6.01 kJ/mol]. For the same block of ice, calculate the entropy change for the system when the ice is warmed from 0.0°C to 25°C. The heat capacity of liquid water over this temperature range is 75.3 J/(mol·°C).
3. Use the data in Table 16.2.1 and CStandard Thermodynamic Quantities for Chemical Substances at 25°C" to calculate Δ*S*° for each reaction.
   a. $H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$
   b. $CH_3OH(l) + HCl(g) \rightarrow CH_3Cl(g) + H_2O(l)$
   c. $H_2(g) + Br_2(l) \rightarrow 2HBr(g)$
   d. $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(s) + H_2(g)$
4. Calculate the entropy change (J/K) when 4.35 g of liquid bromine are heated from 30.0°C to 50.0°C if the molar heat capacity (C_p) of liquid bromine is 75.1 kJ/(mol·K).
5. Calculate the molar heat capacity (C_p) of titanium tetrachloride if the change in entropy when a 6.00 g sample of $TiCl_4(l)$ is heated from 25.0°C to 40.0°C is 0.154 J/K.
6. When a 1.00 g sample of lead is heated from 298.2 K to just below its melting temperature of 600.5 K, the change in entropy is 0.0891 J/K. Determine the molar heat capacity (C_p) of lead over this temperature range.

7. Phosphorus oxychloride ($POCl_3$) is a chlorinating agent that is frequently used in organic chemistry to replace oxygen with chlorine. Given ΔS_{vap} = 93.08 J/(mol·K) and ΔH_{vap} = 35.2 kJ/mol, does $POCl_3$ spontaneously convert from a liquid to a gas at 110°C? Does it spontaneously crystallize at 0.0°C if ΔH_{fus} = 34.3 kJ/mol and ΔS_{fus} = 125 J/(mol·K)? Using the information provided, what is the melting point of $POCl_3$?
8. A useful reagent for the fluorination of alcohols, carboxylic acids, and carbonyl compounds is selenium tetrafluoride (SeF_4). One must be careful when using this compound, however, because it is known to attack glass (such as the glass of a reaction vessel).
    a. Is SeF_4 a liquid or a gas at 100°C given that ΔH_{vap} = 46.9 kJ/mol and ΔS_{vap} = 124 J/(mol·K)?
    b. Determine the boiling point of SeF_4.
    c. Would you use SeF_4 for a solution reaction at 0°C if ΔH_{fus} = 46 kJ/mol and ΔS_{fus} = 178 J/(mol·K)?

Answers

1. 27.8°C; 0.85 J.
2.
3. a. −163.3 J/K
    b. −9.1 J/K
    c. 114.5 J/K
    d. −173.2 J/K
4.
5. 25.0 J/(mol·K)
6.
7. yes; yes; 274 K
8.

Contributors

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Chapter 16.3: Free Energy

Learning Objectives

- To understand the relationship between Gibbs free energy and work.

One of the major goals of chemical thermodynamics is to establish criteria for predicting whether a particular reaction or process will occur spontaneously. We have developed one such criterion, the change in entropy of the universe: if $\Delta S_{univ} > 0$ for a process or a reaction, then the process will occur spontaneously as written. Conversely, if $\Delta S_{univ} < 0$, a process cannot occur spontaneously; if $\Delta S_{univ} = 0$, the system is at equilibrium. The sign of ΔS_{univ} is a universally applicable and infallible indicator of the spontaneity of a reaction. Unfortunately, using ΔS_{univ} requires that we calculate ΔS for *both* a system *and* its surroundings. This is not particularly useful for two reasons: we are normally much more interested in the system than in the surroundings, and it is difficult to make quantitative measurements of the surroundings (i.e., the rest of the universe). A criterion of spontaneity that is based solely on the state functions of a *system* would be much more convenient and is provided by a new state function: the Gibbs free energy.

Gibbs Free Energy and the Direction of Spontaneous Reactions

The Gibbs free energy (G), was named in honor of J. Willard Gibbs (1838–1903), an American physicist who first developed the concept. It is defined in terms of three other state functions with which you are already familiar: enthalpy, temperature, and entropy:

$$G = H - TS \tag{16.3.1}$$

Because it is a combination of state functions, G is also a state function.

J. Willard Gibbs (1839–1903)

Born in Connecticut, Josiah Willard Gibbs attended Yale, as did his father, a professor of sacred literature at Yale, who was involved in the *Amistad* trial. In 1863, Gibbs was awarded the first engineering doctorate granted in the United States. He was appointed professor of mathematical physics at Yale in 1871, the first such professorship in the United States. His series of papers entitled “On the Equilibrium of Heterogeneous Substances” was the foundation of the field of physical chemistry and is considered one of the great achievements of the 19th century. Gibbs, whose work was translated into French by Le Châtelier, lived with his sister and brother-in-law until his death in 1903, shortly before the inauguration of the Nobel Prizes.

The Gibbs free energy determines spontaneity at constant temperature and pressure. While ΔG can be calculated under all conditions it is only at constant temperature and pressure that it determines spontaneity. Since most chemical reactions in the laboratory are carried out at constant pressure and most systems can be brought back to the initial temperature without significantly affecting the value of thermodynamic state functions ΔG is extremely useful. At constant temperature and pressure,

$$\Delta G = \Delta H_{T,P} - T\Delta S_{T,P} \tag{16.3.2}$$

where all thermodynamic quantities are those of the *system*. Recall that at constant pressure, $\Delta H_P = q$, whether a process is reversible or irreversible, and $T\Delta S = q_{rev}$. Using these expressions, we can reduce Equation 16.3.2 to $\Delta G_{T,P} = q - q_{rev}$. Thus ΔG is the difference between the heat released during a process (via a reversible or an irreversible path) and the heat released for the same process occurring in a reversible manner. Under the special condition in which a process occurs reversibly, $q = q_{rev}$ and $\Delta G = 0$. As we shall soon see, if ΔG is zero, the system is at equilibrium, and there will be no net change.

What about processes for which $\Delta G \neq 0$? To understand how the sign of ΔG for a *system* determines the direction in which change is spontaneous, we can rewrite Equation 16.3.2 (where $q_p = \Delta H$, Equation 15.3.7) as follows:

$$\Delta S_{surr} = -\frac{\Delta H_{sys}}{T} \tag{16.3.3}$$

Thus the entropy change of the *surroundings* is related to the enthalpy change of the *system*. We have stated that for a spontaneous reaction, $\Delta S_{univ} > 0$, so substituting we obtain

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0 \tag{16.3.4}$$

$$= \Delta S_{sys} - \frac{\Delta H_{sys}}{T} > 0 \tag{Chapter 16.3.1}$$

Multiplying both sides of the inequality by $-T$ reverses the sign of the inequality; rearranging,

$$\Delta H_{sys} - T\Delta S_{sys} < 0 \tag{Chapter 16.3.2}$$

which is equal to ΔG (Equation 16.3.2). We can therefore see that for a spontaneous process, $\Delta G < 0$.

The relationship between the entropy change of the *surroundings* and the heat gained or lost by the *system* provides the key connection between the thermodynamic properties of the system and the change in entropy of the universe. The relationship shown in Equation 16.3.2 allows us to predict spontaneity by focusing exclusively on the thermodynamic properties and temperature of the system. We predict that highly exothermic processes ($\Delta H << 0$) that increase the disorder of a *system* ($\Delta S_{sys} >> 0$) would therefore occur spontaneously. An example of such a process is the decomposition of ammonium nitrate fertilizer. (Ammonium nitrate explosions destroyed Texas City, Texas, in 1947; and West, Texas in 2013) Ammonium nitrate was also used to destroy the Murrah Federal Building in Oklahoma City, Oklahoma, in 1995.

For a system at constant temperature and pressure, we can summarize the following results:

- If $\Delta G < 0$, the process occurs spontaneously.
- If $\Delta G = 0$, the system is at equilibrium.
- If $\Delta G > 0$, the process is not spontaneous as written but occurs spontaneously in the reverse direction.

To further understand how the various components of ΔG dictate whether a process occurs spontaneously, we now look at a simple and familiar physical change: the conversion of liquid water to water vapor. If this process is carried out at 1 atm and the normal boiling point of 100.00°C (373.15 K), we can calculate ΔG from the experimentally measured value of ΔH_{vap} (40.657 kJ/mol). For vaporizing 1 mol of water, ΔH = 40,657 J, so the process is highly endothermic. From the definition of ΔS (Equation 16.3.2), we know that for 1 mol of water,

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b} = \frac{40,657\ J}{373.15\ K} = 108.96\ J/K \tag{Chapter 16.3.3}$$

Hence there is an increase in the disorder of the system. At the normal boiling point of water,

$$\Delta G_{100°C} = \Delta H_{100°C} - T\Delta S_{100°C} = 40,\ 657\ J - \left[\left(373.15\ \cancel{K}\right)\left(108.96\ J/\cancel{K}\right)\right] = 0 \tag{Chapter 16.3.4}$$

The energy required for vaporization offsets the increase in disorder of the system. Thus ΔG = 0, and the liquid and vapor are in equilibrium, as is true of any liquid at its boiling point under standard conditions. (For more information on standard conditions, see Chapter 6 .)

Now suppose we were to superheat 1 mol of liquid water to 110°C. The value of ΔG for the vaporization of 1 mol of water at 110°C, assuming that ΔH and ΔS do not change significantly with temperature, becomes

$$\Delta G_{110°C} = \Delta H - T\Delta S = 40,\ 657\ J - \left[\left(383.15\ \cancel{K}\right)\left(108.96\ J/\cancel{K}\right)\right] = -1091\ J \tag{Chapter 16.3.5}$$

At 110°C, $\Delta G < 0$, and vaporization is predicted to occur spontaneously and irreversibly.

We can also calculate ΔG for the vaporization of 1 mol of water at a temperature below its normal boiling point—for example, 90°C—making the same assumptions:

$$\Delta G_{90°C} = \Delta H - T\Delta S = 40,\ 657\ J - \left[\left(363.15\ \cancel{K}\right)\left(108.96\ J/\cancel{K}\right)\right] = 1088\ J \tag{Chapter 16.3.6}$$

At 90°C, $\Delta G > 0$, and water does not spontaneously convert to water vapor. When using all the digits in the calculator display in carrying out our calculations, $\Delta G_{110°C}$ = 1090 J = $-\Delta G_{90°C}$, as we would predict

Note the Pattern

$\Delta G = 0$ only if $\Delta H = T\Delta S$.

We can also calculate the temperature at which liquid water is in equilibrium with water vapor. Inserting the values of ΔH and ΔS into the definition of ΔG (Equation 16.3.2), setting $\Delta G = 0$, and solving for T,

$$0\ J = 40,657\ J - T\,(108.96\ J/K) \tag{Chapter 16.3.7}$$

$$T = 373.15\ K \tag{Chapter 16.3.8}$$

Thus $\Delta G = 0$ at $T = 373.15$ K and 1 atm, which indicates that liquid water and water vapor are in equilibrium; this temperature is called the *normal boiling point* of water. At temperatures greater than 373.15 K, ΔG is negative, and water evaporates spontaneously and irreversibly. Below 373.15 K, ΔG is positive, and water does not evaporate spontaneously. Instead, water vapor at a temperature less than 373.15 K and 1 atm will spontaneously and irreversibly condense to liquid water. Figure 16.3.1 shows how the ΔH and $T\Delta S$ terms vary with temperature for the vaporization of water. When the two lines cross, $\Delta G = 0$, and $\Delta H = T\Delta S$.

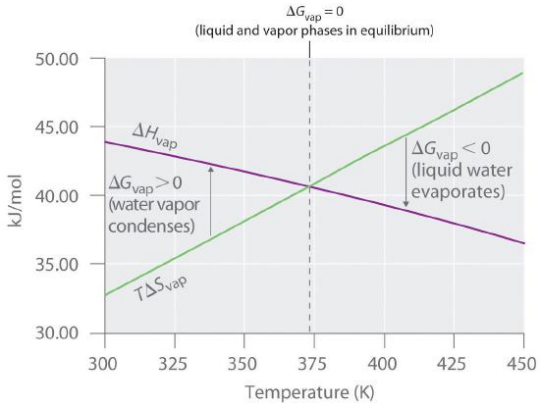


Figure 16.3.1 Temperature Dependence of ΔH and TΔS for the Vaporization of Water *Both ΔH and TΔS are temperature dependent, but the lines have opposite slopes and cross at 373.15 K at 1 atm, where ΔH = TΔS. Because ΔG = ΔH − TΔS, at this temperature ΔG = 0, indicating that the liquid and vapor phases are in equilibrium. The normal boiling point of water is therefore 373.15 K. Above the normal boiling point, the TΔS term is greater than ΔH, making ΔG < 0; hence, liquid water evaporates spontaneously. Below the normal boiling point, the ΔH term is greater than TΔS, making ΔG > 0. Thus liquid water does not evaporate spontaneously, but water vapor spontaneously condenses to liquid.*

A similar situation arises in the conversion of liquid egg white to a solid when an egg is boiled. The major component of egg white is a protein called albumin, which is held in a compact, ordered structure by a large number of hydrogen bonds. Breaking them requires an input of energy ($\Delta H > 0$), which converts the albumin to a highly disordered structure in which the molecules aggregate as a disorganized solid ($\Delta S > 0$). At temperatures greater than 373 K, the $T\Delta S$ term dominates, and $\Delta G < 0$, so the conversion of a raw egg to a hard-boiled egg is an irreversible and spontaneous process above 373 K.

The Relationship between ΔG and Work

In the previous subsection, we learned that the value of ΔG allows us to predict the spontaneity of a physical or a chemical change. In addition, the magnitude of ΔG for a process provides other important information. The change in free energy (ΔG) is equal to the maximum amount of work that a system can perform on the surroundings while undergoing a spontaneous change (at constant temperature and pressure): $\Delta G = w_{max}$. To see why this is true, let's look again at the relationships among free energy, enthalpy, and entropy expressed in Equation 16.3.2. We can rearrange this equation as follows:

$$\Delta H = \Delta G + T\Delta S \tag{16.3.5}$$

This equation tells us that when energy is released during an exothermic process ($\Delta H < 0$), such as during the combustion of a fuel, some of that energy can be used to do work ($\Delta G < 0$), while some is used to increase the entropy of the universe ($T\Delta S > 0$). Only if the process occurs infinitely slowly in a perfectly reversible manner will the entropy of the universe be unchanged. (For more information on entropy and reversibility, see Section 16.4) Because no real system is perfectly reversible, the entropy of the universe increases during all processes that produce energy. As a result, no process that uses stored energy can ever be 100% efficient; that is, ΔH will never equal ΔG because ΔS has a positive value.

One of the major challenges facing engineers is to maximize the efficiency of converting stored energy to useful work or converting one form of energy to another. As indicated in Table 16.3.1 the efficiencies of various energy-converting devices vary widely. For example, an internal combustion engine typically uses only 25%–30% of the energy stored in the hydrocarbon fuel to perform work; the rest of the stored energy is released in an unusable form as heat. In contrast, gas–electric hybrid engines, now used in several models of automobiles, deliver approximately 50% greater fuel efficiency. A large electrical generator is highly efficient (approximately 99%) in converting mechanical to electrical energy, but a typical incandescent light bulb is one of the least efficient devices known (only approximately 5% of the electrical energy is converted to light). In contrast, a mammalian liver cell is a relatively efficient machine and can use fuels such as glucose with an efficiency of 30%–50%.

Table 16.3.1 Approximate Thermodynamic Efficiencies of Various Devices

Device	Energy Conversion	Approximate Efficiency (%)
large electrical generator	mechanical → electrical	99
chemical battery	chemical → electrical	90
home furnace	chemical → heat	65
small electric tool	electrical → mechanical	60
space shuttle engine	chemical → mechanical	50
mammalian liver cell	chemical → chemical	30–50
spinach cell	light → chemical	30
internal combustion engine	chemical → mechanical	25–30
fluorescent light	electrical → light	20
solar cell	light → electricity	10
incandescent light bulb	electricity → light	5
yeast cell	chemical → chemical	2–4

Standard Free-Energy Change

We have seen that there is no way to measure absolute enthalpies, although we can measure *changes* in enthalpy (ΔH) during a chemical reaction. Because enthalpy is one of the components of Gibbs free energy, we are consequently unable to measure absolute free energies; we can measure only changes in free energy. The standard free-energy change ($\Delta G°$) is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The standard free-energy change can be calculated from the definition of free energy, if the standard enthalpy and entropy changes are known, using Equation 16.3.6:

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{16.3.6}$$

If $\Delta S°$ and $\Delta H°$ for a reaction have the same sign, then the sign of $\Delta G°$ depends on the relative magnitudes of the $\Delta H°$ and $T\Delta S°$ terms. It is important to recognize that a positive value of $\Delta G°$ for a reaction does *not* mean that no products will form if the reactants in their standard states are mixed; it means only that at equilibrium the concentrations of the products will be less than the concentrations of the reactants.

Note the Pattern

A positive $\Delta G°$ means that the equilibrium constant is less than 1.

Example 16.3.1

Calculate the standard free-energy change ($\Delta G°$) at 25°C for the reaction $H_2(g)+O_2(g)\rightleftharpoons H_2O_2(l)$ At 25°C, the standard enthalpy change ($\Delta H°$) is −187.78 kJ/mol, and the absolute entropies of the products and reactants are $S°(H_2O_2)$ = 109.6 J/(mol·K), $S°(O_2)$ = 205.2 J/(mol·K), and $S°(H_2)$ = 130.7 J/(mol·K). Is the reaction spontaneous as written?

Given: balanced chemical equation, $\Delta H°$ and $S°$ for reactants and products

Asked for: spontaneity of reaction as written

Strategy:

A Calculate $\Delta S°$ from the absolute molar entropy values given.

B Use Equation 16.3.6, the calculated value of $\Delta S°$, and other data given to calculate $\Delta G°$ for the reaction. Use the value of $\Delta G°$ to determine whether the reaction is spontaneous as written.

Solution:

A To calculate $\Delta G°$ for the reaction, we need to know $\Delta H°$, $\Delta S°$, and T. We are given $\Delta H°$, and we know that T = 298.15 K. We can calculate $\Delta S°$ from the absolute molar entropy values provided using the "products minus reactants" rule:

$$\Delta S^o = S^o(H_2O_2) - [S^o(O_2) + S^o(H_2)]$$

$$= \left[1 \cancel{mol}\ H_2O_2 \times 109.6\ J/\left(\cancel{mol} \cdot K\right)\right]$$

$$-\left\{\left[1 \cancel{mol}\ H_2 \times 130.7\ J/\left(\cancel{mol} \cdot K\right)\right] + \left[1 \cancel{mol}\ O_2 \times 205.27\ J/\left(\cancel{mol} \cdot K\right)\right]\right\}$$

$$= -226.3 J/K\ (per\ mol\ H_2O_2)$$

As we might expect for a reaction in which 2 mol of gas is converted to 1 mol of a much more ordered liquid, $\Delta S°$ is very negative for this reaction.

B Substituting the appropriate quantities into Equation 16.3.6,

$$\Delta G^o = \Delta H^o - T\Delta S^o = -187.78\ kJ/mol - \left(298.15\ \cancel{K}\right)\left[-226.3\ \cancel{J}/\left(mol \cdot \cancel{K}\right) \times 1\ kJ/1000\ \cancel{J}\right]$$

$$= -187.78\ kJ/mol + 67.47\ kJ/mol = -120.31\ kJ/mol$$

The negative value of $\Delta G°$ indicates that the reaction is spontaneous as written. Because $\Delta S°$ and $\Delta H°$ for this reaction have the same sign, the sign of $\Delta G°$ depends on the relative magnitudes of the $\Delta H°$ and $T\Delta S°$ terms. In this particular case, the enthalpy term dominates, indicating that the strength of the bonds formed in the product more than compensates for the unfavorable $\Delta S°$ term and for the energy needed to break bonds in the reactants.

Exercise

Calculate the standard free-energy change ($\Delta G°$) at 25°C for the reaction $2H_2(g)+N_2(g)\rightleftharpoons N_2H_4(l)$ At 25°C, the standard enthalpy change ($\Delta H°$) is 50.6 kJ/mol, and the absolute entropies of the products and reactants are $S°(N_2H_4)$ = 121.2 J/(mol·K), $S°(N_2)$ = 191.6 J/(mol·K), and $S°(H_2)$ = 130.7 J/(mol·K). Is the reaction spontaneous as written?

Answer: 149.5 kJ/mol; no

Tabulated values of standard free energies of formation allow chemists to calculate the values of $\Delta G°$ for a wide variety of chemical reactions rather than having to measure them in the laboratory. The standard free energy of formation ($\Delta G_f°$). of a compound is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. By definition, the standard free energy of formation of an element in its standard state is zero at 298.15 K. One mole of Cl_2 gas at 298.15 K, for example, has $\Delta G_f° = 0$. The standard free energy of formation of a compound can be calculated from the standard enthalpy of formation ($\Delta H_f°$) and the standard entropy of formation ( ) using the definition of free energy:

$$\Delta G_f^o = \Delta H_f^o - T\Delta S_f^o$$

Using standard free energies of formation to calculate the standard free energy of a reaction is analogous to calculating standard enthalpy changes from standard enthalpies of formation using the familiar "products minus reactants" rule:

$$\Delta G_{rxn}^o = \sum m\Delta G_f^o\,(products) - \sum n\Delta G_f^o\,(reactants)$$

where *m* and *n* are the stoichiometric coefficients of each product and reactant in the balanced chemical equation. A very large negative $\Delta G°$ indicates a strong tendency for products to form spontaneously from reactants; *it does not, however, necessarily indicate that the reaction will occur rapidly*. To make this determination, we need to evaluate the kinetics of the reaction. (For more information on chemical kinetics, see Chapter 13.)

Note the Pattern

The $\Delta G°$ of a reaction can be calculated from tabulated $\Delta G_f°$ values using the "products minus reactants" rule.

Example 16.3.2

Calculate $\Delta G°$ for the reaction of isooctane with oxygen gas to give carbon dioxide and water (described in Example 16.2.1). Use the following data:

$\Delta G_f°$(isooctane = -353.2 kJ/mol

$\Delta G_f°$ (CO_{2} = -394.4 kJ/mol and

$\Delta G_f°$ (H_{2}O = -237.1 kJ/mol Is the reaction spontaneous as written?

Given: balanced chemical equation and values of $\Delta G_f°$ for isooctane, CO_2, and H_2O

Asked for: spontaneity of reaction as written

Strategy:

Use the "products minus reactants" rule to obtain $\Delta G_{rxn}°$, remembering that $\Delta G_f°$ for an element in its standard state is zero. From the calculated value, determine whether the reaction is spontaneous as written.

Solution:

From Example 7, we know that the balanced chemical equation for the reaction is as follows: $C_8H_{18}(l) + 25/2\ O_2(g) \rightarrow 8CO_2(g) + 9H_2O(l)$. We are given $\Delta G_f°$ values for all the products and reactants except $O_2(g)$. Because oxygen gas is an element in its standard state, $\Delta G_f°(O_2)$ is zero. Using the "products minus reactants" rule,

$$\Delta G^o = \left[8\Delta G_f^o\,(CO_2) + 9\Delta G_f^o\,(H_2O)\right] - \left[1\Delta G_f^o\,(C_8H_{18}) + \frac{25}{2}\Delta G_f^o\,(O_2)\right]$$

Because $\Delta G°$ is a large negative number, there is a strong tendency for the spontaneous formation of products from reactants (though not necessarily at a rapid rate). Also notice that the magnitude of $\Delta G°$ is largely determined by the $\Delta G_f°$ of the stable products: water and carbon dioxide.

Exercise

Calculate $\Delta G°$ for the reaction of benzene with hydrogen gas to give cyclohexane using the data

$\Delta G_f°$ (benzene) = 124.5 kJ/mol and

$\Delta G_f°$ (cyclohexane) = 217.3 kJ/mol. Is the reaction spontaneous as written?

Answer: 92.8 kJ; no

Calculated values of $\Delta G°$ are extremely useful in predicting whether a reaction will occur spontaneously if the reactants and products are mixed under standard conditions. We should note, however, that very few reactions are actually carried out under standard conditions, and calculated values of $\Delta G°$ may not tell us whether a given reaction will occur spontaneously under nonstandard conditions. What determines whether a reaction will occur spontaneously is the free-energy change (ΔG) under the actual experimental conditions, which are usually different from $\Delta G°$. If the ΔH and $T\Delta S$ terms for a reaction have the same sign, for example, then it may be possible to reverse the sign of ΔG by changing the temperature, thereby converting a reaction that is not thermodynamically spontaneous, having $K_{eq} < 1$, to one that is, having a $K_{eq} > 1$, or vice versa. Because ΔH and ΔS usually do not vary greatly with temperature in the absence of a phase change, we can use tabulated values of $\Delta H°$ and $\Delta S°$ to calculate $\Delta G°$ at various temperatures, as long as no phase change occurs over the temperature range being considered.

Note the Pattern

In the absence of a phase change, neither ΔH nor ΔS vary greatly with temperature.

Example 16.3.3

Calculate (a) $\Delta G°$ and (b) $\Delta G_{300°C}$ for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, assuming that ΔH and ΔS do not change between 25°C and 300°C. Use these data:

$S°(N_2)$ = 191.6 J/(mol·K),

$S°(H_2)$ = 130.7 J/(mol·K),

$S°(NH_3)$ = 192.8 J/(mol·K), and

$\Delta H_f°$ (NH_3) = −45.9 kJ/mol.

Given: balanced chemical equation, temperatures, $S°$ values, and $\Delta H_f°$ for NH_3

Asked for: $\Delta G°$ and ΔG at 300°C

Strategy:

A Convert each temperature to Kelvin. Then calculate $\Delta S°$ for the reaction. Calculate $\Delta H°$ for the reaction, recalling that $\Delta H°$ for any element in its standard state is zero.

B Substitute the appropriate values into Equation 16.3.6 to obtain $\Delta G°$ for the reaction.

C Assuming that ΔH and ΔS are independent of temperature, substitute values into Equation 16.3.2 to obtain ΔG for the reaction at 300°C.

Solution:

1. **A** To calculate $\Delta G°$ for the reaction using Equation 16.3.6, we must know the temperature as well as the values of $\Delta S°$ and $\Delta H°$. At standard conditions, the temperature is 25°C, or 298 K. We can calculate $\Delta S°$ for the reaction from the absolute molar entropy values given for the reactants and the products using the "products minus reactants" rule:

$$\Delta S^o_{rxn} = 2S^o\,(NH_3) - [S^o\,(N_2) + 3S^o\,(H_2)]$$

$$= \left[2\ \cancel{mol}\ NH_3 \times 192.8\ J/\left(\cancel{mol}\cdot K\right)\right]$$

$$-\left\{\left[1\ \cancel{mol}\ N_2 \times 191.6\ J/\left(\cancel{mol}\cdot K\right)\right] + \left[3\ \cancel{mol}\ H_2 \times 130.7\ J/\left(\cancel{mol}\cdot K\right)\right]\right\}$$

$$= -198.1\ J/K\,(per\ mole\ of\ N_2)$$

2. We can also calculate $\Delta H°$ for the reaction using the "products minus reactants" rule. The value of $\Delta H_f°$ (NH_3) is given, and $\Delta H_f°$ is zero for both N_2 and H_2:

3. $$\Delta H^o_{rxn} = 2\Delta H^o_{rxn}\,(NH_3) - [\Delta H^o_{rxn}\,(N_2) + 3\Delta H^o_{rxn}\,(H_2)]$$

$$= [2 \times (-45.9\ KJ/mol)] - [(1 \times 0\ kJ/mol) + 3 \times 0\ kJ/mol]$$

$$-91.8\ kJ\,(per\ mol\ N_2)$$

4. **B** Inserting the appropriate values into Equation 16.3.6,

$$\Delta G_{rxn} = \Delta H^o - T\Delta S^o = -91.8\ kJ - \left(298\ \cancel{K}\right)\left(-198.1\ \cancel{J}/\cancel{K}\right)\left(1\ kJ/1000\ \cancel{J}\right) = -32.7\ kJ\,(per\ mol\ N_2)$$

5. **C** To calculate ΔG for this reaction at 300°C, we assume that ΔH and ΔS are independent of temperature (i.e., $\Delta H_{300°C} = H°$ and $\Delta S_{300°C} = \Delta S°$) and insert the appropriate temperature (573 K) into Equation 16.3.3:

$$\Delta G_{300\ °C} = \Delta H_{300\ °C} - (573\ K)\,(\Delta S_{300\ °C}) = \Delta H^o - (573\ K)\,(\Delta S^o)$$

$$= -91.8\ kJ - 573\ \cancel{K}\left(-198\ \cancel{J}/\cancel{K}\right)\left(1\ kJ/1000\ \cancel{J}\right) = -21.7\ kJ\,(per\ mol\ N_2)$$

In this example, changing the temperature has a major effect on the thermodynamic spontaneity of the reaction. Under standard conditions, the reaction of nitrogen and hydrogen gas to produce ammonia is thermodynamically spontaneous, but in practice, it is too slow to be useful industrially. Increasing the temperature in an attempt to make this reaction occur more rapidly also changes the thermodynamics by causing the $-T\Delta S°$ term to dominate, and the reaction is no longer spontaneous at high temperatures; that is, its K_{eq} is less than one. This is a classic example of the conflict encountered in real systems between thermodynamics and kinetics, which is often unavoidable.

Exercise

Calculate (a) $\Delta G°$ and (b) $\Delta G_{750°C}$ for the reaction $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$, which is important in the formation of urban smog. Assume that ΔH and ΔS do not change between 25.0°C and 750°C and use these data:

$S°(NO)$ = 210.8 J/(mol·K),

$S°(O_2)$ = 205.2 J/(mol·K),

$S°(NO_2)$ = 240.1 J/(mol·K),

$\Delta H_f°(NO_2)$ = 33.2 kJ/mol, and

$\Delta H_f°(NO)$ = 91.3 kJ/mol.

Answer

1. −72.5 kJ/mol of O_2
2. 33.8 kJ/mol of O_2

The effect of temperature on the spontaneity of a reaction, which is an important factor in the design of an experiment or an industrial process, depends on the sign and magnitude of both $\Delta H°$ and $\Delta S°$. The temperature at which a given reaction is at

equilibrium can be calculated by setting $\Delta G° = 0$ in Equation 16.3.6, as illustrated in Example 16.3.4.

Example 16.3.4

As you saw in Example 10, the reaction of nitrogen and hydrogen gas to produce ammonia is one in which $\Delta H°$ and $\Delta S°$ are both negative. Such reactions are predicted to be thermodynamically spontaneous at low temperatures but nonspontaneous at high temperatures. Use the data in Example 10 to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous, assuming that $\Delta H°$ and $\Delta S°$ are independent of temperature.

Given: $\Delta H°$ and $\Delta S°$

Asked for: temperature at which reaction changes from spontaneous to nonspontaneous

Strategy:

Set $\Delta G°$ equal to zero in Equation 16.3.6 and solve for T, the temperature at which the reaction becomes nonspontaneous.

Solution:

In Example 10, we calculated that $\Delta H°$ is −91.8 kJ/mol of N_2 and $\Delta S°$ is −198.1 J/K per mole of N_2, corresponding to $\Delta G°$ = −32.7 kJ/mol of N_2 at 25°C. Thus the reaction is indeed spontaneous at low temperatures, as expected based on the signs of $\Delta H°$ and $\Delta S°$. The temperature at which the reaction becomes nonspontaneous is found by setting $\Delta G°$ equal to zero and rearranging to solve for T:

$$\Delta G^o = \Delta H^o - T\Delta S^o = 0$$

$$\Delta H^o = T\Delta S^o$$

$$T = \frac{\Delta H^o}{\Delta S^o} = \frac{\left(-91.8\ \cancel{kJ}\right)\left(1000\ \cancel{J}/\cancel{kJ}\right)}{-198.1\ \cancel{J}/K} = 463\ K$$

This is a case in which a chemical engineer is severely limited by thermodynamics. Any attempt to increase the rate of reaction of nitrogen with hydrogen by increasing the temperature will cause reactants to be favored over products above 463 K.

Exercise

As you found in the exercise in Example 10, $\Delta H°$ and $\Delta S°$ are both negative for the reaction of nitric oxide and oxygen to form nitrogen dioxide. Use those data to calculate the temperature at which this reaction changes from spontaneous to nonspontaneous.

Answer: 792.6 K

Summary

We can predict whether a reaction will occur spontaneously by combining the entropy, enthalpy, and temperature of a system in a new state function called **Gibbs free energy (*G*)**. The change in free energy (ΔG) is the difference between the heat released during a process and the heat released for the same process occurring in a reversible manner. If a system is at equilibrium, $\Delta G = 0$. If the process is spontaneous, $\Delta G < 0$. If the process is not spontaneous as written but is spontaneous in the reverse direction, $\Delta G > 0$. At constant temperature and pressure, ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. The **standard free-energy change ($\Delta G°$)** is the change in free energy when one substance or a set of substances in their standard states is converted to one or more other substances, also in their standard states. The **standard free energy of formation (**<math display="inline" xml:id="av_1.0-18_m089"><semantics><mrow><mi>Δ</mi><msubsup><mi>G</mi><mtext>f</mtext><mo>°</mo></msubsup></mrow></semantics></math>), is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from

the component elements in their standard states. Tabulated values of standard free energies of formation are used to calculate $\Delta G°$ for a reaction.

Key Takeaway

- The change in Gibbs free energy, which is based solely on changes in state functions, is the criterion for predicting the spontaneity of a reaction.

Key Equations

Free-energy change

Equation 16.3.2: $\Delta G = \Delta H - T\Delta S$

Standard free-energy change

Equation 16.3.5: $\Delta G° = \Delta H° - T\Delta S°$

Conceptual Problems

1. How does each example illustrate the fact that no process is 100% efficient?
   a. burning a log to stay warm
   b. the respiration of glucose to provide energy
   c. burning a candle to provide light
2. Neither the change in enthalpy nor the change in entropy is, by itself, sufficient to determine whether a reaction will occur spontaneously. Why?
3. If a system is at equilibrium, what must be the relationship between ΔH and ΔS?
4. The equilibrium $2AB \rightleftharpoons A_2B_2$ is exothermic in the forward direction. Which has the higher entropy—the products or the reactants? Why? Which is favored at high temperatures?
5. Is ΔG a state function that describes a system or its surroundings? Do its components—ΔH and ΔS—describe a system or its surroundings?
6. How can you use ΔG to determine the temperature of a phase transition, such as the boiling point of a liquid or the melting point of a solid?
7. Occasionally, an inventor claims to have invented a "perpetual motion" machine, which requires no additional input of energy once the machine has been put into motion. Using your knowledge of thermodynamics, how would you respond to such a claim? Justify your arguments.
8. Must the entropy of the universe increase in a spontaneous process? If not, why is no process 100% efficient?
9. The reaction of methyl chloride with water produces methanol and hydrogen chloride gas at room temperature, despite the fact that $\Delta H_f° = 7.3$ kcal/mol. Using thermodynamic arguments, propose an explanation as to why methanol forms.

In order for the reaction to occur spontaneously, ΔG for the reaction must be less than zero. In this case, ΔS must be positive, and the $T\Delta S$ term outweighs the positive value of ΔH.

Answer

1.

Numerical Problems

1. Use the tables in the text to determine whether each reaction is spontaneous under standard conditions. If a reaction is not spontaneous, write the corresponding spontaneous reaction.
   a. $H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$
   b. $2H_2(g) + C_2H_2(g) \rightarrow C_2H_6(g)$
   c. $(CH_3)_2O(g) + H_2O(g) \rightarrow 2CH_3OH(l)$
   d. $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$

2. Use the tables in the text to determine whether each reaction is spontaneous under standard conditions. If a reaction is not spontaneous, write the corresponding spontaneous reaction.
   a. $K_2O_2(s) \rightarrow 2K(s) + O_2(g)$
   b. $PbCO_3(s) \rightarrow PbO(s) + CO_2(g)$
   c. $P_4(s) + 6H_2(g) \rightarrow 4PH_3(g)$
   d. $2AgCl(s) + H_2S(g) \rightarrow Ag_2S(s) + 2HCl(g)$
3. Nitrogen fixation is the process by which nitrogen in the atmosphere is reduced to NH_3 for use by organisms. Several reactions are associated with this process; three are listed in the following table. Which of these are spontaneous at 25°C? If a reaction is not spontaneous, at what temperature does it become spontaneous?

Reaction	$\Delta H°_{298}$ (kcal/mol)	$S°_{298}$[cal/(mol-K)]		
(a) $1/2\ N_2 + O_2 \rightarrow 2NO_2$	8.0	−14.4		
(b) $1/2\ N_2 + 1/2\ O_2 \rightarrow NO$	21.6	2.9		
(c) $1/2\ N_2 + 3/2\ H_2 \rightarrow 2NH_3$	−11.0	−23.7		

4. A student was asked to propose three reactions for the oxidation of carbon or a carbon compound to CO or CO_2. The reactions are listed in the following table. Are any of these reactions spontaneous at 25°C? If a reaction does not occur spontaneously at 25°C, at what temperature does it become spontaneous?

Reaction	$\Delta H°_{rxn}$ (kcal/mol)	S°[cal/(mol-K)]
$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$	42	32
$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$	−9.8	−10.1
$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$	49.3	51.3

5. Tungsten trioxide (WO_3) is a dense yellow powder that, because of its bright color, is used as a pigment in oil paints and water colors (although cadmium yellow is more commonly used in artists' paints). Tungsten metal can be isolated by the reaction of WO_3 with H_2 at 1100°C according to the equation $WO_3(s) + 3H_2(g) \rightarrow W(s) + 3H_2O(g)$. What is the lowest temperature at which the reaction occurs spontaneously? $\Delta H° = 27.4$ kJ/mol and $\Delta S° = 29.8$ J/K.
6. Sulfur trioxide (SO_3) is produced in large quantities in the industrial synthesis of sulfuric acid. Sulfur dioxide is converted to sulfur trioxide by reaction with oxygen gas.
   a. Write a balanced chemical equation for the reaction of SO_2 with $O_2(g)$ and determine its $\Delta G°$.
   b. What is the value of the equilibrium constant at 600°C?
   c. If you had to rely on the equilibrium concentrations alone, would you obtain a higher yield of product at 400°C or at 600°C?
7. Calculate $\Delta G°$ for the general reaction $MCO_3(s) \rightarrow MO(s) + CO_2(g)$ at 25°C, where M is Mg or Ba. At what temperature does each of these reactions become spontaneous?

Compound	$\Delta H_f°$ (kJ/mol)	$S°$ [J/(mol·K)]
MCO_3		
Mg	−1111	65.85
Ba	−1213.0	112.1
MO		
Mg	−601.6	27.0
Ba	−548.0	72.1
CO_2	−393.5	213.8

8. The reaction of aqueous solutions of barium nitrate with sodium iodide is described by the following equation:
   $Ba(NO_3)_2(aq) + 2NaI(aq) \rightarrow BaI_2(aq) + 2NaNO_3(aq)$
   You want to determine the absolute entropy of BaI_2, but that information is not listed in your tables. However, you have been able to obtain the following information:

	$Ba(NO_3)_2$	NaI	BaI_2	$NaNO_3$
$\Delta H°$ (kJ/mol)	−952.36	−295.31	−605.4	−447.5
$S°$ [J/(mol·K)]	302.5	170.3		205.4

   You know that $\Delta G°$ for the reaction at 25°C is 22.64 kJ/mol. What is $\Delta H°$ for this reaction? What is $S°$ for BaI_2?

Answers

1. a. −237.1 kJ/mol; spontaneous as written
   b. −241.9 kJ/mol; spontaneous as written
   c. 8.0 kJ/mol; spontaneous in reverse direction.
   d. 141.9 kJ/mol; spontaneous in reverse direction.
2.
3. a. Not spontaneous at any T
   b. Not spontaneous at 25°C; spontaneous above 7400 K
   c. Spontaneous at 25°C
4.
5. 919 K
6.
7. $MgCO_3$: $\Delta G° = 63$ kJ/mol, spontaneous above 663 K; $BaCO_3$: $\Delta G° = 220$ kJ/mol, spontaneous above 1562 K
8.

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Chapter 16.4: Spontaneity and Equilibrium

Learning Objective

- To know the relationship between free energy and the equilibrium constant.

We have identified three criteria for whether a given reaction will occur spontaneously: $\Delta S_{univ} > 0$, $\Delta G_{sys} < 0$, and the relative magnitude of the reaction quotient Q versus the equilibrium constant K. (For more information on the reaction quotient and the equilibrium constant, see Chapter 15.) Recall that if $Q < K$, then the reaction proceeds spontaneously to the right as written, resulting in the net conversion of reactants to products. Conversely, if $Q > K$, then the reaction proceeds spontaneously to the left as written, resulting in the net conversion of products to reactants. If $Q = K$, then the system is at equilibrium, and no net reaction occurs. Table 16.4.1 summarizes these criteria and their relative values for spontaneous, nonspontaneous, and equilibrium processes. Because all three criteria are assessing the same thing—the spontaneity of the process—it would be most surprising indeed if they were not related. The relationship between ΔS_{univ} and ΔG_{sys} was described in Section 16.3. In this section, we explore the relationship between the standard free energy of reaction ($\Delta G°$) and the equilibrium constant (K).

Table 16.4.1 Criteria for the Spontaneity of a Process as Written

Spontaneous	Equilibrium	Nonspontaneous*
$\Delta S_{univ} > 0$	$\Delta S_{univ} = 0$	$\Delta S_{univ} < 0$
$\Delta G_{sys} < 0$	$\Delta G_{sys} = 0$	$\Delta G_{sys} > 0$
$Q < K$	$Q = K$	$Q > K$
*Spontaneous in the *reverse* direction.		

Free Energy and the Equilibrium Constant

Because $\Delta H°$ and $\Delta S°$ determine the magnitude of $\Delta G°$ (Equation 16.3.6), and because K is a measure of the ratio of the concentrations of products to the concentrations of reactants, we should be able to express K in terms of $\Delta G°$ and vice versa. As you learned in Section 16.3, ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature, thereby eliminating ΔH from the equation for ΔG. Using higher math, the general relationship can be shown as follows:

$$\Delta G = V\Delta P - S\Delta T$$

If a reaction is carried out at constant temperature ($\Delta T = 0$), then Equation 16.4.1 simplifies to

$$\Delta G = V\Delta P$$

Under normal conditions, the pressure dependence of free energy is not important for solids and liquids because of their small molar volumes. For reactions that involve gases, however, the effect of pressure on free energy is very important.

Assuming ideal gas behavior, we can replace the V in Equation 16.4.2 by nRT/P (where n is the number of moles of gas and R is the ideal gas constant) and express ΔG in terms of the initial and final pressures (P_i and P_f, respectively) as in Equation 16.2.3:

$$\Delta G = \left(\frac{nRT}{P}\right)\Delta P = nRT\frac{\Delta P}{P} = nRT\ln\left(\frac{P_f}{P_i}\right)$$

If the initial state is the standard state with $P_i = 1$ atm, then the change in free energy of a substance when going from the standard state to any other state with a pressure P can be written as follows:

$$G - G^o = nRT\ln P$$

This can be rearranged as follows:

$$G = G^o + nRT\ln P$$

As you will soon discover, Equation 16.4.5 allows us to relate $\Delta G°$ and K_p. Any relationship that is true for K_p must also be true for K because K_p and K are simply different ways of expressing the equilibrium constant using different units.

Let's consider the following hypothetical reaction, in which all the reactants and the products are ideal gases and the lowercase letters correspond to the stoichiometric coefficients for the various species:

$$aA + bB \rightleftharpoons cC + dD$$

Because the free-energy change for a reaction is the difference between the sum of the free energies of the products and the reactants, we can write the following expression for ΔG:

$$\Delta G = \sum mG_{products} - \sum mG_{reactants} = (cG_C + dG_D) - (aG_A + bG_B)$$

Substituting Equation 16.4.5 for each term into Equation 16.4.7,

$$\Delta G = [(cG_C + cRT\ln P_C) + (dG_D + dRT\ln P_D)] - [(aG_A + aRT\ln P_A) + (bG_B + bRT\ln P_B)]$$

Combining terms gives the following relationship between ΔG and the reaction quotient Q:

$$\Delta G = \Delta G^o + RT\ln\left(\frac{P_C^c P_D^d}{P_A^a P_B^b}\right) = \Delta G^o + RT\ln Q$$

where $\Delta G°$ indicates that all reactants and products are in their standard states. In Chapter 14, you learned that for gases $Q = K_p$ at equilibrium, and as you've learned in this chapter, $\Delta G = 0$ for a system at equilibrium. Therefore, we can describe the relationship between $\Delta G°$ and K_p for gases as follows:

$$0 = \Delta G^o + RT\ln K_P$$

$$\Delta G^o = RT\ln K_P$$

If the products and reactants are in their standard states and $\Delta G° < 0$, then $K_p > 1$, and products are favored over reactants. Conversely, if $\Delta G° > 0$, then $K_p < 1$, and reactants are favored over products. If $\Delta G° = 0$, then $K_p = 1$, and neither reactants nor products are favored: the system is at equilibrium.

Note the Pattern

For a spontaneous process under standard conditions, K_{eq} and K_p are greater than 1.

Example 16.4.1

In Example 16.3.3, we calculated that $\Delta G° = -32.7$ kJ/mol of N_2 for the reaction $N_2(g)+3H_2(g \rightleftharpoons 2NH_3(g)$ This calculation was for the reaction under standard conditions—that is, with all gases present at a partial pressure of 1 atm and a temperature of 25°C. Calculate ΔG for the same reaction under the following nonstandard conditions: $P(N_2) = 2.00$ atm, $P(H_2) = 7.00$ atm, $P(NH_3) = 0.021$ atm, and $T = 100°C$. Does the reaction favor products or reactants?

Given: balanced chemical equation, partial pressure of each species, temperature, and $\Delta G°$

Asked for: whether products or reactants are favored

Strategy:

A Using the values given and Equation 16.4.8, calculate Q.

B Substitute the values of $\Delta G°$ and Q into Equation 16.4.8 to obtain ΔG for the reaction under nonstandard conditions.

Solution:

A The relationship between $\Delta G°$ and ΔG under nonstandard conditions is given in Equation 16.4.8. Substituting the partial pressures given, we can calculate Q:

$$Q = \frac{P_{NH_3}^2}{P_{N_2}P_{H_2}^3} = \frac{(0.021)^2}{(2.00)\,(7.00)^3} = 6.4 \times 10^{-7}$$

B Substituting the values of $\Delta G°$ and Q into Equation 16.4.8,

$$\Delta G = \Delta G^o + RT\ln Q = -32.7\ kJ + \left[\left(8.314\ \cancel{J}\ \cancel{K}\right)\left(373\ \cancel{K}\right)\left(1\ kJ/1000\ \cancel{kJ}\right)\ln\left(6.4 \times 10^{-7}\right)\right]$$

$$= -32.7\ kJ + (-44\ kJ) = -77\ kJ/mol\ N_2$$

Because $\Delta G < 0$ and $Q < 1.0$, the reaction is spontaneous to the right as written, so products are favored over reactants.

Exercise

Calculate ΔG for the reaction of nitric oxide with oxygen to give nitrogen dioxide under these conditions: T = 50°C, $P(NO)$ = 0.0100 atm, $P(O_2)$ = 0.200 atm, and $P(NO_2)$ = 1.00×10^{-4} atm. The value of $\Delta G°$ for this reaction is −72.5 kJ/mol of O_2. Are products or reactants favored?

Answer: −92.9 kJ/mol of O_2; the reaction is spontaneous to the right as written, so products are favored.

Example 16.4.2

Calculate K_p for the reaction of H_2 with N_2 to give NH_3 at 25°C. As calculated in Example 10, $\Delta G°$ for this reaction is −32.7 kJ/mol of N_2.

Given: balanced chemical equation from Example 10, $\Delta G°$, and temperature

Asked for: K_p

Strategy:

Substitute values for $\Delta G°$ and T (in kelvins) into Equation 16.4.9 to calculate K_p, the equilibrium constant for the formation of ammonia.

Solution:

In Example 10, we used tabulated values of ΔG° to calculate $\Delta G°$ for this reaction (−32.7 kJ/mol of N_2). For equilibrium conditions, rearranging Equation 16.4.9,

$$\Delta G^o = -RT\ln K_P$$

$$\frac{-\Delta G^o}{RT} = \ln K_P$$

Inserting the value of $\Delta G°$ and the temperature (25°C = 298 K) into this equation,

$$\ln K_P = -\frac{\left(-32.7\ \cancel{kJ}\right)\left(1000\ \cancel{J}/\cancel{kJ}\right)}{8.314\ \cancel{J}/\cancel{K}\left(298\ \cancel{K}\right)} = 13.2$$

$$K_P = 5.4 \times 10^5$$

Thus the equilibrium constant for the formation of ammonia at room temperature is favorable. As we saw in Chapter 13, however, the *rate* at which the reaction occurs at room temperature is too slow to be useful.

Exercise

Calculate K_p for the reaction of NO with O_2 to give NO_2 at 25°C. As calculated in the exercise in Example 10, $\Delta G°$ for this reaction is −70.5 kJ/mol of O_2.

Answer: 2.2×10^{12}

Although K_p is defined in terms of the partial pressures of the reactants and the products, the equilibrium constant K is defined in terms of the concentrations of the reactants and the products. We described the relationship between the numerical magnitude of K_p and K in Chapter 14 and showed that they are related:

$$K_P = K(RT)^{\Delta n}$$

where Δn is the number of moles of gaseous product minus the number of moles of gaseous reactant. For reactions that involve only solutions, liquids, and solids, $\Delta n = 0$, so $K_p = K$. For all reactions that do not involve a change in the number of moles of gas present, the relationship in Equation 16.4.9 can be written in a more general form:

$$\Delta G^o = -RT\ln K$$

Only when a reaction results in a net production or consumption of gases is it necessary to correct Equation 16.4.9 for the difference between K_p and K.Although we typically use concentrations or pressures in our equilibrium calculations, recall that

equilibrium constants are generally expressed as unitless numbers because of the use of activities or fugacities in precise thermodynamic work. Systems that contain gases at high pressures or concentrated solutions that deviate substantially from ideal behavior require the use of fugacities or activities, respectively.

Combining Equation 18.26 and Equation 16.4.11 provides insight into how the components of $\Delta G°$ influence the magnitude of the equilibrium constant:

$$\Delta G^o = \Delta H^o - T\Delta S^o = -RT\ln K$$

Notice that K becomes larger as $\Delta S°$ becomes more positive, indicating that the magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder. Moreover, K increases as $\Delta H°$ decreases. Thus the magnitude of the equilibrium constant is also directly influenced by the tendency of a system to seek the lowest energy state possible.

Note the Pattern

The magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder and seek the lowest energy state possible.

Temperature Dependence of the Equilibrium Constant

The fact that $\Delta G°$ and K are related provides us with another explanation of why equilibrium constants are temperature dependent. This relationship is shown explicitly in Equation 16.4.12, which can be rearranged as follows:

$$\ln K = \frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R}$$

Assuming $\Delta H°$ and $\Delta S°$ are temperature independent, for an exothermic reaction ($\Delta H° < 0$), the magnitude of K decreases with increasing temperature, whereas for an endothermic reaction ($\Delta H° > 0$), the magnitude of K increases with increasing temperature. The quantitative relationship expressed in Equation 16.4.13 agrees with the qualitative predictions made by applying Le Châtelier's principle, which we discussed in Chapter 14. Because heat is produced in an exothermic reaction, adding heat (by increasing the temperature) will shift the equilibrium to the left, favoring the reactants and decreasing the magnitude of K. Conversely, because heat is consumed in an endothermic reaction, adding heat will shift the equilibrium to the right, favoring the products and increasing the magnitude of K. Equation 16.4.13 also shows that the *magnitude* of $\Delta H°$ dictates how rapidly K changes as a function of temperature. In contrast, the magnitude and sign of $\Delta S°$ affect the magnitude of K but not its temperature dependence.

If we know the value of K at a given temperature and the value of $\Delta H°$ for a reaction, we can estimate the value of K at any other temperature, even in the absence of information on $\Delta S°$. Suppose, for example, that K_1 and K_2 are the equilibrium constants for a reaction at temperatures T_1 and T_2, respectively. Applying Equation 16.4.13 gives the following relationship at each temperature:

$$\ln K_1 = \frac{\Delta H^o}{RT_1} + \frac{\Delta S^o}{R}$$
$$\ln K_2 = \frac{\Delta H^o}{RT_2} + \frac{\Delta S^o}{R}$$

Subtracting $\ln K_1$ from $\ln K_2$,

$$\ln K_2 - \ln K_1 = \ln\frac{K_2}{K_1} = \frac{\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Thus calculating $\Delta H°$ from tabulated enthalpies of formation and measuring the equilibrium constant at one temperature (K_1) allow us to calculate the value of the equilibrium constant at any other temperature (K_2), assuming that $\Delta H°$ and $\Delta S°$ are independent of temperature.

Example 16.4.3

The equilibrium constant for the formation of NH_3 from H_2 and N_2 at 25°C was calculated to be $K_p = 5.4 \times 10^5$ in Example 13. What is K_p at 500°C? (Use the data from Example 10.)

Given: balanced chemical equation, $\Delta H°$, initial and final T, and K_p at 25°C

Asked for: K_p at 500°C

Strategy:

Convert the initial and final temperatures to kelvins. Then substitute appropriate values into Equation 16.4.13 to obtain K_2, the equilibrium constant at the final temperature.

Solution:

The value of $\Delta H°$ for the reaction obtained using Hess's law is −91.8 kJ/mol of N_2. If we set T_1 = 25°C = 298.K and T_2 = 500°C = 773 K, then from Equation 16.4.13 we obtain the following:

$$= \frac{\left(-91.8\ \cancel{kJ}\right)\left(1000\ J/\cancel{kJ}\right)}{8.314\ J/K}\left(\frac{1}{298\ \cancel{K}} - \frac{1}{773\ \cancel{K}}\right) = -22.8$$

$$\frac{K_2}{K_1} = 1.3 \pm \times 10^{-10}$$

$$K_2 = \left(5.4 \times 10^5\right)\left(1.3 \pm \times 10^{-10}\right) = 7.0 \times 10^{-5}$$

Thus at 500°C, the equilibrium strongly favors the reactants over the products.

Exercise

In the exercise in Example 13, you calculated $K_p = 2.2 \times 10^{12}$ for the reaction of NO with O_2 to give NO_2 at 25°C. Use the $\Delta H_f°$ values in the exercise in Example 10 to calculate K_p for this reaction at 1000°C.

Answer: 5.6×10^{-4}

Summary

For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature. If we assume ideal gas behavior, the ideal gas law allows us to express ΔG in terms of the partial pressures of the reactants and products, which gives us a relationship between ΔG and K_p, the equilibrium constant of a reaction involving gases, or K, the equilibrium constant expressed in terms of concentrations. If $\Delta G° < 0$, then K or $K_p > 1$, and products are favored over reactants. If $\Delta G° > 0$, then K or $K_p < 1$, and reactants are favored over products. If $\Delta G° = 0$, then K or $K_p = 1$, and the system is at equilibrium. We can use the measured equilibrium constant K at one temperature and $\Delta H°$ to estimate the equilibrium constant for a reaction at any other temperature.

Key Takeaway

- The change in free energy of a reaction can be expressed in terms of the standard free-energy change and the equilibrium constant K or K_p and indicates whether a reaction will occur spontaneously under a given set of conditions.

Key Equations

Relationship between standard free-energy change and equilibrium constant

Equation 16.4.9: $\Delta G^o = -RT\ln K$

Temperature dependence of equilibrium constant

Equation 16.4.11: $\ln K = \frac{-\Delta H^o}{RT} + \frac{-\Delta S^o}{R}$

Calculation of K at second temperature

Equation 16.4.13: $\ln \frac{K_2}{K_1} = \frac{-\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

Conceptual Problems

1. Do you expect products or reactants to dominate at equilibrium in a reaction for which $\Delta G°$ is equal to
    1. 1.4 kJ/mol?
    2. 105 kJ/mol?
    3. −34 kJ/mol?

2. The change in free energy enables us to determine whether a reaction will proceed spontaneously. How is this related to the extent to which a reaction proceeds?
3. What happens to the change in free energy of the reaction $N_2(g) + 3F_2(g) \rightarrow 2NF_3(g)$ if the pressure is increased while the temperature remains constant? if the temperature is increased at constant pressure? Why are these effects not so important for reactions that involve liquids and solids?
4. Compare the expressions for the relationship between the change in free energy of a reaction and its equilibrium constant where the reactants are gases versus liquids. What are the differences between these expressions?

Numerical Problems

1. Carbon monoxide, a toxic product from the incomplete combustion of fossil fuels, reacts with water to form CO_2 and H_2, as shown in the equation $CO(g)+H_2O(g) \rightleftharpoons CO_2(g)+H_2(g)$, for which $\Delta H° = -41.0$ kJ/mol and $\Delta S° = -42.3$ J cal/(mol·K) at 25°C and 1 atm.
    1. What is $\Delta G°$ for this reaction?
    2. What is ΔG if the gases have the following partial pressures: $P(CO) = 1.3$ atm, $P(H_2O) = 0.8$ atm, $P(CO_2) = 2.0$ atm, and $P(H_2) = 1.3$ atm?
    3. What is ΔG if the temperature is increased to 150°C assuming no change in pressure?
2. Methane and water react to form carbon monoxide and hydrogen according to the equation $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$
    1. What is the standard free energy change for this reaction?
    2. What is K_p for this reaction?
    3. What is the carbon monoxide pressure if 1.3 atm of methane reacts with 0.8 atm of water, producing 1.8 atm of hydrogen gas?
    4. What is the hydrogen gas pressure if 2.0 atm of methane is allowed to react with 1.1 atm of water?
    5. At what temperature does the reaction become spontaneous?
3. Calculate the equilibrium constant at 25°C for each equilibrium reaction and comment on the extent of the reaction.
    1. $CCl_4(g) + 6\ H_2O(l) \rightleftharpoons CO_2(g) + 4HCl(aq)$; $\Delta G° = -377$ kJ/mol
    2. $Xe(g) + 2F_2(g) \rightleftharpoons XeF_4(s)$; $\Delta H° = -66.3$ kJ/mol, $\Delta S° = -102.3$ J/(mol·K)
    3. $PCl_3(g) + S \rightleftharpoons PSCl_3(l)$; $\Delta G_f°(PCl_3) = -272.4$ kJ/mol, $\Delta G_f°(PSCl_3) = -363.2$ kJ/mol
4. Calculate the equilibrium constant at 25°C for each equilibrium reaction and comment on the extent of the reaction.
    1. $2KClO_3(s) \rightleftharpoons 2KCl(s) + 3O_2(g)$; $\Delta G° = -225.8$ kJ/mol
    2. $CoCl2(s) + 6\ H_2O(l) \rightleftharpoons 6CoCl_2 \cdot 6\ H_2O(s)$; $\Delta H_{rxn}° = -352$ kJ/mol, $\Delta S_{rxn}° = -899$ J/(mol·K)
    3. $PCl_3(g) + O_2(g) \rightleftharpoons 2POCl_3(g)$; (PCl_3); $\Delta G_f°(PCl_3) = -272.4$ kJ/mol, $\Delta G_f°(POCl_3) = -558.5$ kJ/mol
5. The gas-phase decomposition of N_2O_4 to NO_2 is an equilibrium reaction with $K_p = 4.66 \times 10^{-3}$. Calculate the standard free-energy change for the equilibrium reaction between N_2O_4 and NO_2.
6. The standard free-energy change for the dissolution $K_4Fe(CN)_6 \cdot H_2O(s) \rightleftharpoons 4K^+(aq) + Fe(CN)_6^{4-}(aq) + H_2O(l)$ is 26.1 kJ/mol. What is the equilibrium constant for this process at 25°C?
7. Ammonia reacts with water in liquid ammonia solution (am) according to the equation $NH_3(g) + H_2O(am) \rightleftharpoons NH_4^+(am) + OH^-(am)$ The change in enthalpy for this reaction is 21 kJ/mol, and $\Delta S° = -303$ J/(mol·K). What is the equilibrium constant for the reaction at the boiling point of liquid ammonia (−31°C)?
8. At 25°C, a saturated solution of barium carbonate is found to have a concentration of $[Ba^{2+}] = [CO_3^{2-}] = 5.08 \times 10^{-5}$ M. Determine $\Delta G°$ for the dissolution of $BaCO_3$.
9. Lead phosphates are believed to play a major role in controlling the overall solubility of lead in acidic soils. One of the dissolution reactions is $Pb_3(PO_4)_2(s) + 4H^+(aq) \rightleftharpoons 3Pb^{2+}(aq) + 2H_2PO_4^-(aq)$ for which $\log K = -1.80$. What is $\Delta G°$ for this reaction?
10. The conversion of butane to 2-methylpropane is an equilibrium process with $\Delta H° = -2.05$ kcal/mol and $\Delta G° = -0.89$ kcal/mol.

1. What is the change in entropy for this conversion?
2. Based on structural arguments, are the sign and magnitude of the entropy change what you would expect? Why?
3. What is the equilibrium constant for this reaction?

11. The reaction of $CaCO_3(s)$ to produce $CaO(s)$ and $CO_2(g)$ has an equilibrium constant at 25°C of 2×10^{-23}. Values of $\Delta H_f°$ are as follows: $CaCO_3$, −1207.6 kJ/mol; CaO, −634.9 kJ/mol; and CO_2, −393.5 kJ/mol.
    1. What is $\Delta G°$ for this reaction?
    2. What is the equilibrium constant at 900°C?
    3. What is the partial pressure of $CO_2(g)$ in equilibrium with CaO and $CaCO_3$ at this temperature?
    4. Are reactants or products favored at the lower temperature? at the higher temperature?
12. In acidic soils, dissolved Al^{3+} undergoes a complex formation reaction with SO_4^{2-} to form $[AlSO_4^+]$. The equilibrium constant at 25°C for the reaction $Al^{3+}(aq) + SO_4^{2-}(aq) \rightleftharpoons AlSO_4^+(aq)$ is 1585.
    1. What is $\Delta G°$ for this reaction?
    2. How does this value compare with $\Delta G°$ for the reaction $Al^{3+}(aq) + F^-(aq) \rightleftharpoons AlF^{2+}(aq)$ for which $K = 10^7$ at 25°C?
    3. Which is the better ligand to use to trap Al^{3+} from the soil?

Answers

1. 1. −28.4 kJ/mol
    2. −26.1 kJ/mol
    3. −19.9 kJ/mol
2.
3. 1. 1.21×10^{66}; equilibrium lies far to the right.
    2. 1.89×10^{6}; equilibrium lies to the right.
    3. 5.28×10^{16}; equilibrium lies far to the right.
4.
5. 13.3 kJ/mol
6.
7. 5.1×10^{-21}
8.
9. 10.3 kJ/mol
10.
11. 1. 129.5 kJ/mol
    2. 6
    3. 6.0 atm
    4. Products are favored at high T; reactants are favored at low T.
12.

Contributors

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Chapter 16.5: Comparing Thermodynamics and Kinetics

Learning Objective

- To understand the differences between the information that thermodynamics and kinetics provide about a system.

Because thermodynamics deals with state functions, it can be used to describe the overall properties, behavior, and equilibrium composition of a system. It is *not* concerned with the particular pathway by which physical or chemical changes occur, however, so it cannot address the *rate* at which a particular process will occur. Although thermodynamics provides a significant constraint on what *can* occur during a reaction process, it does not describe the detailed steps of what *actually* occurs on an atomic or a molecular level.

Note the Pattern

Thermodynamics focuses on the energetics of the products and the reactants, whereas kinetics focuses on the pathway from reactants to products.

Table 16.5.1 gives the numerical values of the equilibrium constant (K) that correspond to various approximate values of $\Delta G°$. Note that $\Delta G° \geq +10$ kJ/mol or $\Delta G° \leq -10$ kJ/mol ensures that an equilibrium lies essentially all the way to the left or to the right, respectively, under standard conditions, corresponding to a reactant-to-product ratio of approximately 10,000:1 (or vice versa). Only if $\Delta G°$ is quite small (±10 kJ/mol) are significant amounts of both products and reactants present at equilibrium. Most reactions that we encounter have equilibrium constants substantially greater or less than 1, with the equilibrium strongly favoring either products or reactants. In many cases, we will encounter reactions that are strongly favored by thermodynamics but do not occur at a measurable rate. In contrast, we may encounter reactions that are not thermodynamically favored under standard conditions but nonetheless do occur under certain nonstandard conditions.

Table 16.5.1 The Relationship between K and $\Delta G°$ at 25°C

$\Delta G°$ (kJ/mol)	K	Physical Significance
500	3×10^{-88}	For all intents and purposes, the reaction does not proceed in the forward direction: only reactants are present at equilibrium.
100	3×10^{-18}	
10	2×10^{-2}	Both forward and reverse reactions occur: significant amounts of both products and reactants are present at equilibrium.
0	1	
−10	60	
−100	3×10^{17}	For all intents and purposes, the forward reaction proceeds to completion: only products are present at equilibrium.
−500	4×10^{87}	

A typical challenge in industrial processes is a reaction that has a large negative value of $\Delta G°$ and hence a large value of K but that is too slow to be practically useful. In such cases, mixing the reactants results in only a physical mixture, not a chemical reaction. An example is the reaction of carbon tetrachloride with water to produce carbon dioxide and hydrochloric acid, for which $\Delta G°$ is −232 kJ/mol:

$$CCl_4\,(l) + 2H_2O\,(l) \rightleftharpoons CO_2\,(g) + 2HCl\,(g)$$

The value of K for this reaction is 5×10^{40} at 25°C, yet when CCl_4 and water are shaken vigorously at 25°C, nothing happens: the two immiscible liquids form separate layers, with the denser CCl_4 on the bottom. In comparison, the analogous reaction of $SiCl_4$ with water to give SiO_2 and HCl, which has a similarly large equilibrium constant, occurs almost explosively. Although the two reactions have comparable thermodynamics, they have very different kinetics!

There are also many reactions for which $\Delta G° << 0$ but that do not occur as written because another possible reaction occurs more rapidly. For example, consider the reaction of lead sulfide with hydrogen peroxide. One possible reaction is as follows:

$$PbS\,(s) + 4H_2O_2\,(l) \rightleftharpoons PbO_2\,(s) + SO_2\,(g) + 4H_2O\,(l)$$

for which $\Delta G°$ is −886 kJ/mol and K is 10^{161}. Yet when lead sulfide is mixed with hydrogen peroxide, the ensuing vigorous reaction does *not* produce PbO_2 and SO_2. Instead, the reaction that actually occurs is as follows:

$$PbS\,(s) + 4H_2O_2\,(l) \rightleftharpoons PbSO_4\,(s) + 4H_2O\,(l)$$

This reaction has a $\Delta G°$ value of −1181 kJ/mol, within the same order of magnitude as the reaction in Equation 16.5.2, but it occurs much more rapidly.

Now consider reactions with $\Delta G° > 0$. Thermodynamically, such reactions do not occur spontaneously under standard conditions. Nonetheless, these reactions can be made to occur under nonstandard conditions. An example is the reduction of chromium(III) chloride by hydrogen gas:

$$CrCl_3\,(s) + \frac{1}{2}H_2\,(g) \rightleftharpoons CrCl_2\,(s) + HCl\,(g)$$

At 25°C, $\Delta G°$ = 35 kJ/mol and $K_p = 7 \times 10^{-7}$. However, at 730°C, $\Delta G°$ = −52 kJ/mol and $K_p = 5 \times 10^2$; at this elevated temperature, the reaction is a convenient way of preparing chromium(II) chloride in the laboratory. Moreover, removing HCl gas from the system drives the reaction to completion, as predicted by Le Châtelier's principle. Although the reaction is not thermodynamically spontaneous under standard conditions, it becomes spontaneous under nonstandard conditions.

There are also cases in which a compound whose formation appears to be thermodynamically prohibited can be prepared using a different reaction. The reaction for the preparation of chlorine monoxide from its component elements, for example, is as follows:

$$\frac{1}{2}O_2\,(g) + Cl_2\,(g) \rightleftharpoons Cl_2O\,(g)$$

for which $\Delta G_f°$ is 97.9 kJ/mol. The large positive value of $\Delta G_f°$ for this reaction indicates that mixtures of chlorine and oxygen do not react to any extent to form Cl_2O. Nonetheless, Cl_2O is easily prepared using the reaction

$$HgO\,(s) + 2Cl_2\,(g) \rightleftharpoons Cl_2O\,(g) + HgCl_2\,(s)$$

which has a $\Delta G°$ of −22.2 kJ/mol and a K_p of approximately 1×10^4.

Finally, the $\Delta G°$ values for some reactions are so positive that the only way to make them proceed in the desired direction is to supply external energy, often in the form of electricity. Consider, for example, the formation of metallic lithium from molten lithium chloride:

$$LiCl\,(s) \rightleftharpoons Li\,(l) + \frac{1}{2}Cl_2\,(s)$$

Even at 1000°C, ΔG is very positive (324 kJ/mol), and there is no obvious way to obtain lithium metal using a different reaction. Hence in the industrial preparation of metallic lithium, electrical energy is used to drive the reaction to the right, as described in Chapter 17 .

Note the Pattern

A reaction that does not occur under standard conditions can be made to occur under nonstandard conditions, such as by driving the reaction to completion using Le Châtelier's principle or by providing external energy.

Often reactions that are not thermodynamically spontaneous under standard conditions can be made to occur spontaneously if coupled, or connected, in some way to another reaction for which $\Delta G° << 0$. Because the overall value of $\Delta G°$ for a series of reactions is the sum of the $\Delta G°$ values for the individual reactions, virtually any unfavorable reaction can be made to occur by chemically coupling it to a sufficiently favorable reaction or reactions. In the preparation of chlorine monoxide from mercuric oxide and chlorine (Equation 16.5.6), we have already encountered one example of this phenomenon of *coupled reactions*, although we did not describe it as such at the time. We can see how the chemical coupling works if we write Equation 16.5.6 as the sum of three separate reactions:

$$\cancel{\frac{1}{2}O_2(g)} + Cl_2(g) \rightleftharpoons Cl_2O(g) \qquad \Delta G^o = 97.9\ kJ/mol \quad (1)$$

$$HgO(s) \rightleftharpoons \cancel{Hg(l)} + \cancel{\frac{1}{2}O_2(g)} \qquad \Delta G^o = 58.5\ kJ/mol \quad (2)$$

$$\cancel{Hg(l)} + Cl_2(g) \rightleftharpoons HgCl_2(s) \qquad \Delta G^o = -178.6\ kJ/mol \quad (3)$$

$$HgO(s) + 2Cl_2(g) \rightleftharpoons Cl_2O + HgCl_2(s) \qquad \Delta G^o = -22.2\ kJ/mol$$

Comparing the $\Delta G°$ values for the three reactions shows that reaction 3 is so energetically favorable that it more than compensates for the other two energetically unfavorable reactions. Hence the overall reaction is indeed thermodynamically spontaneous as written.

Note the Pattern

By coupling reactions, a reaction that is thermodynamically nonspontaneous can be made spontaneous.

Example 16.5.1

Bronze Age metallurgists were accomplished practical chemists who unknowingly used coupled reactions to obtain metals from their ores. Realizing that different ores of the same metal required different treatments, they heated copper oxide ore in the presence of charcoal (carbon) to obtain copper metal, whereas they pumped air into the reaction system if the ore was copper sulfide. Assume that a particular copper ore consists of pure cuprous oxide (Cu_2O). Using the $\Delta G_f°$ values given for each, calculate

1. $\Delta G°$ and K_p for the decomposition of Cu_2O to metallic copper and oxygen gas
   $\Delta G_f°(Cu_2O)$= -146.0 kJ/mol
2. $\Delta G°$ and K_p for the reaction of Cu_2O with carbon to produce metallic copper and carbon monoxide
   $\Delta G_f°(CO)$= -137.2 kJ/mol

Given: reactants and products$\Delta G_f°$and K_p values for Cu_2O and CO, and temperature

Asked for: $\Delta G°$ and K_p for the formation of metallic copper from Cu_2O in the absence and presence of carbon

Strategy:

A Write the balanced equilibrium equation for each reaction. Using the "products minus reactants" rule, calculate $\Delta G°$ for the reaction.

B Substitute appropriate values into Equation 16.4.9 to obtain K_p.

Solution:

1. **A** The chemical equation for the decomposition of cuprous oxide is as follows:

   $$Cu_2O(s) \rightleftharpoons 2Cu(s) + \frac{1}{2}O_2(g)$$

   The substances on the right side of this equation are pure elements in their standard states, so their $\Delta G_f°$ values are zero. $\Delta G°$ for the reaction is therefore

   $$\Delta G^o = \left[2\Delta G_f^o(Cu) + \frac{1}{2}\Delta G_f^o(O_2)\right] - \Delta G_f^o(Cu_2O)$$
   $$= \left[\left(2\ \cancel{mol}\right)\left(0\ kJ/\cancel{mol}\right) + \left(\frac{1}{2}\ \cancel{mol}\right)\left(0\ kJ/\cancel{mol}\right)\right] - \left(1\ \cancel{mol}\right)\left(-146.0\ kJ/\cancel{mol}\right)$$
   $$= 146\ kJ$$

2. **B** Rearranging and substituting the appropriate values into Equation 16.4.9,

   $$ln\ K_p = -\frac{\Delta G^o}{RT} = -\frac{146.0\ \cancel{kJ}\left(1000\ \cancel{J}/\cancel{kJ}\right)}{\left(8.314\ \cancel{J}/K\right)\left(298.15\ \cancel{K}\right)} = -58.90$$

3. $K_p = 2.6 \times 10^{-26}$

This is a very small number, indicating that Cu_2O does not spontaneously decompose to a significant extent at room temperature.

4. **A** The O_2 produced in the decomposition of Cu_2O can react with carbon to form CO:

$$\frac{1}{2}O_2(g) + C(s) \rightleftharpoons CO(g)$$

Because $\Delta G°$ for this reaction is equal to $<\Delta G_f°$ for CO (−137.2 kJ/mol), it is energetically more feasible to produce metallic copper from cuprous oxide by coupling the two reactions:

$$Cu_2O(s) \rightleftharpoons 2Cu(s) + \frac{1}{2}O_2(g) \quad \Delta G^o = 146.0\ kJ/mol \quad (1)$$

$$\frac{1}{2}O_2(g) + C(s) \rightleftharpoons CO(g) \quad \Delta G^o = -137.2\ kJ/mol \quad (2)$$

$$Cu_2O(s) + Cl(s) \rightleftharpoons 2Cu(s) + CO(g) \quad \Delta G_f^o = 8.8\ kJ/mol$$

B We can find the corresponding value of K_p:

$$ln\ K_p = -\frac{\Delta G^o}{RT} = -\frac{8.8\ \cancel{kJ}\left(1000\ J/\cancel{kJ}\right)}{\left(8.314\ J/K\right)\left(298.15\ \cancel{K}\right)} = -3.6$$

$$K_p = -0.03$$

Although this value is still less than 1, indicating that reactants are favored over products at room temperature, it is about 24 orders of magnitude greater than K_p for the production of copper metal in the absence of carbon. Because both $\Delta H°$ and $\Delta S°$ are positive for this reaction, it becomes thermodynamically feasible at slightly elevated temperatures (greater than about 80°C). At temperatures of a few hundred degrees Celsius, the reaction occurs spontaneously, proceeding smoothly and rapidly to the right as written and producing metallic copper and carbon monoxide from cuprous oxide and carbon.

Exercise

Use the $\Delta G_f°$ values given to calculate $\Delta G°$ and K_p for each reaction.

1. the decomposition of cuprous sulfide to copper metal and elemental sulfur
   $\Delta G_f°(Cu_2S)$= -86.2 kJ/mol
2. the reaction of cuprous sulfide with oxygen gas to produce sulfur dioxide and copper metal
   $\Delta G_f°(SO_2(g))$= -300.1 kJ/mol

Answer:

1. $\Delta G°$ = 86.2 kJ/mol; $K_p = 7.90 \times 10^{-16}$
2. $\Delta G°$ = −213.9 kJ/mol; $K_p = 2.99 \times 10^{37}$

Summary

Thermodynamics describes the overall properties, behavior, and equilibrium composition of a system; kinetics describes the rate at which a particular process will occur and the pathway by which it will occur. Whereas thermodynamics tells us what can occur during a reaction process, kinetics tells us what actually occurs on an atomic or a molecular level. A reaction that is not thermodynamically spontaneous under standard conditions can often be made to occur spontaneously by varying the reaction conditions; using a different reaction to obtain the same product; supplying external energy, such as electricity; or coupling the unfavorable reaction to another reaction for which $\Delta G° << 0$.

Key Takeaway

- Thermodynamics describes the overall properties, behavior, and equilibrium composition of a system, whereas kinetics describes the particular pathway by which a physical or a chemical change actually occurs.

Conceptual Problem

1. You are in charge of finding conditions to make the reaction A(l) + B(l) → C(l) + D(g) favorable because it is a critical step in the synthesis of your company's key product. You have calculated that $\Delta G°$ for the reaction is negative, yet the ratio of products to reactants is very small. What have you overlooked in your scheme? What can you do to drive the reaction to increase your product yield?

Contributors

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Chapter 16.6: End of Chapter Material

+ H_2O \rightarrow \underset{lactic acid}{4CH_{3}CH\left (OH \right)CO_{2}H} \)

The combustion of sucrose, however, occurs as follows:

$C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(l)$

1. Which reaction is thermodynamically more favorable—the anaerobic conversion of sucrose to lactic acid or the aerobic oxidation to CO_2 and H_2O? The values of ΔH_f are as follows: lactic acid, −694.1 kJ/mol; sucrose, −222 kJ/mol; CO_2, −393.5 kJ/mol; and H_2O, −285.8 kJ/mol.
2. What is ΔE for the combustion of 12.0 g of sucrose at normal body temperature (37°C)?

•

Phosphorus exists as several allotropes, the most common being red, black, and white phosphorus. White phosphorus consists of tetrahedral P_4 molecules and melts at 44.15°C; it is converted to red phosphorus by heating at 400°C for several hours. The chemical differences between red and white phosphorus are considerable: white phosphorus burns in air, whereas red phosphorus is stable; white phosphorus is soluble in organic compounds, whereas red phosphorus is not; white phosphorus melts at 44.15°C, whereas red phosphorus melts at 597°C. If the enthalpy of fusion of white phosphorus is 0.659 kJ/mol, what is its ΔS? Black phosphorus is even less reactive than red. Based on this information, which allotrope would you predict to have the highest entropy? the lowest? Why?

•

♦ Ruby and sapphire have a common mineral name: corundum (Al_2O_3). Although they are crystalline versions of the same compound, the nature of the imperfections determines the identity of the gem. Outline a method for measuring and comparing the entropy of a ruby with the entropy of a sapphire. How would you expect the entropies to compare with the entropy of a perfect corundum crystal?

•

♦ Tin has two crystalline forms—α and β—represented in the following equilibrium equation:

$$\underset{gray}{\alpha - tin} + H_2O \overset{18°C}{\rightleftharpoons} \underset{white}{\beta - tin} \overset{232°C}{\rightleftharpoons} Sn\,(l)$$

The earliest known tin artifacts were discovered in Egyptian tombs of the 18th dynasty (1580–1350 BC), although archaeologists are surprised that so few tin objects exist from earlier eras. It has been suggested that many early tin objects were either oxidized to a mixture of stannous and stannic oxides or transformed to powdery, gray tin. Sketch a thermodynamic cycle similar to part (b) in Figure 18.4.3 to show the conversion of liquid tin to gray tin. Then calculate the change in entropy that accompanies the conversion of Sn(l) to α-Sn using the following data: C_p(white) = 26.99, C_p(gray) = 25.77 J/(mol·K), ΔH_{fus} = 7.0 kJ/mol, $\Delta H_{\beta \rightarrow \alpha}$ = −2.2 kJ/mol.

•

The reaction of SO_2 with O_2 to produce SO_3 has great industrial significance because SO_3 is converted to H_2SO_4 by reaction with water. Unfortunately, the reaction is also environmentally important because SO_3 from industrial smokestacks is a primary source of acid rain. ΔH for the reaction of SO_2 with O_2 to form SO_3 is −23.49 kJ/mol, and ΔS is −22.66 J/(mol·K). Does this reaction occur spontaneously at 25°C? Does it occur spontaneously at 800°C assuming no change in ΔH and ΔS? Why is this reaction usually carried out at elevated temperatures?

•

Pollutants from industrial societies pose health risks to individuals from exposure to metals such as lead, mercury, and cadmium. The biological effects of a toxic metal may be reduced by removing it from the system using a chelating agent, which binds to the metal and forms a complex that is eliminated from the system without causing more damage. In designing a suitable chelating agent, one must be careful, however, because some chelating agents form metal complexes that are more toxic than the metal itself. Both methylamine (CH_3NH_2) and ethylenediamine ($H_2NCH_2CH_2NH_2$, abbreviated en) could, in principle, be used to treat heavy metal poisoning. In the case of cadmium, the reactions are as follows:

$$Cd^{2+} + 2CH_3NH_2 \rightarrow Cd\left(CH_3NH_2\right)_2^{2+}$$

$$\Delta H = -7.03\ kcal/mol \quad \Delta S = -1.58\ cal/\left(mol \cdot K\right)$$

$$Cd^{2+} + en \rightarrow Cd\left(en\right)_2^{2+}$$

$$\Delta H = -7.02\ kcal/mol \quad \Delta S = -3.15\ cal/\left(mol \cdot K\right)$$

Based strictly on thermodynamic arguments, which would you choose to administer to a patient suffering from cadmium toxicity? Why? Assume a body temperature of 37°C.

•

♦ Explosive reactions often have a large negative enthalpy change and a large positive entropy change, but the reaction must also be kinetically favorable. For example, the following equation represents the reaction between hydrazine, a rocket propellant, and the oxidizer dinitrogen tetroxide:

$2N_2H_4(l) + N_2O_4(l) \rightarrow 4H_2O(g) + 3N_2(g)$ $\Delta H°$ = −249 kJ/mol, $\Delta S°$ = 218 J/(mol·K)

1. How much free energy is produced from this reaction at 25°C?
2. Is the reaction thermodynamically favorable?
3. What is K?
4. This reaction requires thermal ignition. Why?

•

♦ Cesium, a silvery-white metal used in the manufacture of vacuum tubes, is produced industrially by the reaction of CsCl with CaC_2:

$2CsCl(l) + CaC_2(s) \rightarrow CaCl_2(l) + 2C(s) + 2Cs(g)$

Compare the free energy produced from this reaction at 25°C and at 1227°C, the temperature at which it is normally run, given these values:

$\Delta H_{298\ K}°$ = 32.0 kJ/mol, $\Delta S_{298\ K}°$= 8.0 J/(mol·K); $\Delta H_{1500\ K}°$ = −0.6 kJ/mol, $\Delta S_{1500\ K}°$ = 3.6 J/(mol·K).

1. If you wanted to minimize energy costs in your production facility by reducing the temperature of the reaction, what is the lowest temperature at which products are favored over reactants (assuming the reaction is kinetically favorable at the lower temperature)? Assume $\Delta H°$ and $\Delta S°$ vary linearly with temperature.
2. What is the ratio $K_{1500\ K}/K_{298\ K}$?

•

Dessicants (drying agents) can often be regenerated by heating, although it is generally not economically worthwhile to do so. A dessicant that is commonly regenerated is $CaSO_4 \cdot 2H_2O$:

$$CaSO_4 \cdot 2H_2O\left(s\right) \rightarrow CaSO_4\left(s\right) + 2H_2O\left(g\right)$$

$$\Delta H_{298}^{o} = -7.02\ kcal/mol \quad \Delta S_{298}^{o} = -3.15\ cal/\left(mol \cdot K\right)$$

Regeneration is carried out at 250°C.

1. What is $\Delta G°$ for this reaction?
2. What is the equilibrium constant at 25°C?
3. What is the ratio $K_{250°C}/K_{25°C}$?
4. What is the equilibrium constant at 250°C?
5. Is regeneration of $CaSO_4(s) \cdot 2H_2O$ an enthalpy- or entropy-driven process? Explain your answer.

•

The nitrogen triiodide complex with ammonia ($NI_3 \cdot NH_3$) is a simple explosive that can be synthesized from common household products. When detonated, it produces N_2 and I_2. It can be painted on surfaces when wet, but it is shock sensitive when dry (even touching it with a feather can cause an explosion). Do you expect ΔG for the explosion reaction to be positive or negative? Why doesn't $NI_3 \cdot NH_3$ explode spontaneously?

•

Adenosine triphosphate (ATP) contains high-energy phosphate bonds that are used in energy metabolism, coupling energy-yielding and energy-requiring processes. Cleaving a phosphate link by hydrolysis (ATP hydrolysis) can be described by the reaction ATP + H_2O ⇌ ADP + Pi + H^+ where P_i symbolizes phosphate. Glycerol and ATP react to form glycerol-3-phosphate, ADP, and H^+, with an overall K = 6.61 × 10^5 at 37°C. The reaction of glycerol with phosphate to form glycerol-3-phosphate and water has an equilibrium constant of 2.82 × 10^{-2}. What is the equilibrium constant for ATP hydrolysis? How much free energy is released from the hydrolysis of ATP?

•

♦ Consider the biological reduction of molecular nitrogen, for which the following is the minimal reaction stoichiometry under optimal conditions (P_i = phosphate):

$8H^+ + 8e^- + N_2 + 16ATP \rightarrow H_2 + 2NH_3 + 16ADP + 16P_i$

1. What is the approximate ratio of K_{eq} for this reaction and for the same reaction in the absence of ATP?
2. Given the fact that at pH 7 both the reaction of protons and electrons to give H_2 and the reaction of H_2 with N_2 to give ammonia are thermodynamically spontaneous (i.e., K >> 1), suggest a reason that nitrogen-fixing bacteria use such a large energy input to drive a reaction that is already spontaneous.

3. 1. −4315 kJ/mol B_5H_9
   2. 1340 kJ

Answers

1. 3. −1.55 × 10^6 kJ per 50 lb of B_5H_9
4.
5. −2046 kJ/mol
6.
7. 1. aerobic conversion
   2. −268 kJ
8.
9.
10.
11. Yes, the reaction is spontaneous at 25°C, but its rate is *very* slow. The reaction is not spontaneous at 800°C (ΔG = 0.82 kJ/mol), but the reaction rate is much greater.
12.
13. 1. −314 kJ/mol
    2. yes
    3. 2.10 × 10^{45}
    4. Ignition is required to overcome the high activation energy to reaction.
14.
15. 1. 4.4 kJ/mol
    2. 0.17
    3. 78.3
    4. 13
    5. entropy-driven; $\Delta H°$ > 0, so $\Delta S°$ must be positive for the reaction to be spontaneous.
16.
17. 2.34 × 10^7; −43.7 kJ/mol
18.

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CHAPTER OVERVIEW

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Chapter 17.0: Introduction

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In oxidation–reduction (redox) reactions, electrons are transferred from one species (the reductant) to another (the oxidant). This transfer of electrons provides a means for converting chemical energy to electrical energy or vice versa. The study of the relationship between electricity and chemical reactions is called electrochemistry, an area of chemistry we introduced in Section 12.7). In this chapter, we describe electrochemical reactions in more depth and explore some of their applications.

In the first three sections, we review redox reactions; describe how they can be used to generate an electrical potential, or *voltage*; and discuss factors that affect the magnitude of the potential. We then explore the relationships among the electrical potential, the change in free energy, and the equilibrium constant for a redox reaction, which are all measures of the thermodynamic driving force for a reaction. Finally, we examine two kinds of applications of electrochemical principles: (1) those in which a spontaneous reaction is used to provide electricity and (2) those in which electrical energy is used to drive a thermodynamically nonspontaneous reaction. By the end of this chapter, you will understand why different kinds of batteries are used in cars, flashlights, cameras, and portable computers; how rechargeable batteries operate; and why corrosion occurs and how to slow—if not prevent—it. You will also discover how metal objects can be plated with silver or chromium for protection; how silver polish removes tarnish; and how to calculate the amount of electricity needed to produce aluminum, chlorine, copper, and sodium on an industrial scale.



A view from the top of the Statue of Liberty, showing the green patina coating the statue. *The patina is formed by corrosion of the copper skin of the statue, which forms a thin layer of an insoluble compound that contains copper(II), sulfate, and hydroxide ions.*

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Chapter 17.1: Describing Electrochemical Cells

Learning Objective

- To distinguish between galvanic and electrolytic cells.

In any electrochemical process, electrons flow from one chemical substance to another, driven by an oxidation–reduction (redox) reaction. As we described in Section 12.7, a redox reaction occurs when electrons are transferred from a substance that is oxidized to one that is being reduced. The reductant (a substance that is capable of donating electrons and in the process is oxidized) is the substance that loses electrons and is oxidized in the process; the oxidant (A substance that is capable of accepting electrons and in the process is reduced) is the species that gains electrons and is reduced in the process. The associated potential energy is determined by the potential difference between the valence electrons in atoms of different elements.

Because it is impossible to have a reduction without an oxidation and vice versa, a redox reaction can be described as two half-reactions (reactions that represent either the oxidation half or the reduction half of an oxidation–reduction (redox) reaction), one representing the oxidation process and one the reduction process. For the reaction of zinc with bromine, the overall chemical reaction is as follows:

$$Zn\,(s) + Br_2\,(l) \rightarrow Zn^{2+}\,(aq) + 2Br^-\,(aq) \tag{17.1.1}$$

<\div>

The half-reactions are as follows:

$$reduction\ half\ reaction: Br_2\,(l) + 2e^- \rightarrow 2Br^-\,(aq) \tag{17.1.2}$$

$$oxidation\ half\ reaction: Zn\,(s) \rightarrow Zn^{2+}\,(aq) + 2e^- \tag{17.1.3}$$

Each half-reaction is written to show what is actually occurring in the system; Zn is the reductant in this reaction (it loses electrons), and Br_2 is the oxidant (it gains electrons). Adding the two half-reactions gives the overall chemical reaction (Equation 17.1.1). A redox reaction is balanced when *the number of electrons lost by the reductant equals the number of electrons gained by the oxidant*. Like any balanced chemical equation, the overall process is electrically neutral; that is, the net charge is the same on both sides of the equation.

Note the Pattern

In any redox reaction, the number of electrons lost by the reductant equals the number of electrons gained by the oxidant.

In most of our discussions of chemical reactions, we have assumed that the reactants are in intimate physical contact with one another. Acid–base reactions, for example, are usually carried out with the acid and the base dispersed in a single phase, such as a liquid solution. With redox reactions, however, it is possible to physically separate the oxidation and reduction half-reactions in space, as long as there is a complete circuit, including an external electrical connection, such as a wire, between the two half-reactions. As the reaction progresses, the electrons flow from the reductant to the oxidant over this electrical connection, producing an electric current that can be used to do work. An apparatus that is used to generate electricity from a spontaneous redox reaction or, conversely, that uses electricity to drive a nonspontaneous redox reaction is called an electrochemical cell (an apparatus that generates electricity from a spontaneous oxidation–reduction (redox) reaction or, conversely, uses electricity to drive a nonspontaneous redox reaction).

There are two types of electrochemical cells: galvanic cells and electrolytic cells. A galvanic (voltaic) cell (an electrochemical cell that uses the energy released during a spontaneous oxidation–reduction (redox) reaction (ΔG^o) to generate electricity). Galvanic cells are named for the Italian physicist and physician Luigi Galvani (1737–1798), who observed that dissected frog leg muscles twitched when a small electric shock was applied, demonstrating the electrical nature of nerve impulses. uses the energy released during a spontaneous redox reaction ($\Delta G < 0$) to *generate* electricity. This type of electrochemical cell is often called a *voltaic cell* after its inventor, the Italian physicist Alessandro Volta (1745–1827). In contrast, an electrolytic cellAn electrochemical cell that consumes electrical energy from an external source to drive a nonspontaneous (ΔG^o) oxidation–reduction (redox) reaction. *consumes* electrical energy from an external source, using it to cause a nonspontaneous redox reaction to occur ($\Delta G > 0$). Both types contain two electrodesA solid metal connected by an electrolyte and an external circuit that provides an electrical connection

between systems in an electrochemical cell (galvanic or electrolytic)., which are solid metals connected to an external circuit that provides an electrical connection between the two parts of the system Figure 17.1.1). The oxidation half-reaction occurs at one electrode (the anodeOne of two electrodes in an electrochemical cell, it is the site of the oxidation half-reaction.), and the reduction half-reaction occurs at the other (the cathodeOne of two electrodes in an electrochemical cell, it is the site of the reduction half-reaction.). When the circuit is closed, electrons flow from the anode to the cathode. The electrodes are also connected by an *electrolyte*, an ionic substance or solution that allows ions to transfer between the electrode compartments, thereby maintaining the system's electrical neutrality. In this section, we focus on reactions that occur in galvanic cells. We discuss electrolytic cells in Section 17.7.

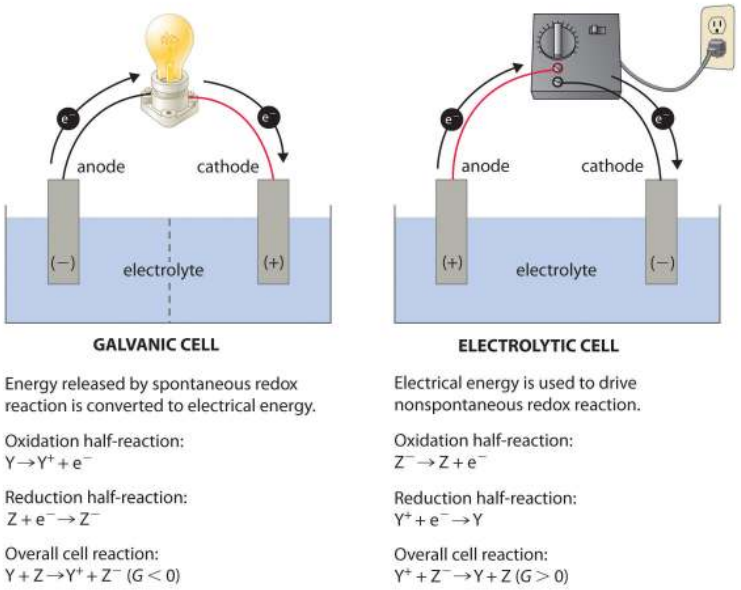


Figure 17.1.1 Electrochemical Cells *A galvanic cell (left) transforms the energy released by a spontaneous redox reaction into electrical energy that can be used to perform work. The oxidative and reductive half-reactions usually occur in separate compartments that are connected by an external electrical circuit; in addition, a second connection that allows ions to flow between the compartments (shown here as a vertical dashed line to represent a porous barrier) is necessary to maintain electrical neutrality. The potential difference between the electrodes (voltage) causes electrons to flow from the reductant to the oxidant through the external circuit, generating an electric current. In an electrolytic cell (right), an external source of electrical energy is used to generate a potential difference between the electrodes that forces electrons to flow, driving a nonspontaneous redox reaction; only a single compartment is employed in most applications. In both kinds of electrochemical cells, the anode is the electrode at which the oxidation half-reaction occurs, and the cathode is the electrode at which the reduction half-reaction occurs.*

Galvanic (Voltaic) Cells

To illustrate the basic principles of a galvanic cell, let's consider the reaction of metallic zinc with cupric ion (Cu^{2+}) to give copper metal and Zn^{2+} ion. The balanced chemical equation is as follows:

$$Zn\,(s) + Cu^{2+}\,(aq) \rightarrow Zn^{2+}\,(aq) + Cu\,(s)$$

We can cause this reaction to occur by inserting a zinc rod into an aqueous solution of copper(II) sulfate. As the reaction proceeds, the zinc rod dissolves, and a mass of metallic copper forms (Figure 17.1.2). These changes occur spontaneously, but all the energy released is in the form of heat rather than in a form that can be used to do work.

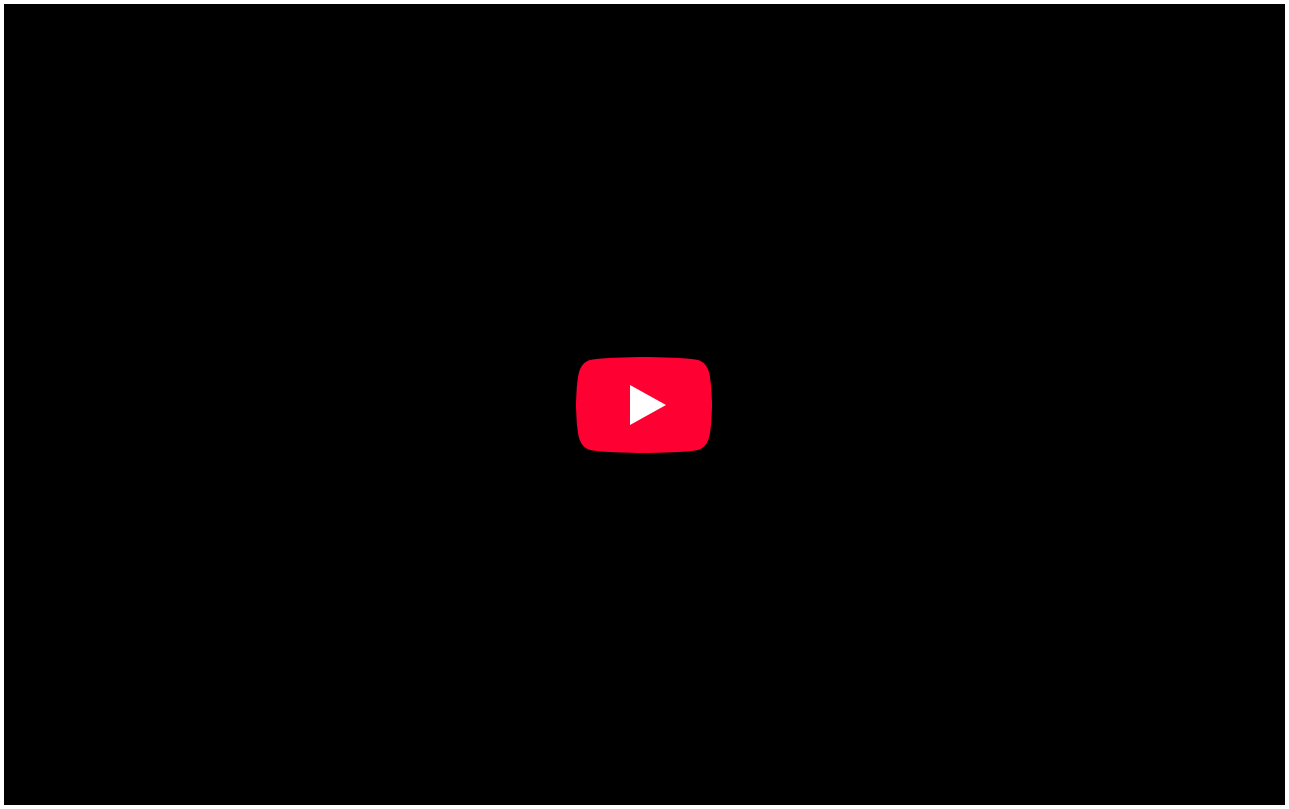




Figure 17.1.2 The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Single Compartment *When a zinc plate is inserted into a beaker that contains an aqueous solution of copper(II) sulfate, a spontaneous redox reaction occurs: the zinc electrode dissolves to give $Zn^{2+}(aq)$ ions, while $Cu^{2+}(aq)$ ions are simultaneously reduced to metallic copper. The reaction occurs so rapidly that the copper is deposited as very fine particles that appear black, rather than the usual reddish color of copper. Video from CMUChemVideos*

This same reaction can be carried out using the galvanic cell illustrated in part (a) in Figure 17.1.3. To assemble the cell, a copper strip is inserted into a beaker that contains a 1 M solution of Cu^{2+} ions, and a zinc strip is inserted into a different beaker that contains a 1 M solution of Zn^{2+} ions. The two metal strips, which serve as electrodes, are connected by a wire, and the compartments are connected by a salt bridge (a U-shaped tube inserted into both solutions of a galvanic cell that contains a concentrated liquid or gelled electrolyte and completes the circuit between the anode and the cathode), a U-shaped tube inserted into both solutions that contains a concentrated liquid or gelled electrolyte. The ions in the salt bridge are selected so that they do not interfere with the electrochemical reaction by being oxidized or reduced themselves or by forming a precipitate or complex; commonly used cations and anions are Na^+ or K^+ and NO_3^- or SO_4^{2-}, respectively. (The ions in the salt bridge do *not* have to be the same as those in the redox couple in either compartment.) When the circuit is closed, a spontaneous reaction occurs: zinc metal

is oxidized to Zn^{2+} ions at the zinc electrode (the anode), and Cu^{2+} ions are reduced to Cu metal at the copper electrode (the cathode). As the reaction progresses, the zinc strip dissolves, and the concentration of Zn^{2+} ions in the Zn^{2+} solution increases; simultaneously, the copper strip gains mass, and the concentration of Cu^{2+} ions in the Cu^{2+} solution decreases (part (b) in Figure 17.1.3). Thus we have carried out the same reaction as we did using a single beaker, but this time the oxidative and reductive half-reactions are physically separated from each other. The electrons that are released at the anode flow through the wire, producing an electric current. Galvanic cells therefore transform chemical energy into electrical energy that can then be used to do work.

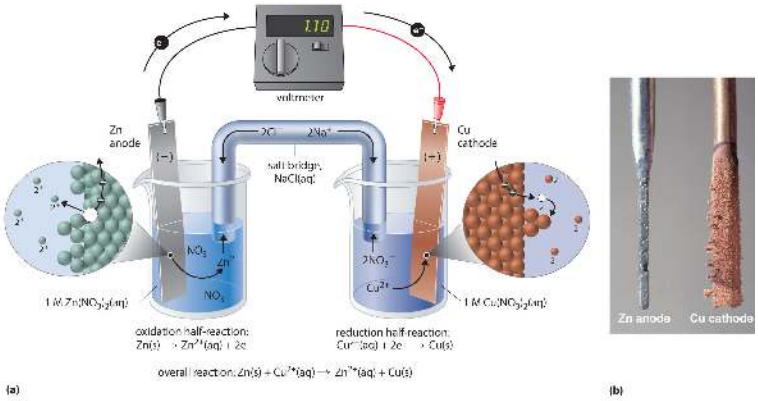
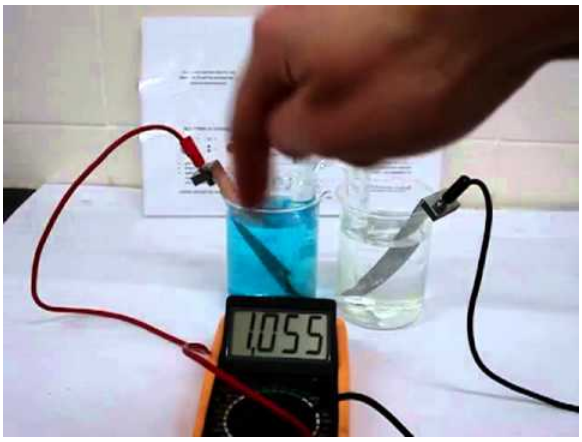


Figure 17.1.3 The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Galvanic Cell *(a) A galvanic cell can be constructed by inserting a copper strip into a beaker that contains an aqueous 1 M solution of Cu^{2+} ions and a zinc strip into a different beaker that contains an aqueous 1 M solution of Zn^{2+} ions. The two metal strips are connected by a wire that allows electricity to flow, and the beakers are connected by a salt bridge. When the switch is closed to complete the circuit, the zinc electrode (the anode) is spontaneously oxidized to Zn^{2+} ions in the left compartment, while Cu^{2+} ions are simultaneously reduced to copper metal at the copper electrode (the cathode). (b) As the reaction progresses, the Zn anode loses mass as it dissolves to give $Zn^{2+}(aq)$ ions, while the Cu cathode gains mass as $Cu^{2+}(aq)$ ions are reduced to copper metal that is deposited on the cathode.*

The electrolyte in the salt bridge serves two purposes: it completes the circuit by carrying electrical charge and maintains electrical neutrality in both solutions by allowing ions to migrate between them. The identity of the salt in a salt bridge is unimportant, as long as the component ions do not react or undergo a redox reaction under the operating conditions of the cell. Without such a connection, the total positive charge in the Zn^{2+} solution would increase as the zinc metal dissolves, and the total positive charge in the Cu^{2+} solution would decrease. The salt bridge allows charges to be neutralized by a flow of anions into the Zn^{2+} solution and a flow of cations into the Cu^{2+} solution. In the absence of a salt bridge or some other similar connection, the reaction would rapidly cease because electrical neutrality could not be maintained.



A galvanic cell. *This galvanic cell illustrates the use of a salt bridge to connect two solutions generating a voltage. Video from Angela Stott*

A *voltmeter* can be used to measure the difference in electrical potential between the two compartments. Opening the switch that connects the wires to the anode and the cathode prevents a current from flowing, so no chemical reaction occurs. With the switch closed, however, the external circuit is closed, and an electric current can flow from the anode to the cathode. The potential (E_{cell})Related to the energy needed to move a charged particle in an electric field, it is the difference in electrical potential beween two half-reactions. of the cell, measured in volts, is the difference in electrical potential between the two half-reactions and is related to the energy needed to move a charged particle in an electric field. In the cell we have described, the voltmeter indicates a potential of 1.10 V (part (a) in Figure 17.1.3). Because electrons from the oxidation half-reaction are released at the anode, the anode in a galvanic cell is negatively charged. The cathode, which attracts electrons, is positively charged.

Not all electrodes undergo a chemical transformation during a redox reaction. The electrode can be made from an inert, highly conducting metal such as platinum to prevent it from reacting during a redox process, where it does not appear in the overall electrochemical reaction. This phenomenon is illustrated in Example 1.

Note the Pattern

A galvanic (voltaic) cell converts the energy released by a spontaneous chemical reaction to electrical energy. An electrolytic cell consumes electrical energy from an external source to drive a nonspontaneous chemical reaction.

Example 17.1.1

A chemist has constructed a galvanic cell consisting of two beakers. One beaker contains a strip of tin immersed in aqueous sulfuric acid, and the other contains a platinum electrode immersed in aqueous nitric acid. The two solutions are connected by a salt bridge, and the electrodes are connected by a wire. Current begins to flow, and bubbles of a gas appear at the platinum electrode. The spontaneous redox reaction that occurs is described by the following balanced chemical equation:

$$3Sn(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3Sn^{2+}(aq) + 2NO(g) + 4H_2O(l)$$

For this galvanic cell,

1. write the half-reaction that occurs at each electrode.
2. indicate which electrode is the cathode and which is the anode.
3. indicate which electrode is the positive electrode and which is the negative electrode.

Given: galvanic cell and redox reaction

Asked for: half-reactions, identity of anode and cathode, and electrode assignment as positive or negative

Strategy:

A Identify the oxidation half-reaction and the reduction half-reaction. Then identify the anode and cathode from the half-reaction that occurs at each electrode.

B From the direction of electron flow, assign each electrode as either positive or negative.

Solution:

1. **A** In the reduction half-reaction, nitrate is reduced to nitric oxide. (The nitric oxide would then react with oxygen in the air to form NO_2, with its characteristic red-brown color.) In the oxidation half-reaction, metallic tin is oxidized. The half-reactions corresponding to the actual reactions that occur in the system are as follows:

   reduction: $NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$ oxidation: $Sn(s) \rightarrow Sn^{2+}(aq) + 2e^-$

   Thus nitrate is reduced to NO, while the tin electrode is oxidized to Sn^{2+}.

2. Because the reduction reaction occurs at the Pt electrode, it is the cathode. Conversely, the oxidation reaction occurs at the tin electrode, so it is the anode.
3. **B** Electrons flow from the tin electrode through the wire to the platinum electrode, where they transfer to nitrate. The electric circuit is completed by the salt bridge, which permits the diffusion of cations toward the cathode and anions toward the anode. Because electrons flow *from* the tin electrode, it must be electrically negative. In contrast, electrons flow *toward* the Pt electrode, so that electrode must be electrically positive.

Exercise

Consider a simple galvanic cell consisting of two beakers connected by a salt bridge. One beaker contains a solution of MnO_4^- in dilute sulfuric acid and has a Pt electrode. The other beaker contains a solution of Sn^{2+} in dilute sulfuric acid, also with a Pt electrode. When the two electrodes are connected by a wire, current flows and a spontaneous reaction occurs that is described by the following balanced chemical equation:

$$2MnO_4^-(aq) + 5Sn^{2+}(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5Sn^{4+}(aq) + 8H_2O(l)$$

For this galvanic cell,

1. write the half-reaction that occurs at each electrode.
2. indicate which electrode is the cathode and which is the anode.
3. indicate which electrode is positive and which is negative.

Answer:

1. $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$; $Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-$
2. The Pt electrode in the permanganate solution is the cathode; the one in the tin solution is the anode.

3. The cathode (electrode in beaker that contains the permanganate solution) is positive, and the anode (electrode in beaker that contains the tin solution) is negative.

Constructing a Cell Diagram

Because it is somewhat cumbersome to describe any given galvanic cell in words, a more convenient notation has been developed. In this line notation, called a *cell diagram*, the identity of the electrodes and the chemical contents of the compartments are indicated by their chemical formulas, with the anode written on the far left and the cathode on the far right. Phase boundaries are shown by single vertical lines, and the salt bridge, which has two phase boundaries, by a double vertical line. Thus the cell diagram for the Zn/Cu cell shown in part (a) in Figure 17.1.3 is written as follows:

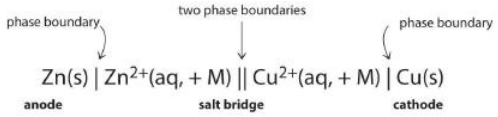


Figure 17.1.4 *A cell diagram includes solution concentrations when they are provided.*

Galvanic cells can have arrangements other than the examples we have seen so far. For example, the voltage produced by a redox reaction can be measured more accurately using two electrodes immersed in a single beaker containing an electrolyte that completes the circuit. This arrangement reduces errors caused by resistance to the flow of charge at a boundary, called the *junction potential*. One example of this type of galvanic cell is as follows:

$$Pt\,(s)\,|\,H_2\,(g)\,|\,HCl\,(aq)\,|\,AgCl\,(s)\,|\,Ag\,(s)$$

This cell diagram does not include a double vertical line representing a salt bridge because there is no salt bridge providing a junction between two dissimilar solutions. Moreover, solution concentrations have not been specified, so they are not included in the cell diagram. The half-reactions and the overall reaction for this cell are as follows:

$$cathode\ reaction: AgCl\,(s) + e^- \rightarrow Ag\,(s) + Cl^-\,(aq)$$

$$anode\ reaction: \frac{1}{2}H_2\,(g) \rightarrow H^+\,(aq) + e^-$$

$$overall: AgCl\,(s) + \frac{1}{2}H_2\,(g) \rightarrow Ag\,(s) + Cl^-\,(aq) + H^+\,(aq)$$

A single-compartment galvanic cell will initially exhibit the same voltage as a galvanic cell constructed using separate compartments, but it will discharge rapidly because of the direct reaction of the reactant at the anode with the oxidized member of the cathodic redox couple. Consequently, cells of this type are not particularly useful for producing electricity.

Example 17.1.2

Draw a cell diagram for the galvanic cell described in Example 1. The balanced chemical reaction is as follows:

$$3Sn(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3Sn^{2+}(aq) + 2NO(g) + 4H_2O(l)$$

Given: galvanic cell and redox reaction

Asked for: cell diagram

Strategy:

Using the symbols described, write the cell diagram beginning with the oxidation half-reaction on the left.

Solution:

The anode is the tin strip, and the cathode is the Pt electrode. Beginning on the left with the anode, we indicate the phase boundary between the electrode and the tin solution by a vertical bar. The anode compartment is thus $Sn(s)|Sn^{2+}(aq)$. We could include $H_2SO_4(aq)$ with the contents of the anode compartment, but the sulfate ion (as HSO_4^-) does not participate in the overall reaction, so it does not need to be specifically indicated. The cathode compartment contains aqueous nitric acid, which does participate in the overall reaction, together with the product of the reaction (NO) and the Pt electrode. These are written as $HNO_3(aq)|NO(g)|Pt(s)$, with single vertical bars indicating the phase boundaries. Combining the two compartments and using a double vertical bar to indicate the salt bridge,

$$Sn(s)\,|\,Sn^{2+}(aq)\,\|\,HNO_3(aq)\,|\,NO(g)\,|\,Pt(s)$$

The solution concentrations were not specified, so they are not included in this cell diagram.

Exercise

Draw a cell diagram for the following reaction, assuming the concentration of Ag^+ and Mg^{2+} are each 1 M:

$$Mg(s) + 2Ag^+(aq) \rightarrow Mg^{2+}(aq) + 2Ag(s)$$

Answer: $Mg(s)\,|\,Mg^{2+}(aq,\ 1\ M)\,\|\,Ag^+(aq,\ 1\ M)\,|\,Ag(s)$

Summary

Electrochemistry is the study of the relationship between electricity and chemical reactions. The oxidation–reduction reaction that occurs during an electrochemical process consists of two **half-reactions**, one representing the oxidation process and one the reduction process. The sum of the half-reactions gives the overall chemical reaction. The overall redox reaction is balanced when the number of electrons lost by the **reductant** equals the number of electrons gained by the **oxidant**. An electric current is produced from the flow of electrons from the reductant to the oxidant. An **electrochemical cell** can either generate electricity from a spontaneous redox reaction or consume electricity to drive a nonspontaneous reaction. In a **galvanic (voltaic) cell**, the energy from a spontaneous reaction generates electricity, whereas in an **electrolytic cell**, electrical energy is consumed to drive a nonspontaneous redox reaction. Both types of cells use two **electrodes** that provide an electrical connection between systems that are separated in space. The oxidative half-reaction occurs at the **anode**, and the reductive half-reaction occurs at the **cathode**. A **salt bridge** connects the separated solutions, allowing ions to migrate to either solution to ensure the system's electrical neutrality. A voltmeter is a device that measures the flow of electric current between two half-reactions. The **potential** of a cell, measured in volts, is the energy needed to move a charged particle in an electric field. An electrochemical cell can be described using line notation called a cell diagram, in which vertical lines indicate phase boundaries and the location of the salt bridge. Resistance to the flow of charge at a boundary is called the junction potential.

Key Takeaway

- A galvanic (voltaic) cell uses the energy released during a spontaneous redox reaction to generate electricity, whereas an electrolytic cell consumes electrical energy from an external source to force a reaction to occur.

Conceptual Problems

1. Is $2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$ an oxidation–reduction reaction? Why or why not?
2. If two half-reactions are physically separated, how is it possible for a redox reaction to occur? What is the name of the apparatus in which two half-reactions are carried out simultaneously?
3. What is the difference between a galvanic cell and an electrolytic cell? Which would you use to generate electricity?
4. What is the purpose of a salt bridge in a galvanic cell? Is it always necessary to use a salt bridge in a galvanic cell?
5. One criterion for a good salt bridge is that it contains ions that have similar rates of diffusion in aqueous solution, as K^+ and Cl^- ions do. What would happen if the diffusion rates of the anions and cations differed significantly?
6. It is often more accurate to measure the potential of a redox reaction by immersing two electrodes in a single beaker rather than in two beakers. Why?

5. A large difference in cation/anion diffusion rates would increase resistance in the salt bridge and limit electron flow through the circuit.
4.
3.
6.
2.

Answer

1.

Numerical Problems

1. Copper(I) sulfate forms a bright blue solution in water. If a piece of zinc metal is placed in a beaker of aqueous $CuSO_4$ solution, the blue color fades with time, the zinc strip begins to erode, and a black solid forms around the zinc strip. What is happening? Write half-reactions to show the chemical changes that are occurring. What will happen if a piece of copper metal is placed in a colorless aqueous solution of $ZnCl_2$?
2. Consider the following spontaneous redox reaction: $NO_3^-(aq) + H^+(aq) + SO_3^{2-}(aq) \rightarrow SO_4^{2-}(aq) + HNO_2(aq)$.
    1. Write the two half-reactions for this overall reaction.

2. If the reaction is carried out in a galvanic cell using an inert electrode in each compartment, which electrode corresponds to which half-reaction?
3. Which electrode is negatively charged, and which is positively charged?

3. The reaction $Pb(s) + 2VO^{2+}(aq) + 4H^{+}(aq) \rightarrow Pb^{2+}(aq) + 2V^{3+}(aq) + 2H_2O(l)$ occurs spontaneously.
    1. Write the two half-reactions for this redox reaction.
    2. If the reaction is carried out in a galvanic cell using an inert electrode in each compartment, which reaction occurs at the cathode and which occurs at the anode?
    3. Which electrode is positively charged, and which is negatively charged?
4. Phenolphthalein is an indicator that turns pink under basic conditions. When an iron nail is placed in a gel that contains $[Fe(CN)_6]^{3-}$, the gel around the nail begins to turn pink. What is occurring? Write the half-reactions and then write the overall redox reaction.
5. Sulfate is reduced to HS^{-} in the presence of glucose, which is oxidized to bicarbonate. Write the two half-reactions corresponding to this process. What is the equation for the overall reaction?
6. Write the spontaneous half-reactions and the overall reaction for each proposed cell diagram. State which half-reaction occurs at the anode and which occurs at the cathode.
    1. $Pb(s)\,|\,PbSO_4(s)\,|\,SO_4^{2-}(aq)\,\|\,Cu^{2+}(aq)\,|\,Cu(s)$
    2. $Hg(l)\,|\,Hg_2Cl_2(s)\,|\,Cl^{-}(aq)\,\|\,Cd^{2+}(aq)\,|\,Cd(s)$
7. For each galvanic cell represented by these cell diagrams, determine the spontaneous half-reactions and the overall reaction. Indicate which reaction occurs at the anode and which occurs at the cathode.
    1. $Zn(s)\,|\,Zn^{2+}(aq)\,\|\,H^{+}(aq)\,|\,H_2(g)$, $Pt(s)$
    2. $Ag(s)\,|\,AgCl(s)\,|\,Cl^{-}(aq)\,\|\,H^{+}(aq)\,|\,H_2(g)\,|\,Pt(s)$
    3. $Pt(s)\,|\,H_2(g)\,|\,H^{+}(aq)\,\|\,Fe^{2+}(aq)$, $Fe^{3+}(aq)\,|\,Pt(s)$
8. For each redox reaction, write the half-reactions and draw the cell diagram for a galvanic cell in which the overall reaction occurs spontaneously. Identify each electrode as either positive or negative.
    1. $Ag(s) + Fe^{3+}(aq) \rightarrow Ag^{+}(aq) + Fe^{2+}(aq)$
    2. $Fe^{3+}(aq) + 1/2H_2(g) \rightarrow Fe^{2+}(aq) + H^{+}(aq)$
9. Write the half-reactions for each overall reaction, decide whether the reaction will occur spontaneously, and construct a cell diagram for a galvanic cell in which a spontaneous reaction will occur.
    1. $2Cl^{-}(aq) + Br_2(l) \rightarrow Cl_2(g) + 2Br^{-}(aq)$
    2. $2NO_2(g) + 2OH^{-}(aq) \rightarrow NO_2^{-}(aq) + NO_3^{-}(aq) + H_2O(l)$
    3. $2H_2O(l) + 2Cl^{-}(aq) \rightarrow H_2(g) + Cl_2(g) + 2OH^{-}(aq)$
    4. $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$
10. Write the half-reactions for each overall reaction, decide whether the reaction will occur spontaneously, and construct a cell diagram for a galvanic cell in which a spontaneous reaction will occur.
    1. $Co(s) + Fe^{2+}(aq) \rightarrow Co^{2+}(aq) + Fe(s)$
    2. $O_2(g) + 4H^{+}(aq) + 4Fe^{2+}(aq) \rightarrow 2H_2O(l) + 4Fe^{3+}(aq)$
    3. $6Hg^{+}(aq) + 2NO_3^{-}(aq) + 8H^{+} \rightleftharpoons 3Hg_2^{2+}(aq) + 2NO(g) + 4H_2O(l)$
    4. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

5. reduction: $SO_4^{2-}(aq) + 9H^{+}(aq) + 8e^{-} \rightarrow HS^{-}(aq) + 4H_2O(l)$; oxidation: $C_6H_{12}O_6(aq) + 12H_2O(l) \rightarrow 6HCO_3^{-}(g) + 30H^{+}(aq) + 24e^{-}$; overall: $C_6H_{12}O_6(aq) + 3SO_4^{2-}(aq) \rightarrow 6HCO_3^{-}(g) + 3H^{+}(aq) + 3HS^{-}(aq)$

6.

7.

Answers

1. 1. reduction: $2H^{+}(aq) + 2e^{-} \rightarrow H_2(aq)$; cathode;

       oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$; anode;

       overall: $Zn(s) + 2H^{+}(aq) \rightarrow Zn^{2+}(aq) + H_2(aq)$

    2. reduction: $AgCl(s) + e^{-} \rightarrow Ag(s) + Cl^{-}(aq)$; cathode;

oxidation: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$; anode;

overall: $AgCl(s) + H_2(g) \rightarrow 2H^+(aq) + Ag(s) + Cl^-(aq)$

3. reduction: $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$; cathode;

   oxidation: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$; anode;

   overall: $2Fe^{3+}(aq) + H_2(g) \rightarrow 2H^+(aq) + 2Fe^{2+}(aq)$

8.
9.
10.

Contributors

- Anonymous

Modified by Joshua Halpern (Howard University), Scott Sinex, and Scott Johnson (PGCC)

The reaction between Zn and Cu^{2+} from YouTube courtesy of UC Berkeley Chemistry and Respect Chemistry

Galvanic Cell demonstration from YouTube courtesy of Angela Stott

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Chapter 17.2: Standard Potentials

Learning Objective

- To use redox potentials to predict whether a reaction is spontaneous.
- To balance redox reactions using half-reactions.

In a galvanic cell, current is produced when electrons flow externally through the circuit from the anode to the cathode because of a difference in potential energy between the two electrodes in the electrochemical cell. In the Zn/Cu system, the valence electrons in zinc have a substantially higher potential energy than the valence electrons in copper because of shielding of the *s* electrons of zinc by the electrons in filled *d* orbitals. (For more information on atomic orbitals, see Section 2.5.) Hence electrons flow spontaneously from zinc to copper(II) ions, forming zinc(II) ions and metallic copper (Figure 17.2.1). Just like water flowing spontaneously downhill, which can be made to do work by forcing a waterwheel, the flow of electrons from a higher potential energy to a lower one can also be harnessed to perform work.

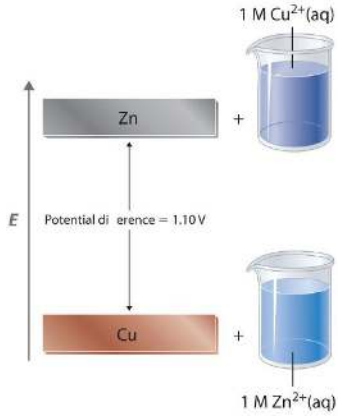


Figure 17.2.1 Potential Energy Difference in the Zn/Cu System The potential energy of a system consisting of metallic Zn and aqueous Cu^{2+} ions is greater than the potential energy of a system consisting of metallic Cu and aqueous $Zn^{2+\ ions}$. Much of this potential energy difference is because the valence electrons of metallic Zn are higher in energy than the valence electrons of metallic Cu. Because the Zn(s) + Cu^{2+}(aq) system is higher in energy by 1.10 V than the Cu(s) + Zn^{2+}(aq) system, energy is released when electrons are transferred from Zn to Cu^{2+} to form Cu and Zn^{2+}.

Because the potential energy of valence electrons differs greatly from one substance to another, the voltage of a galvanic cell depends partly on the identity of the reacting substances. If we construct a galvanic cell similar to the one in part (a) in Figure 17.1.3 but instead of copper use a strip of cobalt metal and 1 M Co^{2+} in the cathode compartment, the measured voltage is not 1.10 V but 0.51 V. Thus we can conclude that the difference in potential energy between the valence electrons of cobalt and zinc is less than the difference between the valence electrons of copper and zinc by 0.59 V.

The measured potential of a cell also depends strongly on the *concentrations* of the reacting species and the *temperature* of the system. To develop a scale of relative potentials that will allow us to predict the direction of an electrochemical reaction and the magnitude of the driving force for the reaction, the potentials for oxidations and reductions of different substances must be measured under comparable conditions. To do this, chemists use the standard cell potentialThe potential of an electrochemical cell measured under standard conditions (1 M for solutions, 1 atm for gases, and pure solids or pure liquids for other substances) and at a fixed temperature (usually 298 K). ($E°_{cell}$), defined as the potential of a cell measured under standard conditions—that is, with all species in their standard states (1 M for solutions,Concentrated solutions of salts (about 1 M) generally do not exhibit ideal behavior, and the actual standard state corresponds to an *activity* of 1 rather than a concentration of 1 M. Corrections for nonideal behavior are important for precise quantitative work but not for the more qualitative approach that we are taking here. 1 atm for gases, pure solids or pure liquids for other substances) and at a fixed temperature, usually 25°C.

Note the Pattern

Measured redox potentials depend on the potential energy of valence electrons, the concentrations of the species in the reaction, and the temperature of the system.

Measuring Standard Electrode Potentials

It is physically impossible to measure the potential of a single electrode: only the *difference* between the potentials of two electrodes can be measured. (This is analogous to measuring absolute enthalpies or free energies. Recall from Chapter 16 that only *differences* in enthalpy and free energy can be measured.) We can, however, compare the standard cell potentials for two different galvanic cells that have one kind of electrode in common. This allows us to measure the potential difference between two dissimilar electrodes. For example, the measured standard cell potential ($E°$) for the Zn/Cu system is 1.10 V, whereas $E°$ for the corresponding Zn/Co system is 0.51 V. This implies that the potential difference between the Co and Cu electrodes is 1.10 V − 0.51 V = 0.59 V. In fact, that is exactly the potential measured under standard conditions if a cell is constructed with the following cell diagram:

$$Co\,(s)\mid Co^{2+}\,(aq,\ 1M)\parallel Cu^{2+}\,(aq,\ 1M)\mid Cu\,(s)$$

This cell diagram corresponds to the oxidation of a cobalt anode and the reduction of Cu^{2+} in solution at the copper cathode.

All tabulated values of *standard electrode potentials* by convention are listed for a reaction written as a reduction, not as an oxidation, to be able to compare standard potentials for different substances. (Standard electrode potentials for various reduction reactions are given in Standard Reduction Potentials at 25°C".) The standard cell potential ($E°_{cell}$) is therefore the *difference* between the tabulated reduction potentials of the two half-reactions, not their sum:

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

In contrast, recall that half-reactions are written to show the reduction and oxidation reactions that actually occur in the cell, so the overall cell reaction is written as the *sum* of the two half-reactions. According to Equation 17.2.2, when we know the standard potential for any single half-reaction, we can obtain the value of the standard potential of many other half-reactions by measuring the standard potential of the corresponding cell.

Note the Pattern

The overall cell reaction is the sum of the two half-reactions, but the cell potential is the difference between the reduction potentials: $E°_{cell} = E°_{cathode} - E°_{anode}$.

Although it is impossible to measure the potential of any electrode directly, we can choose a reference electrode whose potential is defined as 0 V under standard conditions. The standard hydrogen electrode (SHE)The electrode chosen as the reference for all other electrodes, which has been assigned a standard potential of 0 V and consists of a Pt wire in contact with an aqueous solution that contains 1 M H^+ in equilibrium with H_2 gas at a pressure of 1 atm at the Pt-solution interface. is universally used for this purpose and is assigned a standard potential of 0 V. It consists of a strip of platinum wire in contact with an aqueous solution containing 1 M H^+. The [H^+] in solution is in equilibrium with H_2 gas at a pressure of 1 atm at the Pt-solution interface (Figure 17.2.2). Protons are reduced or hydrogen molecules are oxidized at the Pt surface according to the following equation:

$$2H^+\,(aq) + 2e^- \rightleftharpoons H_2\,(g)$$

One especially attractive feature of the SHE is that the Pt metal electrode is not consumed during the reaction.

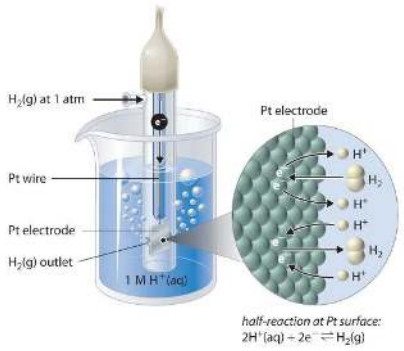


Figure 17.2.2 The Standard Hydrogen Electrode The SHE consists of platinum wire that is connected to a Pt surface in contact with an aqueous solution containing 1 M H^+ in equilibrium with H_2 gas at a pressure of 1 atm. In the molecular view, the Pt surface catalyzes the oxidation of hydrogen molecules to protons or the reduction of protons to hydrogen gas. (Water is omitted for clarity.) The standard potential of the SHE is arbitrarily assigned a value of 0 V.

Figure 17.2.3 shows a galvanic cell that consists of a SHE in one beaker and a Zn strip in another beaker containing a solution of Zn^{2+} ions. When the circuit is closed, the voltmeter indicates a potential of 0.76 V. The zinc electrode begins to dissolve to form Zn^{2+}, and H^+ ions are reduced to H_2 in the other compartment. Thus the hydrogen electrode is the cathode, and the zinc electrode is the anode. The diagram for this galvanic cell is as follows:

$$Zn\,(s)\mid Zn^{2+}\,(aq)\parallel H^+\,(aq,\ 1M)\mid H_2\,(g, 1\ atm)\mid Pt\,(s)$$

The half-reactions that actually occur in the cell and their corresponding electrode potentials are as follows:

$$cathode: 2H^+\,(aq,\ 1M) + 2e^- \rightarrow H_2\,(g) \quad E^o_{cathode} = 0\ V$$

$$anode: Zn\,(s) \rightarrow Zn^{2+}\,(aq) + 2e^- \quad E^o_{anode} = -0.76\ V$$

$$overall: Zn\,(s) + 2H^+\,(aq) \rightarrow Zn^{2+}\,(aq) + H_2\,(g)$$

$$E^o_{cell} = E^o_{cathode} - E^o_{anode} = 0.76$$

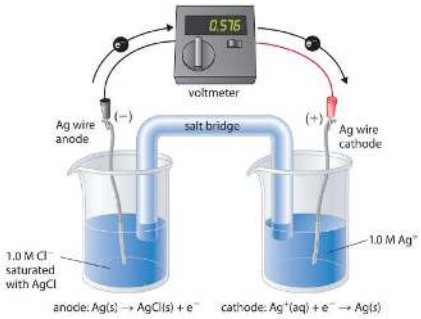


Figure 17.2.3 Determining a Standard Electrode Potential Using a Standard Hydrogen Electrode The voltmeter shows that the standard cell potential of a galvanic cell consisting of a SHE and a Zn/Zn^{2+} couple is $E°_{cell}$ = 0.76 V. Because the zinc electrode in this cell dissolves spontaneously to form Zn^{2+}(aq) ions while H^+(aq) ions are reduced to H_2 at the platinum surface, the standard electrode potential of the Zn^{2+}/Zn couple is −0.76 V.

Although the reaction at the anode is an oxidation, by convention its tabulated $E°$ value is reported as a *reduction* potential. The potential of a half-reaction measured against the SHE under standard conditions is called the standard electrode potentialThe potential of a half-reaction measured against the SHE under standard conditions. for that half-reaction.In this example, the standard reduction potential for Zn^{2+}(aq) + $2e^-$ → Zn(s) is −0.76 V, which means that the standard electrode potential for the reaction that occurs at the anode, the *oxidation* of Zn to Zn^{2+}, often called the Zn/Zn^{2+} *redox couple*, or the Zn/Zn^{2+} *couple*, is −(−0.76 V) = 0.76 V. We must therefore subtract $E°_{anode}$ from $E°_{cathode}$ to obtain $E°_{cell}$: 0 − (−0.76 V) = 0.76 V.

Because electrical potential is the energy needed to move a charged particle in an electric field, standard electrode potentials for half-reactions are intensive properties and do not depend on the amount of substance involved. Consequently, *$E°$ values are independent of the stoichiometric coefficients for the half-reaction*, and, most important, the coefficients used to produce a balanced overall reaction do not affect the value of the cell potential.

Note the Pattern

$E°$ values do not depend on the stoichiometric coefficients for a half-reaction.

To measure the potential of the Cu/Cu^{2+} couple, we can construct a galvanic cell analogous to the one shown in Figure 17.2.3 but containing a Cu/Cu^{2+} couple in the sample compartment instead of Zn/Zn^{2+}. When we close the circuit this time, the measured potential for the cell is negative (−0.34 V) rather than positive. The negative value of $E°_{cell}$ indicates that the direction of spontaneous electron flow is the opposite of that for the Zn/Zn^{2+} couple. Hence the reactions that occur spontaneously, indicated by a positive $E°_{cell}$, are the reduction of Cu^{2+} to Cu at the copper electrode. The copper electrode gains mass as the reaction proceeds,

and H_2 is oxidized to H^+ at the platinum electrode. In this cell, the copper strip is the *cathode*, and the hydrogen electrode is the *anode*. The cell diagram therefore is written with the SHE on the left and the Cu^{2+}/Cu couple on the right:

$$Pt\,(s)\mid H_2\,(g, 1\ atm)\mid H^+\,(aq,\ 1M)\parallel Cu^{2+}\,(aq)\mid Cu\,(s)$$

The half-cell reactions and potentials of the spontaneous reaction are as follows:

$$cathode: Cu^{2+}\,(aq) + 2e^- \rightarrow Cu\,(s) \quad E^o_{cathode} = 0.34\ V$$

$$anode: H_2\,(g) \rightarrow 2H^+\,(aq) + 2e^- \quad E^o_{anode} = 0\ V$$

$$overall: H_2\,(g) + Cu^{2+}\,(aq) \rightarrow Cu\,(s) + 2H^+\,(aq)$$

$$E^o_{cell} = E^o_{cathode} - E^o_{anode} = 0.34$$

Thus the standard electrode potential for the Cu^{2+}/Cu couple is 0.34 V.

Balancing Redox Reactions Using the Half-Reaction Method

In Chapter 12.7, we described a method for balancing redox reactions using oxidation numbers. Oxidation numbers were assigned to each atom in a redox reaction to identify any changes in the oxidation states. Here we present an alternative approach to balancing redox reactions, the half-reaction method, in which the overall redox reaction is divided into an oxidation half-reaction and a reduction half-reaction, each balanced for mass and charge. This method more closely reflects the events that take place in an electrochemical cell, where the two half-reactions may be physically separated from each other.

We can illustrate how to balance a redox reaction using half-reactions with the reaction that occurs when Drano, a commercial solid drain cleaner, is poured into a clogged drain. Drano contains a mixture of sodium hydroxide and powdered aluminum, which in solution reacts to produce hydrogen gas:

$$Al\,(s) + OH^-\,(aq) \rightarrow Al\,(OH)_4^-\,(aq) + H_2\,(g)$$

In this reaction, Al(s) is oxidized to Al^{3+}, and H^+ in water is reduced to H_2 gas, which bubbles through the solution, agitating it and breaking up the clogs.

The overall redox reaction is composed of a reduction half-reaction and an oxidation half-reaction. From the standard electrode potentials listed in Standard Reduction Potentials at 25°C, we find the corresponding half-reactions that describe the reduction of H^+ ions in water to H_2 and the oxidation of Al to Al^{3+} in basic solution:

$$reduction:\ 2H_2O\,(l) + 2e^- \rightarrow 2OH^-\,(aq) + H_2\,(g)$$

$$oxidation:\ Al\,(s) + 4OH^-\,(aq) \rightarrow Al(OH)_4^-\,(aq) + 3e^-$$

The half-reactions chosen must exactly reflect the reaction conditions, such as the basic conditions shown here. Moreover, the physical states of the reactants and the products must be identical to those given in the overall reaction, whether gaseous, liquid, solid, or in solution.

In Equation 17.2.13, two H^+ ions gain one electron each in the reduction; in Equation 17.2.14, the aluminum atom loses three electrons in the oxidation. The charges are balanced by multiplying the reduction half-reaction (Equation 17.2.13) by 3 and the oxidation half-reaction (Equation 17.2.14) by 2 to give the same number of electrons in both half-reactions:

$$reduction:\ 6H_2O\,(l) + 6e^- \rightarrow 6OH^-\,(aq) + 3H_2\,(g)$$

$$oxidation:\ 2Al\,(s) + 8OH^-\,(aq) \rightarrow 2Al(OH)_4^-\,(aq) + 6e^-$$

$$6H_2O\,(l) + 2Al\,(s) + 8OH^-\,(aq) \rightarrow 2Al(OH)_4^-\,(aq) + 6OH^-\,(aq) + 3H_2\,(g)$$

Simplifying by canceling substances that appear on both sides of the equation,

$$6H_2O\,(l) + 2Al\,(s) + 2OH^-\,(aq) \rightarrow 2Al(OH)_4^-\,(aq) + 3H_2\,(g)$$

We have a −2 charge on the left side of the equation and a −2 charge on the right side. Thus the charges are balanced, but we must also check that atoms are balanced:

$$2Al + 8O + 14H = 2Al + 8O + 14H$$

The atoms also balance, so Equation 17.2.18 is a balanced chemical equation for the redox reaction depicted in Equation 17.2.12.

Note the Pattern

The half-reaction method requires that half-reactions exactly reflect reaction conditions, and the physical states of the reactants and the products must be identical to those in the overall reaction.

We can also balance a redox reaction by first balancing the atoms in each half-reaction and then balancing the charges. With this alternative method, we do not need to use the half-reactions listed in Standard Reduction Potentials at 25°C" but instead focus on the atoms whose oxidation states change, as illustrated in the following steps:

Step 1: Write the reduction half-reaction and the oxidation half-reaction.

For the reaction shown in Equation 17.2.12, hydrogen is reduced from H^+ in OH^- to H_2, and aluminum is oxidized from Al^0 to Al^{3+}:

$$reduction: \ OH^-(aq) \rightarrow H_2(g)$$

$$oxidation: \ Al(s) \rightarrow Al(OH)_4^-(aq)$$

Step 2: Balance the atoms by balancing elements other than O and H. Then balance O atoms by adding H_2O and balance H atoms by adding H^+.

Elements other than O and H in the previous two equations are balanced as written, so we proceed with balancing the O atoms. We can do this by adding water to the appropriate side of each half-reaction:

$$reduction: \ OH^-(aq) \rightarrow H_2(g) + H_2O(l)$$

$$oxidation: \ Al(s) + 4H_2O(l) \rightarrow Al(OH)_4^-(aq)$$

Balancing H atoms by adding H^+, we obtain the following:

$$reduction: \ OH^-(aq) + 3H^+(aq) \rightarrow H_2(g) + H_2O(l)$$

$$oxidation: \ Al(s) + 4H_2O(l) \rightarrow Al(OH)_4^-(aq) + 4H^+(aq)$$

We have now balanced the atoms in each half-reaction, but the charges are not balanced.

Step 3: Balance the charges in each half-reaction by adding electrons.

Two electrons are gained in the reduction of H^+ ions to H_2, and three electrons are lost during the oxidation of Al^0 to Al^{3+}:

$$reduction: \ OH^-(aq) + 3H^+(aq) + 2e^- \rightarrow H_2(g) + H_2O(l)$$

$$oxidation: \ Al(s) + 4H_2O(l) \rightarrow Al(OH)_4^-(aq) + 4H^+(aq) + 3e^-$$

Step 4: Multiply the reductive and oxidative half-reactions by appropriate integers to obtain the same number of electrons in both half-reactions.

In this case, we multiply Equation 17.2.26 (the reductive half-reaction) by 3 and Equation 17.2.27 (the oxidative half-reaction) by 2 to obtain the same number of electrons in both half-reactions:

$$reduction: \ 3OH^-(aq) + 9H^+(aq) + 6e^- \rightarrow 3H_2(g) + 3H_2O(l)$$

$$oxidation: \ 2Al(s) + 8H_2O(l) \rightarrow 2Al(OH)_4^-(aq) + 8H^+(aq) + 6e^-$$

Step 5: Add the two half-reactions and cancel substances that appear on both sides of the equation.

Adding and, in this case, canceling $8H^+$, $3H_2O$, and $6e^-$,

$$oxidation: \ 2Al(s) + 5H_2O(l) + 3OH^-(aq) + H^+(aq) \rightarrow 2Al(OH)_4^-(aq) + 3H_2(g)$$

We have three OH^- and one H^+ on the left side. Neutralizing the H^+ gives us a total of $5H_2O + H_2O = 6H_2O$ and leaves $2OH^-$ on the left side:

$$oxidation: \ 2Al(s) + 6H_2O(l) + 2OH^-(aq) \rightarrow 2Al(OH)_4^-(aq) + 3H_2(g)$$

Step 6: Check to make sure that all atoms and charges are balanced.

Equation 17.2.31 is identical to Equation 17.2.18, obtained using the first method, so the charges and numbers of atoms on each side of the equation balance.

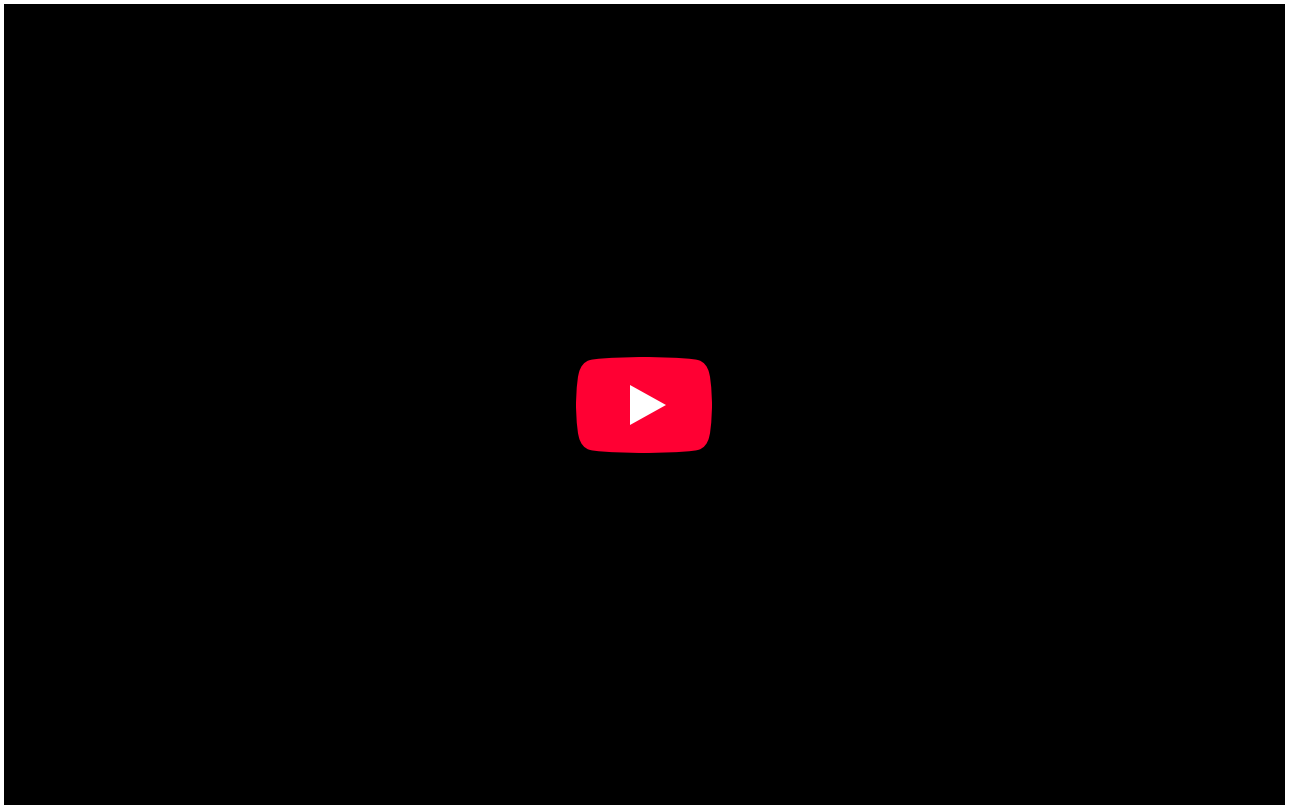




Figure 17.2.4 The Reaction of Dichromate with Iodide The reaction of a yellow solution of sodium dichromate with a colorless solution of sodium iodide produces a deep amber solution that contains a green Cr^{3+}(aq) complex and brown I_2(aq) ions. From Ling Lee on YouTube

Example 17.2.1

In acidic solution, the redox reaction of dichromate ion ($Cr_2O_7^{2-}$) and iodide (I^-) can be monitored visually. The yellow dichromate solution reacts with the colorless iodide solution to produce a solution that is deep amber due to the presence of a green Cr^{3+}(aq) complex and brown I_2(aq) ions (Figure 17.2.4.):

$$Cr_2O_7^{2-}\,(aq) + I^-\,(aq) \rightarrow Cr^{3+}\,(aq) + 3I_2\,(aq)$$

Balance this equation using half-reactions.

Given: redox reaction and Standard Reduction Potentials at 25°C"

Asked for: balanced chemical equation using half-reactions

Strategy:

Follow the steps to balance the redox reaction using the half-reaction method.

Solution:

From the standard electrode potentials listed in Standard Reduction Potentials at 25°C", we find the half-reactions corresponding to the overall reaction:

$$reduction: \ Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

$$oxidation: \ 2I^-(aq) \rightarrow I_2(aq) + 2e^-$$

Balancing the number of electrons by multiplying the oxidation reaction by 3,

$$oxidation: \ 6I^-(aq) \rightarrow 3I_2(aq) + 6e^-$$

oxidation: $6I^-(aq) \rightarrow 3I_2(aq) + 6e^-$

Adding the two half-reactions and canceling electrons,

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6I^-(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3I_2(aq)$$

We must now check to make sure the charges and atoms on each side of the equation balance:

$$\begin{array}{ll} (-2) + 14 + (-6) & = +6 \\ +6 & = +6 \\ 2Cr + 7O + 14H + 6I & 2Cr + 7O + 14H + 6I \end{array}$$

The charges and atoms balance, so our equation is balanced.

We can also use the alternative procedure, which does not require the half-reactions listed in Standard Reduction Potentials at 25°C".

Step 1: Chromium is reduced from Cr^{6+} in $Cr_2O_7^{2-}$to Cr^{3+}, and I^- ions are oxidized to I_2. Dividing the reaction into two half-reactions,

$$reduction: \ Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$$

$$oxidation: \ I^-(aq) \rightarrow I_2(aq)$$

Step 2: Balancing the atoms other than oxygen and hydrogen,

$$reduction: \ Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq)$$

$$oxidation: \ 2I^-(aq) \rightarrow I_2(aq)$$

We now balance the O atoms by adding H_2O—in this case, to the right side of the reduction half-reaction. Because the oxidation half-reaction does not contain oxygen, it can be ignored in this step.

Next we balance the H atoms by adding H^+ to the left side of the reduction half-reaction. Again, we can ignore the oxidation half-reaction.

$$reduction: \ Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

Step 3: We must now add electrons to balance the charges. The reduction half-reaction ($2Cr^{+6}$ to $2Cr^{+3}$) has a +12 charge on the left and a +6 charge on the right, so six electrons are needed to balance the charge. The oxidation half-reaction ($2I^-$ to I_2) has a −2 charge on the left side and a 0 charge on the right, so it needs two electrons to balance the charge:

$$reduction: \ Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

Step 4: To have the same number of electrons in both half-reactions, we must multiply the oxidation half-reaction by 3:

$$oxidation: \ 6I^-(aq) \rightarrow 3I_2(aq) + 6e^-$$

Step 5: Adding the two half-reactions and canceling substances that appear in both reactions,

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6I^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3I_2(aq)$$

Step 6: This is the same equation we obtained using the first method. Thus the charges and atoms on each side of the equation balance.

Exercise

Copper is commonly found as the mineral covellite (CuS). The first step in extracting the copper is to dissolve the mineral in nitric acid (HNO_3), which oxidizes sulfide to sulfate and reduces nitric acid to NO:

$$CuS\,(s) + HNO_3 \rightarrow NO\,(g) + CuSO_4$$

Balance this equation using the half-reaction method.

Answer: $3CuS\,(s) + 8HNO_3 \rightarrow 8NO\,(g) + 3CuSO_4 + 4H_2O\,(l)$

Calculating Standard Cell Potentials

The standard cell potential for a redox reaction ($E°_{cell}$) is a measure of the tendency of reactants in their standard states to form products in their standard states; consequently, it is a measure of the driving force for the reaction, which earlier we called *voltage*. We can use the two standard electrode potentials we found earlier to calculate the standard potential for the Zn/Cu cell represented by the following cell diagram:

$$Zn\,(s) \mid Zn^{2+}\,(aq, 1M) \parallel Cu^{2+}\,(aq, 1M) \mid Cu\,(s)$$

We know the values of $E°_{anode}$ for the reduction of Zn^{2+} and $E°_{cathode}$ for the reduction of Cu^{2+}, so we can calculate $E°_{cell}$:

$$cathode:\ Cu^{2+}\,(aq, 1M) + 2e^- \rightarrow Cu\,(s) \quad E°_{cathode} = 0.34\ V$$

$$anode:\ Zn\,(s) \rightarrow Zn^{2+}\,(aq, 1M) + 2e^- \quad E°_{anode} = -0.76\ V$$

$$overall\ Zn\,(s) + Cu^{2+}\,(aq, 1M) \rightarrow Zn^{2+}\,(aq, 1M) + Cu\,(s)$$

$$E_{cell} = E°_{cathode} - E_{anode} = 1.10\ V$$

This is the same value that is observed experimentally. If the value of $E°_{cell}$ is positive, the reaction will occur spontaneously as written. If the value of $E°_{cell}$ is negative, then the reaction is not spontaneous, and it will not occur as written under standard conditions; it will, however, proceed spontaneously in the opposite direction.As we shall see in Section 17.7, this does not mean that the reaction cannot be made to occur at all under standard conditions. With a sufficient input of electrical energy, virtually any reaction can be forced to occur. Example 4 and its corresponding exercise illustrate how we can use measured cell potentials to calculate standard potentials for redox couples.

Note the Pattern

A positive $E°_{cell}$ means that the reaction will occur spontaneously as written. A negative $E°_{cell}$ means that the reaction will proceed spontaneously in the opposite direction.

Example 17.2.2

A galvanic cell with a measured standard cell potential of 0.27 V is constructed using two beakers connected by a salt bridge. One beaker contains a strip of gallium metal immersed in a 1 M solution of $GaCl_3$, and the other contains a piece of nickel immersed in a 1 M solution of $NiCl_2$. The half-reactions that occur when the compartments are connected are as follows:

$$cathode:\ Ni^{2+}\,(aq) + 2e^- \rightarrow Ni\,(s)$$
$$anode:\ Ga\,(s) \rightarrow Ga^{3+}\,(aq) + 3e^-$$

If the potential for the oxidation of Ga to Ga^{3+} is 0.55 V under standard conditions, what is the potential for the oxidation of Ni to Ni^{2+}?

Given: galvanic cell, half-reactions, standard cell potential, and potential for the oxidation half-reaction under standard conditions

Asked for: standard electrode potential of reaction occurring at the cathode

Strategy:

A Write the equation for the half-reaction that occurs at the anode along with the value of the standard electrode potential for the half-reaction.

B Use Equation 17.2.2 to calculate the standard electrode potential for the half-reaction that occurs at the cathode. Then reverse the sign to obtain the potential for the corresponding oxidation half-reaction under standard conditions.

Solution:

A We have been given the potential for the oxidation of Ga to Ga^{3+} under standard conditions, but to report the standard electrode potential, we must reverse the sign. For the reduction reaction $Ga^{3+}(aq) + 3e^- \rightarrow Ga(s)$, $E°_{anode} = -0.55$ V.

B Using the value given for $E°_{cell}$ and the calculated value of $E°_{anode}$, we can calculate the standard potential for the reduction of Ni^{2+} to Ni from Equation 17.2.2:

$$\begin{aligned} E_{cell} &= E^o_{cathode} - E_{anode} \\ 0.27\ V &= E^o_{cathode} - (-0.55\ V) \\ E^o_{cathode} &= -0.28\ V \end{aligned}$$

This is the standard electrode potential for the reaction $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$. Because we are asked for the potential for the *oxidation* of Ni to Ni^{2+} under standard conditions, we must reverse the sign of $E°_{cathode}$. Thus $E° = -(-0.28\ V) = 0.28$ V for the oxidation. With three electrons consumed in the reduction and two produced in the oxidation, the overall reaction is not balanced. Recall, however, that standard potentials are *independent* of stoichiometry.

Exercise

A galvanic cell is constructed with one compartment that contains a mercury electrode immersed in a 1 M aqueous solution of mercuric acetate [$Hg(CH_3CO_2)_2$] and one compartment that contains a strip of magnesium immersed in a 1 M aqueous solution of $MgCl_2$. When the compartments are connected, a potential of 3.22 V is measured and the following half-reactions occur:

$$\begin{aligned} &cathode: \ Hg^{2+}(aq) + 2e^- \rightarrow Hg(l) \\ &anode: \ Mg(s) \rightarrow Mg^{2+}(aq) + 2e^- \end{aligned}$$

If the potential for the oxidation of Mg to Mg^{2+} is 2.37 V under standard conditions, what is the standard electrode potential for the reaction that occurs at the anode?

Answer: 0.85 V

Reference Electrodes and Measuring Concentrations

When using a galvanic cell to measure the concentration of a substance, we are generally interested in the potential of only one of the electrodes of the cell, the so-called indicator electrodeThe electrode of a galvanic cell whose potential is related to the concentration of the substance being measured., whose potential is related to the concentration of the substance being measured. To ensure that any change in the measured potential of the cell is due to only the substance being analyzed, the potential of the other electrode, the reference electrodeAn electrode in an galvanic cell whose potential is unaffected by the properties of the solution., must be constant. You are already familiar with one example of a reference electrode: the SHE. The potential of a reference electrode must be unaffected by the properties of the solution, and if possible, it should be physically isolated from the solution of interest. To measure the potential of a solution, we select a reference electrode and an appropriate indicator electrode. Whether reduction or oxidation of the substance being analyzed occurs depends on the potential of the half-reaction for the substance of interest (the sample) and the potential of the reference electrode.

Note the Pattern

The potential of any reference electrode should not be affected by the properties of the solution to be analyzed, and it should also be physically isolated.

There are many possible choices of reference electrode other than the SHE. The SHE requires a constant flow of highly flammable hydrogen gas, which makes it inconvenient to use. Consequently, two other electrodes are commonly chosen as reference electrodes. One is the silver–silver chloride electrodeA reference electrode that consists of a silver wire coated with a very thin layer of AgCl and dipped into a chloride ion solution with a fixed concentration., which consists of a silver wire coated with a very thin layer of AgCl that is dipped into a chloride ion solution with a fixed concentration. The cell diagram and reduction half-reaction are as follows:

$$Cl^-(aq) \mid AgCl(s) \mid Ag(s)$$
$$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$$

If a saturated solution of KCl is used as the chloride solution, the potential of the silver–silver chloride electrode is 0.197 V versus the SHE. That is, 0.197 V must be subtracted from the measured value to obtain the standard electrode potential measured against the SHE.

A second common reference electrode is the saturated calomel electrode (SCE)A reference electrode that consists of a platinum wire inserted into a moist paste of liquid mercury (calomel; <math display="inline" xml:id="av_1.0-19_m021"><semantics><mrow><msub><mrow><mtext>Hg</mtext></mrow><mn>2</mn></msub><msub><mrow><mtext>Cl</mtext></mrow><mn>2</mn></msub></mrow></semantics></math>) and KCl in an interior cell, which is surrounded by an aqueous KCl solution., which has the same general form as the silver–silver chloride electrode. The SCE consists of a platinum wire inserted into a moist paste of liquid mercury (Hg_2Cl_2; called *calomel* in the old chemical literature) and KCl. This interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior cell and the exterior solution (part (a) in Figure 17.2.5). Although it sounds and looks complex, this cell is actually easy to prepare and maintain, and its potential is highly reproducible. The SCE cell diagram and corresponding half-reaction are as follows:

$$Pt(s) \mid Hg_2Cl_2(s) \mid KCl(aq, sat)$$
$$Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^-(aq)$$

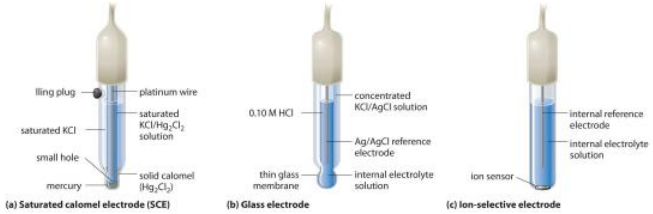


Figure 17.2.5 Three Common Types of Electrodes: (a) The SCE is a reference electrode that consists of a platinum wire inserted into a moist paste of liquid mercury (calomel; Hg_2Cl_2) and KCl. The interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior cell and the exterior solution. (b) In a glass electrode, an internal Ag/AgCl electrode is immersed in a 1 M HCl solution that is separated from the sample solution by a very thin glass membrane. The potential of the electrode depends on the H^+ ion concentration of the sample. (c) The potential of an ion-selective electrode depends on the concentration of only a single ionic species in solution.

At 25°C, the potential of the SCE is 0.2415 V versus the SHE, which means that 0.2415 V must be subtracted from the potential versus an SCE to obtain the standard electrode potential.

One of the most common uses of electrochemistry is to measure the H^+ ion concentration of a solution. A glass electrodeAn electrode used to measure the <math display="inline" xml:id="av_1.0-19_m022"><semantics><mrow><msup><mtext>H</mtext><mo>+</mo></msup></mrow></semantics></math> ion concentration of a solution and consisting of an internal Ag/AgCl electrode immersed in a 1 M HCl solution that is separated from the solution by a very thin glass membrane. is generally used for this purpose, in which an internal Ag/AgCl electrode is immersed in a 0.10 M HCl solution that is separated from the solution by a very thin glass membrane (part (b) in Figure 17.2.5). The glass membrane absorbs protons, which affects the measured potential. The extent of the adsorption on the inner side is fixed because $[H^+]$ is fixed inside the electrode, but the adsorption of protons on the outer surface depends on the pH of the solution. The potential of the glass electrode depends on $[H^+]$ as follows (recall that pH = −log$[H^+]$:

$$E_{glass} = E' + (0.0591\ V \times log\,[H^+]) = E' - 0.0591\ V \times pH$$

The voltage E' is a constant that depends on the exact construction of the electrode. Although it can be measured, in practice, a glass electrode is *calibrated*; that is, it is inserted into a solution of known pH, and the display on the pH meter is adjusted to the known value. Once the electrode is properly calibrated, it can be placed in a solution and used to determine an unknown pH.

Ion-selective electrodesAn electrode whose potential depends on only the concentration of a particular species in solution. are used to measure the concentration of a particular species in solution; they are designed so that their potential depends on only the concentration of the desired species (part (c) in Figure 17.2.5). These electrodes usually contain an internal reference electrode that

is connected by a solution of an electrolyte to a crystalline inorganic material or a membrane, which acts as the sensor. For example, one type of ion-selective electrode uses a single crystal of Eu-doped LaF_3 as the inorganic material. When fluoride ions in solution diffuse to the surface of the solid, the potential of the electrode changes, resulting in a so-called *fluoride electrode*. Similar electrodes are used to measure the concentrations of other species in solution. Some of the species whose concentrations can be determined in aqueous solution using ion-selective electrodes and similar devices are listed in Table 17.2.1.

Table 17.2.1 Some Species Whose Aqueous Concentrations Can Be Measured Using Electrochemical Methods

Species	Type of Sample
H^+	laboratory samples, blood, soil, and ground and surface water
NH_3/NH_4^+	wastewater and runoff water
K^+	blood, wine, and soil
CO_2/HCO_3^-	blood and groundwater
F^-	groundwater, drinking water, and soil
Br^-	grains and plant extracts
I^-	milk and pharmaceuticals
NO_3^-	groundwater, drinking water, soil, and fertilizer

Summary

The flow of electrons in an electrochemical cell depends on the identity of the reacting substances, the difference in the potential energy of their valence electrons, and their concentrations. The potential of the cell under standard conditions (1 M for solutions, 1 atm for gases, pure solids or liquids for other substances) and at a fixed temperature (25°C) is called the **standard cell potential ($E°_{cell}$)**. Only the *difference* between the potentials of two electrodes can be measured. By convention, all tabulated values of *standard electrode potentials* are listed as standard reduction potentials. The overall cell potential is the reduction potential of the reductive half-reaction minus the reduction potential of the oxidative half-reaction ($E°_{cell} = E°_{cathode} - E°_{anode}$). The potential of the **standard hydrogen electrode (SHE)** is defined as 0 V under standard conditions. The potential of a half-reaction measured against the SHE under standard conditions is called its **standard electrode potential**. The standard cell potential is a measure of the driving force for a given redox reaction. All $E°$ values are independent of the stoichiometric coefficients for the half-reaction. Redox reactions can be balanced using the half-reaction method, in which the overall redox reaction is divided into an oxidation half-reaction and a reduction half-reaction, each balanced for mass and charge. The half-reactions selected from tabulated lists must exactly reflect reaction conditions. In an alternative method, the atoms in each half-reaction are balanced, and then the charges are balanced. Whenever a half-reaction is reversed, the sign of $E°$ corresponding to that reaction must also be reversed. If $E°_{cell}$ is positive, the reaction will occur spontaneously under standard conditions. If $E°_{cell}$ is negative, then the reaction is not spontaneous under standard conditions, although it will proceed spontaneously in the opposite direction. The potential of an **indicator electrode** is related to the concentration of the substance being measured, whereas the potential of the **reference electrode** is held constant. Whether reduction or oxidation occurs depends on the potential of the sample versus the potential of the reference electrode. In addition to the SHE, other reference electrodes are the **silver–silver chloride electrode**; the **saturated calomel electrode (SCE)**; the **glass electrode**, which is commonly used to measure pH; and **ion-selective electrodes**, which depend on the concentration of a single ionic species in solution. Differences in potential between the SHE and other reference electrodes must be included when calculating values for $E°$.

Key Takeaways

- Redox reactions can be balanced using the half-reaction method.
- The standard cell potential is a measure of the driving force for the reaction.

Key Equation

Standard cell potential

Equation 17.2.2: $E°_{cell} = E°_{cathode} - E°_{anode}$

Conceptual Problems

1. Is a hydrogen electrode chemically inert? What is the major disadvantage to using a hydrogen electrode?
2. List two factors that affect the measured potential of an electrochemical cell and explain their impact on the measurements.
3. What is the relationship between electron flow and the potential energy of valence electrons? If the valence electrons of substance A have a higher potential energy than those of substance B, what is the direction of electron flow between them in a galvanic cell?
4. If the components of a galvanic cell include aluminum and bromine, what is the predicted direction of electron flow? Why?
5. Write a cell diagram representing a cell that contains the Ni/Ni^{2+} couple in one compartment and the SHE in the other compartment. What are the values of $E°_{cathode}$, $E°_{anode}$, and $E°_{cell}$?
6. Explain why $E°$ values are independent of the stoichiometric coefficients in the corresponding half-reaction.
7. Identify the oxidants and the reductants in each redox reaction.
    1. $Cr(s) + Ni^{2+}(aq) \rightarrow Cr^{2+}(aq) + Ni(s)$
    2. $Cl_2(g) + Sn^{2+}(aq) \rightarrow 2Cl^-(aq) + Sn^{4+}(aq)$
    3. $H_3AsO_4(aq) + 8H^+(aq) + 4Zn(s) \rightarrow AsH_3(g) + 4H_2O(l) + 4Zn^{2+}(aq)$
    4. $2NO_2(g) + 2OH^-(aq) \rightarrow NO_2^-(aq) + NO_3^-(aq) + H_2O(l)$
8. Identify the oxidants and the reductants in each redox reaction.
    1. $Br_2(l) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(s)$
    2. $Cu^{2+}(aq) + 2Ag(s) \rightarrow Cu(s) + 2Ag^+(aq)$
    3. $H^+(aq) + 2MnO_4^-(aq) + 5H_2SO_3(aq) \rightarrow 2Mn^{2+}(aq) + 3H_2O(l) + 5HSO_4^-(aq)$
    4. $IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \rightarrow 3I_2(s) + 3H_2O(l)$
9. All reference electrodes must conform to certain requirements. List the requirements and explain their significance.
10. For each application, describe the reference electrode you would use and explain why. In each case, how would the measured potential compare with the corresponding $E°$?
    1. measuring the potential of a Cl^-/Cl_2 couple
    2. measuring the pH of a solution
    3. measuring the potential of a Zn^{2+}/Zn couple

Answers

5. $Ni(s) \mid Ni^{2+}(aq) \parallel H^+(aq, 1\ M) \mid H_2(g, 1\ atm) \mid Pt(s)$

E^o_{anode}	$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	$-0.257\ V$
$E^o_{cathode}$	$2H^+(aq) + 2e^- \rightarrow H_2(g,)$	$0.000\ V$
E^o_{cell}	$2H^+(aq) + Ni(s) \rightarrow H_2(g,) + Ni^{2+}(aq)$	$0.257\ V$

6.
7. 1. oxidant: $Ni^{2+}(aq)$; reductant: Cr(s)
    2. oxidant: $Cl_2(g)$; reductant: $Sn^{2+}(aq)$
    3. oxidant: $H_3AsO_4(aq)$; reductant: Zn(s)
    4. oxidant: $NO_2(g)$; reductant: $NO_2(g)$
8.
9.
10.

Numerical Problems

1. Draw the cell diagram for a galvanic cell with an SHE and a copper electrode that carries out this overall reaction:

$$H_2(g) + Cu^{2+}(aq) \rightarrow 2H^+(aq) + Cu(s).$$

2. Draw the cell diagram for a galvanic cell with an SHE and a zinc electrode that carries out this overall reaction:

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g).$$

3. Balance each reaction and calculate the standard electrode potential for each. Be sure to include the physical state of each product and reactant.

    1. $Cl_2(g) + H_2(g) \rightarrow 2Cl^-(aq) + 2H^+(aq)$
    2. $Br_2(aq) + Fe^{2+}(aq) \rightarrow 2Br^-(aq) + Fe^{3+}(aq)$
    3. $Fe^{3+}(aq) + Cd(s) \rightarrow Fe^{2+}(aq) + Cd^{2+}(aq)$

4. Balance each reaction and calculate the standard reduction potential for each. Be sure to include the physical state of each product and reactant.

    1. $Cu^+(aq) + Ag^+(aq) \rightarrow Cu^{2+}(aq) + Ag(s)$
    2. $Sn(s) + Fe^{3+}(aq) \rightarrow Sn^{2+}(aq) + Fe^{2+}(aq)$
    3. $Mg(s) + Br_2(l) \rightarrow 2Br^-(aq) + Mg^{2+}(aq)$

5. Write a balanced chemical equation for each redox reaction.

    1. $H_2PO_2^-(aq) + SbO_2^-(aq) \rightarrow HPO_3^{2-}(aq) + Sb(s)$ in basic solution
    2. $HNO_2(aq) + I^-(aq) \rightarrow NO(g) + I_2(s)$ in acidic solution
    3. $N_2O(g) + ClO^-(aq) \rightarrow Cl^-(aq) + NO_2^-(aq)$ in basic solution
    4. $Br_2(l) \rightarrow Br^-(aq) + BrO_3^-(aq)$ in basic solution
    5. $Cl(CH_2)_2OH(aq) + K_2Cr_2O_7(aq) \rightarrow ClCH_2CO_2H(aq) + Cr^{3+}(aq)$ in acidic solution

6. Write a balanced chemical equation for each redox reaction.

    1. $I^-(aq) + HClO_2(aq) \rightarrow IO_3^-(aq) + Cl_2(g)$ in acidic solution
    2. $Cr^{2+}(aq) + O_2(g) \rightarrow Cr^{3+}(aq) + H_2O(l)$ in acidic solution
    3. $CrO_2^-(aq) + ClO^-(aq) \rightarrow CrO_4^{2-}(aq) + Cl^-(aq)$ in basic solution
    4. $S(s) + HNO_2(aq) \rightarrow H_2SO_3(aq) + N_2O(g)$ in acidic solution
    5. $F(CH_2)_2OH(aq) + K_2Cr_2O_7(aq) \rightarrow FCH_2CO_2H(aq) + Cr^{3+}(aq)$ in acidic solution

7. The standard cell potential for the oxidation of Pb to Pb^{2+} with the concomitant reduction of Cu^+ to Cu is 0.39 V. You know that $E°$ for the Pb^{2+}/Pb couple is −0.13 V. What is $E°$ for the Cu^+/Cu couple?

8. You have built a galvanic cell similar to the one in Figure 17.2.3 using an iron nail, a solution of $FeCl_2$, and an SHE. When the cell is connected, you notice that the iron nail begins to corrode. What else do you observe? Under standard conditions, what is E_{cell}?

9. Carbon is used to reduce iron ore to metallic iron. The overall reaction is as follows:

$$2Fe_2O_3{\cdot}xH_2O(s) + 3C(s) \rightarrow 4Fe(l) + 3CO_2(g) + 2xH_2O(g)$$

    Write the two half-reactions for this overall reaction.

10. Will each reaction occur spontaneously under standard conditions?

    1. $Cu(s) + 2H^+(aq) \rightarrow Cu^{2+}(aq) + H_2(g)$
    2. $Zn^{2+}(aq) + Pb(s) \rightarrow Zn(s) + Pb^{2+}(aq)$

11. Each reaction takes place in acidic solution. Balance each reaction and then determine whether it occurs spontaneously as written under standard conditions.

    1. $Se(s) + Br_2(l) \rightarrow H_2SeO_3(aq) + Br^-(aq)$
    2. $NO_3^-(aq) + S(s) \rightarrow HNO_2(aq) + H_2SO_3(aq)$
    3. $Fe^{3+}(aq) + Cr^{3+}(aq) \rightarrow Fe^{2+}(aq) + Cr_2O_7^{2-}(aq)$

12. Calculate $E°_{cell}$ and $\Delta G°$ for the redox reaction represented by the cell diagram $Pt(s)\,|\,Cl_2(g, 1\ atm)\,\|\,ZnCl_2(aq, 1\ M)\,|\,Zn(s)$. Will this reaction occur spontaneously?

13. If you place Zn-coated (galvanized) tacks in a glass and add an aqueous solution of iodine, the brown color of the iodine solution fades to a pale yellow. What has happened? Write the two half-reactions and the overall balanced chemical equation for this reaction. What is $E°_{cell}$?
14. Your lab partner wants to recover solid silver from silver chloride by using a 1.0 M solution of HCl and 1 atm H_2 under standard conditions. Will this plan work?

Answers

1. $Pt(s)\,|\,H_2(g, 1\ atm)\,|\,H^+(aq, 1M)\,\|\,Cu^{2+}(aq)\,|\,Cu(s)$
2.
3.
   1. $Cl_2(g) + H_2(g) \rightarrow 2Cl^-(aq) + 2H^+(aq)$; $E° = 1.358$ V
   2. $Br_2(l) + 2Fe^{2+}(aq) \rightarrow 2Br^-(aq) + 2Fe^{3+}(aq)$; $E° = 0.316$ V
   3. $2Fe^{3+}(aq) + Cd(s) \rightarrow 2Fe^{2+}(aq) + Cd^{2+}(aq)$; $E° = 1.174$ V
4.
5.
6.
7.
8.
9.
10.
11.
12.
13.
14.

Contributors

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Chapter 17.3: Comparing Strengths of Oxidants and Reductants

Learning Objective

- To know how to predict the relative strengths of various oxidants and reductants.

We can use the procedure described in Section 17.2 to measure the standard potentials for a wide variety of chemical substances, some of which are listed in Table 17.3.1 . (Standard Reduction Potentials at 25°C" contains a more extensive listing.) These data allow us to compare the oxidative and reductive strengths of a variety of substances. The half-reaction for the standard hydrogen electrode (SHE) lies more than halfway down the list in Table 17.3.1 . All reactants that lie *above* the SHE in the table are stronger oxidants than H^+, and all those that lie below the SHE are weaker. The strongest oxidant in the table is F_2, with a standard electrode potential of 2.87 V. This high value is consistent with the high electronegativity of fluorine and tells us that fluorine has a stronger tendency to accept electrons (it is a stronger oxidant) than any other element.

Table 17.3.1 Standard Potentials for Selected Reduction Half-Reactions at 25°C

Half-Reaction	$E°$ (V)
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$	1.78
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	1.72
$PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$	1.69
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.23
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	1.23
$MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)$	1.22
$Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$	1.09
$NO_3^-(aq) + 3H^+(aq) + 2e^- \rightarrow HNO_2(aq) + H_2O(l)$	0.93
$Ag^+(aq) + e^- \rightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	0.77
$H_2SeO_3(aq) + 4H^+ + 4e^- \rightarrow Se(s) + 3H_2O(l)$	0.74
$O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O_2(aq)$	0.70
$MnO_4^-(aq) + 2H_2O(l) + 3e^- \rightarrow MnO_2(s) + 4OH^-(aq)$	0.60
$MnO_4^{2-}(aq) + 2H_2O(l) + 2e^- \rightarrow MnO_2(s) + 4OH^-(aq)$	0.60
$I_2(s) + 2e^- \rightarrow 2I^-(aq)$	0.54
$H_2SO_3(aq) + 4H^+(aq) + 4e^- \rightarrow S(s) + 3H_2O(l)$	0.45
$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	0.34
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	0.22
$Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$	0.15
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	0.15
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	−0.14
$2SO_4^{2-}(aq) + 4H+(aq) + 2e^- \rightarrow S_2O_6^{2-}(aq) + 2H_2O(l)$	−0.22
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	−0.26
$PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$	−0.36
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	−0.40
$Cr^{3+}(aq) + e^- \rightarrow Cr^{2+}(aq)$	−0.41
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	−0.45

Half-Reaction	$E°$ (V)
$Ag_2S(s) + 2e^- \rightarrow 2Ag(s) + S^{2-}(aq)$	−0.69
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	−0.76
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	−1.662
$Be^{2+}(aq) + 2e^- \rightarrow Be(s)$	−1.85
$Li^+(aq) + e^- \rightarrow Li(s)$	−3.04

Similarly, all species in Table 17.3.1 that lie *below* H_2 are stronger reductants than H_2, and those that lie above H_2 are weaker. The strongest reductant in the table is thus metallic lithium, with a standard electrode potential of −3.04 V. This fact might be surprising because cesium, not lithium, is the least electronegative element. The apparent anomaly can be explained by the fact that electrode potentials are measured in aqueous solution, where intermolecular interactions are important, whereas ionization potentials and electron affinities are measured in the gas phase. Due to its small size, the Li^+ ion is stabilized in aqueous solution by strong electrostatic interactions with the negative dipole end of water molecules. These interactions result in a significantly greater $\Delta H_{hydration}$ for Li^+ compared with Cs^+. Lithium metal is therefore the strongest reductant (most easily oxidized) of the alkali metals in aqueous solution.

Note the Pattern

Species in Table 17.3.1 that lie below H_2 are stronger reductants (more easily oxidized) than H_2. Species that lie above H_2 are stronger oxidants.

Because the half-reactions shown in Table 17.3.1 are arranged in order of their $E°$ values, we can use the table to quickly predict the relative strengths of various oxidants and reductants. Any species on the left side of a half-reaction will spontaneously oxidize any species on the right side of another half-reaction that lies *below* it in the table. Conversely, any species on the right side of a half-reaction will spontaneously reduce any species on the left side of another half-reaction that lies *above* it in the table. We can use these generalizations to predict the spontaneity of a wide variety of redox reactions ($E°_{cell} > 0$), as illustrated in Example 5.

Example 5

The black tarnish that forms on silver objects is primarily Ag_2S. The half-reaction for reversing the tarnishing process is as follows:

$$Ag_2S(s) + 2e^- \rightarrow 2Ag(s) + S^{2-}(aq) \quad E° = -0.69\ V$$



1. Referring to Table 17.3.1 , predict which species—H_2O_2(aq), Zn(s), I^-(aq), Sn^{2+}(aq)—can reduce Ag_2S to Ag under standard conditions.
2. Of these species—H_2O_2(aq), Zn(s), I^-(aq), Sn^{2+}(aq), identify which is the strongest reducing agent in aqueous solution and thus the best candidate for a commercial product.
3. From the data in Table 17.3.1 , suggest an alternative reducing agent that is readily available, inexpensive, and possibly more effective at removing tarnish.

Given: reduction half-reaction, standard electrode potential, and list of possible reductants

Asked for: reductants for Ag_2S, strongest reductant, and potential reducing agent for removing tarnish

Strategy:

A From their positions in Table 17.3.1, decide which species can reduce Ag_2S. Determine which species is the strongest reductant.

B Use Table 17.3.1 to identify a reductant for Ag_2S that is a common household product.

Solution:

We can solve the problem in one of two ways: (1) compare the relative positions of the four possible reductants with that of the Ag_2S/Ag couple in Table 17.3.1 or (2) compare $E°$ for each species with $E°$ for the Ag_2S/Ag couple (−0.69 V).

1. **A** The species in Table 17.3.1 are arranged from top to bottom in order of increasing reducing strength. Of the four species given in the problem, $I^-(aq)$, $Sn^{2+}(aq)$, and $H_2O_2(aq)$ lie above Ag_2S, and one [Zn(s)] lies below it. We can therefore conclude that Zn(s) can reduce $Ag_2S(s)$ under standard conditions, whereas $I^-(aq)$, $Sn^{2+}(aq)$, and $H_2O_2(aq)$ cannot. $Sn^{2+}(aq)$ and $H_2O_2(aq)$ appear twice in the table: on the left side (oxidant) in one half-reaction and on the right side (reductant) in another.
2. The strongest reductant is Zn(s), the species on the right side of the half-reaction that lies closer to the bottom of Table 17.3.1 than the half-reactions involving $I^-(aq)$, $Sn^{2+}(aq)$, and $H_2O_2(aq)$. (Commercial products that use a piece of zinc are often marketed as a "miracle product" for removing tarnish from silver. All that is required is to add warm water and salt for electrical conductivity.)
3. **B** Of the reductants that lie below Zn(s) in Table 17.3.1 , and therefore are stronger reductants, only one is commonly available in household products: Al(s), which is sold as aluminum foil for wrapping foods.

Exercise

Refer to Table 17.3.1 to predict

1. which species—$Sn^{4+}(aq)$, $Cl^-(aq)$, $Ag^+(aq)$, $Cr^{3+}(aq)$, and/or $H_2O_2(aq)$—can oxidize $MnO_2(s)$ to MNO_4^- under standard conditions.
2. which species—$Sn^{4+}(aq)$, $Cl^-(aq)$, $Ag^+(aq)$, $Cr^{3+}(aq)$, and/or $H_2O_2(aq)$—is the strongest oxidizing agent in aqueous solution.

Answer:

1. $Ag^+(aq)$; $H_2O_2(aq)$
2. $H_2O_2(aq)$

Example 17.3.1

Use the data in Table 17.3.1 to determine whether each reaction is likely to occur spontaneously under standard conditions:

1. $Sn(s) + Be^{2+}(aq) \rightarrow Sn^{2+}(aq) + Be(s)$
2. $MnO_2(s) + H_2O_2(aq) + 2H^+(aq) \rightarrow O_2(g) + Mn^{2+}(aq) + 2H_2O(l)$

Given: redox reaction and list of standard electrode potentials (Table 17.3.1)

Asked for: reaction spontaneity

Strategy:

A Identify the half-reactions in each equation. Using Table 17.3.1, determine the standard potentials for the half-reactions in the appropriate direction.

B Use Equation 17.2.2 to calculate the standard cell potential for the overall reaction. From this value, determine whether the overall reaction is spontaneous.

Solution:

1. **A** Metallic tin is oxidized to $Sn^{2+}(aq)$, and $Be^{2+}(aq)$ is reduced to elemental beryllium. We can find the standard electrode potentials for the latter (reduction) half-reaction (−1.85 V) and for the former (oxidation) half-reaction (−0.14 V) directly from Table 17.3.1.

   B Adding the two half-reactions gives the overall reaction:

$$\begin{array}{lll} cathode: & MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l) & E^o_{cathode} = 1.22\ V \\ anode: & H_2O_2(aq) \rightarrow O_2(g) + 2H^+(aq) + 2e^- & E^o_{anode} = 1.22\ V \\ overall: & MnO_2(s) + 2H^+(aq) + H_2O_2(aq) \rightarrow & E^o_{cell} = E^o_{cathode} - E^o_{anode} \\ & O_2(g) + Mn^{2+}(aq) + 2H_2O(l) & -0.53\ V \end{array}$$

   The standard cell potential is quite negative, so the reaction will *not* occur spontaneously as written. That is, metallic tin cannot be used to reduce Be^{2+} to beryllium metal under standard conditions. Instead, the reverse process, the reduction of stannous ions (Sn^{2+}) by metallic beryllium, which has a positive value of $E°_{cell}$, will occur spontaneously.

2. **A** MnO_2 is the oxidant (Mn^{4+} is reduced to Mn^{2+}), while H_2O_2 is the reductant (O^{2-} is oxidized to O_2). We can obtain the standard electrode potentials for the reduction and oxidation half-reactions directly from Standard Potentials for Selected

Reduction Half-Reactions at 25°C.

B The two half-reactions and their corresponding potentials are as follows:

$$\begin{array}{lcc} cathode: & MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l) & E^o_{cathode} = 1.22\ V \\ anode: & H_2O_2(aq) \rightarrow O_2(g) + 2H^+(aq) + 2e^- & E^o_{anode} = 1.22\ V \\ overall: & MnO_2(s) + 2H^+(aq) + H_2O_2(aq) \rightarrow & E^o_{cell} = E^o_{cathode} - E^o_{anode} \\ & O_2(g) + Mn^{2+}(aq) + 2H_2O(l) & -0.53\ V \end{array}$$

The standard potential for the reaction is positive, indicating that under standard conditions, it will occur spontaneously as written. Hydrogen peroxide will reduce MnO_2, and oxygen gas will evolve from the solution.

Exercise

Use the data in Table 17.3.2 to determine whether each reaction is likely to occur spontaneously under standard conditions:

1. $2Ce^{4+}(aq) + 2Cl^-(aq) \rightarrow 2Ce^{3+}(aq) + Cl_2(g)$
2. $4MnO_2(s) + 3O_2(g) + 4OH^-(aq) \rightarrow 4MnO_4^-(aq) + 2H_2O$

Answer:

1. spontaneous ($E°_{cell}$ = 0.36 V)
2. nonspontaneous ($E°_{cell}$ = −0.20 V)

Although the sign of $E°_{cell}$ tells us whether a particular redox reaction will occur spontaneously under standard conditions, it does not tell us to what *extent* the reaction proceeds, and it does not tell us what will happen under nonstandard conditions. To answer these questions requires a more quantitative understanding of the relationship between electrochemical cell potential and chemical thermodynamics, as described in Section 17.4.

Summary

The oxidative and reductive strengths of a variety of substances can be compared using standard electrode potentials. Apparent anomalies can be explained by the fact that electrode potentials are measured in aqueous solution, which allows for strong intermolecular electrostatic interactions, and not in the gas phase.

Key Takeaway

- The relative strengths of various oxidants and reductants can be predicted using $E°$ values.

Conceptual Problems

1. The order of electrode potentials cannot always be predicted by ionization potentials and electron affinities. Why? Do you expect sodium metal to have a higher or a lower electrode potential than predicted from its ionization potential? What is its approximate electrode potential?
2. Without referring to tabulated data, of Br_2/Br^-, Ca^{2+}/Ca, O_2/OH^-, and Al^{3+}/Al, which would you expect to have the *least* negative electrode potential and which the *most* negative? Why?
3. Because of the sulfur-containing amino acids present in egg whites, eating eggs with a silver fork will tarnish the fork. As a chemist, you have all kinds of interesting cleaning products in your cabinet, including a 1 M solution of oxalic acid ($H_2C_2O_4$). Would you choose this solution to clean the fork that you have tarnished from eating scrambled eggs?
4. The electrode potential for the reaction $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ is 0.34 V under standard conditions. Is the potential for the oxidation of 0.5 mol of Cu equal to −0.34/2 V? Explain your answer.

Answer

3. No; $E°$ = −0.691 V for $Ag_2S(s) + 2e^- \rightarrow Ag(s) + S^{2-}(aq)$, which is too negative for Ag_2S to be spontaneously reduced by oxalic acid [$E°$ = 0.49 V for $2CO_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2C_2O_4(aq)$]

4.

Contributors

- Anonymous

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Chapter 17.4: Electrochemical Cells and Thermodynamics

Learning Objective

- To understand the relationship between cell potential and the equilibrium constant.
- To use cell potentials to calculate solution concentrations.

Changes in reaction conditions can have a tremendous effect on the course of a redox reaction. For example, under standard conditions, the reaction of Co(s) with Ni^{2+}(aq) to form Ni(s) and Co^{2+}(aq) occurs spontaneously, but if we reduce the concentration of Ni^{2+} by a factor of 100, so that [Ni^{2+}] is 0.01 M, then the reverse reaction occurs spontaneously instead. The relationship between voltage and concentration is one of the factors that must be understood to predict whether a reaction will be spontaneous.

The Relationship between Cell Potential and Free Energy

Electrochemical cells convert chemical energy to electrical energy and vice versa. The total amount of energy produced by an electrochemical cell, and thus the amount of energy available to do electrical work, depends on both the cell potential and the total number of electrons that are transferred from the reductant to the oxidant during the course of a reaction. The resulting electric current is measured in coulombs (C)The SI unit of measure for the number of electrons that pass a given point in 1 second; it is defined as 6.25×10^{18} e^-/s and relates electron potential (in volts) to energy (in joules): 1 J/1 V = 1 C., an SI unit that measures the number of electrons passing a given point in 1 s. A coulomb relates energy (in joules) to electrical potential (in volts). Electric current is measured in amperes (A)The fundamental SI unit of electric current; it is defined as the flow of 1 C/s past a given point: 1A = 1 C/s.; 1 A is defined as the flow of 1 C/s past a given point (1 C = 1 A·s):

$$\frac{1\ J}{1\ V} = 1\ C = 1\ A \cdot s$$

In chemical reactions, however, we need to relate the coulomb to the charge on a *mole* of electrons. Multiplying the charge on the electron by Avogadro's number gives us the charge on 1 mol of electrons, which is called the faraday (*F*)The charge on 1 mol of electrons; it is obtained by multiplying the charge on the electron by Avogadro's number., named after the English physicist and chemist Michael Faraday (1791–1867):

$$F = \left(1.60218 \times 10^{-19}\ C\right) \frac{6.02214 \times 10^{23}}{1\ mole}$$

$$F = 9.64855 \times 10^{4}\ C/mole \simeq 96,486 C/\left(mol\ e^{-}\right)$$

The total charge transferred from the reductant to the oxidant is therefore *nF*, where *n* is the number of moles of electrons.

Michael Faraday (1791–1867)

Faraday was a British physicist and chemist who was arguably one of the greatest experimental scientists in history. The son of a blacksmith, Faraday was self-educated and became an apprentice bookbinder at age 14 before turning to science. His experiments in electricity and magnetism made electricity a routine tool in science and led to both the electric motor and the electric generator. He discovered the phenomenon of electrolysis and laid the foundations of electrochemistry. In fact, most of the specialized terms introduced in this chapter (electrode, anode, cathode, and so forth) are due to Faraday. In addition, he discovered benzene and invented the system of oxidation state numbers that we use today. Faraday is probably best known for "The Chemical History of a Candle," a series of public lectures on the chemistry and physics of flames.

The maximum amount of work that can be produced by an electrochemical cell (w_{max}) is equal to the product of the cell potential (E_{cell}) and the total charge transferred during the reaction (*nF*):

$$w_{max} = nFE_{cell}$$

Work is expressed as a negative number because work is being done *by* a system (an electrochemical cell with a positive potential) *on* its surroundings.

As you learned in Chapter 16, the change in free energy (ΔG) is also a measure of the maximum amount of work that can be performed during a chemical process ($\Delta G = w_{max}$). Consequently, there must be a relationship between the potential of an electrochemical cell and ΔG, the most important thermodynamic quantity discussed in Chapter 16. This relationship is as follows:

$$\Delta G = -nFE_{cell}$$

A spontaneous redox reaction is therefore characterized by a *negative* value of ΔG and a *positive* value of E_{cell}, consistent with our earlier discussions. When both reactants and products are in their standard states, the relationship between $\Delta G°$ and $E°_{cell}$ is as follows:

$$\Delta G^o = -nFE^o_{cell}$$

Note the Pattern

A spontaneous redox reaction is characterized by a negative value of $\Delta G°$, which corresponds to a positive value of $E°_{cell}$.

Example 17.4.1

Suppose you want to prepare elemental bromine from bromide using the dichromate ion as an oxidant. Using the data in Table 17.3.1, calculate the free-energy change ($\Delta G°$) for this redox reaction under standard conditions. Is the reaction spontaneous?

Given: redox reaction

Asked for: $\Delta G°$ for the reaction and spontaneity

Strategy:

A From the relevant half-reactions and the corresponding values of $E°$, write the overall reaction and calculate $E°_{cell}$ using Equation 17.2.2.

B Determine the number of electrons transferred in the overall reaction. Then use Equation 17.4.5 to calculate $\Delta G°$. If $\Delta G°$ is negative, then the reaction is spontaneous.

Solution:

A As always, the first step is to write the relevant half-reactions and use them to obtain the overall reaction and the magnitude of $E°$. From the Standard Reduction Potentials Table, we can find the reduction and oxidation half-reactions and corresponding $E°$ values:

$$\begin{array}{lll} cathode: & Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) & E^o_{cathode} = 1.23\ V \\ anode: & 2Br^-(aq) \rightarrow Br_2(aq) + 2e^- & E^o_{anode} = 1.09\ V \end{array}$$

To obtain the overall balanced chemical equation, we must multiply both sides of the oxidation half-reaction by 3 to obtain the same number of electrons as in the reduction half-reaction, remembering that the magnitude of $E°$ is not affected:

$$\begin{array}{lll} cathode: & Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) & E^o_{cathode} = 1.23\ V \\ anode: & 6Br^-(aq) \rightarrow 3Br_2(aq) + 6e^- & E^o_{anode} = 1.09\ V \\ overall: & Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6BrI^- \rightarrow & E^o_{cell} = 0.14\ V \\ & 2Cr^{3+}(aq) + 7H_2O(l) + 3Br_2(aq) & \end{array}$$

B We can now calculate $\Delta G°$ using Equation 17.4.5 Because six electrons are transferred in the overall reaction, the value of n is 6:

$$\begin{aligned} \Delta G^o = -nFE^o_{cell} &= \left(6\ \cancel{mol}\right)\left(96,468\ J/\left(\cancel{V}\cdot\cancel{mol}\right)\right)\left(0.14\ \cancel{V}\right) \\ &-8.1 \times 10^4\ J \\ &-81\ kJ/mol\ Cr_2O_7 \end{aligned}$$

Thus $\Delta G°$ is −81 kJ for the reaction as written, and the reaction is spontaneous.

Exercise

Use the data in Table 17.3.1 to calculate $\Delta G°$ for the reduction of ferric ion by iodide:

$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(s)$

Is the reaction spontaneous?

Answer: −44 kJ/mol I_2; yes

Potentials for the Sums of Half-Reactions

Although Table 17.3.1 and Standard Reduction Potentials at 25°C" list several half-reactions, many more are known. When the standard potential for a half-reaction is not available, we can use relationships between standard potentials and free energy to obtain

the potential of any other half-reaction that can be written as the sum of two or more half-reactions whose standard potentials are available. For example, the potential for the reduction of Fe^{3+}(aq) to Fe(s) is not listed in the table, but two related reductions are given:

$$Fe^{3+}\,(aq) + e^- \rightarrow Fe^{2+}\,(aq) \quad E^o = 0.77\ V$$

$$Fe^{2+}\,(aq) + 2e^- \rightarrow Fe\,(aq) \quad E^o = -0.45\ V$$

Although the sum of these two half-reactions gives the desired half-reaction, we cannot simply add the potentials of two reductive half-reactions to obtain the potential of a third reductive half-reaction *because E° is not a state function*. However, because Δ*G*° is a state function, the sum of the Δ*G*° values for the individual reactions gives us Δ*G*° for the overall reaction, which is proportional to *both* the potential *and* the number of electrons (*n*) transferred. To obtain the value of *E*° for the overall half-reaction, we first must add the values of Δ*G*° (= −*nFE*°) for each individual half-reaction to obtain Δ*G*° for the overall half-reaction:

$$Fe^{3+}\,(aq) + e^- \rightarrow \cancel{Fe^{2+}\,(aq)} \quad \Delta G^o = (-1)\,F\,(0.77\ V)$$

$$\cancel{Fe^{2+}\,(aq)} + 2e^- \rightarrow Fe\,(s) \quad \Delta G^o = (-2)\,F\,(-0.457\ V)$$

$$Fe^{3+}\,(aq) + e^- \rightarrow Fe\,(s) \quad \Delta G^o = (-1)\,F\,(0.77\ V) + (-2)\,F\,(-0.457\ V)$$

Solving the last expression for Δ*G*° for the overall half-reaction,

$$\Delta G^o = F\,[(-0.77\ V) + (-2)\,(-0.457\ V)] = F\,(0.13\ V)$$

Three electrons (*n* = 3) are transferred in the overall reaction (Equation 17.4.8), so substituting into Equation 17.4.5 and solving for *E*° gives the following:

$$\Delta G^o = -nFE^o_{cell}$$

$$F\,(0.13\ V) = -3FE^o_{cell}$$

$$E^o_{cell} = -\frac{0.13\ V}{3} = -0.043\ V$$

This value of *E*° is *very* different from the value that is obtained by simply adding the potentials for the two half-reactions (0.32 V) and even has the opposite sign.

Note the Pattern

Values of *E*° for half-reactions cannot be added to give *E*° for the sum of the half-reactions; only values of Δ*G*° = −*nFE*°$_{cell}$ for half-reactions can be added.

The Relationship between Cell Potential and the Equilibrium Constant

We can use the relationship between Δ*G*° and the equilibrium constant *K*, defined in Chapter 16, to obtain a relationship between *E*°$_{cell}$ and *K*. Recall that for a general reaction of the type *a*A + *b*B → *c*C + *d*D, the standard free-energy change and the equilibrium constant are related by the following equation:

$$\Delta G^o = -RT\ln K$$

Given the relationship between the standard free-energy change and the standard cell potential (Equation 17.4.5), we can write

$$-nFE^o_{cell} = -RT\ln K$$

Rearranging this equation,

$$E^o_{cell} = \left(\frac{RT}{nF}\right)\ln K$$

For *T* = 298 K, Equation 17.4.12 can be simplified as follows:

$$E^o_{cell} = \left(\frac{RT}{nF}\right)\ln K = \left[\frac{8.314\ \cancel{J}/\left(\cancel{mol}\cdot\cancel{K}\right)\left(298\ \cancel{K}\right)}{n\left[96,486\ \cancel{J}/\left(V\cdot\cancel{mol}\right)\right]}\right] 2.303\ \log K = \left(\frac{0.0591}{n}\right)\log K$$

Thus *E*°$_{cell}$ is directly proportional to the logarithm of the equilibrium constant. This means that large equilibrium constants correspond to large positive values of *E*°$_{cell}$ and vice versa.

Example 17.4.2

Use the data in Table 17.3.1 to calculate the equilibrium constant for the reaction of metallic lead with PbO_2 in the presence of sulfate ions to give $PbSO_4$ under standard conditions. (This reaction occurs when a car battery is discharged.) Report your answer to two significant figures.

Given: redox reaction

Asked for: K

Strategy:

A Write the relevant half-reactions and potentials. From these, obtain the overall reaction and $E°_{cell}$.

B Determine the number of electrons transferred in the overall reaction. Use Equation 17.4.13 to solve for log K and then K.

Solution:

A The relevant half-reactions and potentials from Table 17.3.1 are as follows:

$$\begin{aligned} cathode: &\quad PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l) && E°_{cathode} = 1.69\ V \\ anode: &\quad Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^- && E°_{anode} = 0.36\ V \\ overall: &\quad Pb(s)\,PbO_2(s) + 2SO_4^{2-}(aq) + 4H^+(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l) && E°_{cell} = 2.05\ V \end{aligned}$$

B Two electrons are transferred in the overall reaction, so $n = 2$. Solving Equation 17.4.13 for log K and inserting the values of n and $E°$,

$$\ln K = \frac{nE°}{0.0591\ V} = \frac{2\left(2.05\ \cancel{V}\right)}{0.0591\ \cancel{V}} = 69.37$$

$$K = 2.3 \times 10^{69}$$

Thus the equilibrium lies far to the right, favoring a discharged battery (as anyone who has ever tried unsuccessfully to start a car after letting it sit for a long time will know).

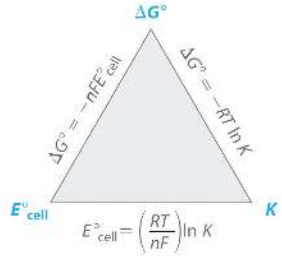
Exercise

Use the data in Table 17.3.1 to calculate the equilibrium constant for the reaction of Sn^{2+}(aq) with oxygen to produce Sn^{4+}(aq) and water under standard conditions. Report your answer to two significant figures. The reaction is as follows:

$$2Sn^{2+}(aq) + O_2(g) + 4H^+(aq) \rightleftharpoons 2Sn^{4+}(aq) + 2H_2O(l)$$

Answer: 1.2×10^{73}

Figure 17.4.1 summarizes the relationships that we have developed based on properties of the *system*—that is, based on the equilibrium constant, standard free-energy change, and standard cell potential—and the criteria for spontaneity ($\Delta G° < 0$). Unfortunately, these criteria apply only to systems in which all reactants and products are present in their standard states, a situation that is seldom encountered in the real world. A more generally useful relationship between cell potential and reactant and product concentrations, as we are about to see, uses the relationship between ΔG and the reaction quotient Q developed in Chapter 16 .



$\Delta G°$	$E°_{cell}$	K	Direction of Reaction
< 0	> 0	> 1	spontaneous in forward direction
> 0	< 0	< 1	spontaneous in reverse direction
0	0	1	no net reaction: system at equilibrium

Figure 17.4.1 The Relationships among Criteria for Thermodynamic Spontaneity The three properties of a system that can be used to predict the spontaneity of a redox reaction under standard conditions are K, $\Delta G°$, and $E°_{cell}$. If we know the value of one of these quantities, then these relationships enable us to calculate the value of the other two. The signs of $\Delta G°$ and $E°_{cell}$ and the magnitude of K determine the direction of spontaneous reaction under standard conditions.

The Effect of Concentration on Cell Potential: The Nernst Equation

Recall from Chapter 16 that the *actual* free-energy change for a reaction under nonstandard conditions, ΔG, is given as follows:

$$\Delta G = \Delta G^o + RT\ ln\ Q$$

We also know that $\Delta G = -nFE_{cell}$ and $\Delta G° = -nFE°_{cell}$. Substituting these expressions into Equation 17.4.14, we obtain

$$-nFE_{cell} = -nFE^o_{cell} + RT\ ln\ Q$$

Dividing both sides of this equation by $-nF$,

$$E_{cell} = E^o_{cell} - \frac{RT}{nF}\ ln\ Q$$

Equation 17.4.16 is called the Nernst equationAn equation for calculating cell potentials E_{cell} under nonstandard conditions; it can be used to determine the direction of spontaneous reaction for any redox reaction under an conditions:E_{cell}=</mo><msubsup><mi>E°−(RT/nF)lnQ, after the German physicist and chemist Walter Nernst (1864–1941), who first derived it. The Nernst equation is arguably the most important relationship in electrochemistry. When a redox reaction is at equilibrium ($\Delta G = 0$), Equation 17.4.16 reduces to Equation 17.4.12 because $Q = K$, and there is no net transfer of electrons (i.e., $E_{cell} = 0$).

Substituting the values of the constants into Equation 17.4.16 with T = 298 K and converting to base-10 logarithms give the relationship of the actual cell potential (E_{cell}), the standard cell potential ($E°_{cell}$), and the reactant and product concentrations at room temperature (contained in Q):

$$E_{cell} = E^o_{cell} - \frac{0.0591\ V}{F}\ ln\ Q$$

Note the Pattern

The Nernst equation can be used to determine the value of E_{cell}, and thus the direction of spontaneous reaction, for any redox reaction under any conditions.

Equation 17.4.17 allows us to calculate the potential associated with any electrochemical cell at 298 K for any combination of reactant and product concentrations under any conditions. We can therefore determine the spontaneous direction of any redox reaction under any conditions, as long as we have tabulated values for the relevant standard electrode potentials. Notice in Equation 17.4.17 that the cell potential changes by 0.0591/n V for each 10-fold change in the value of Q because log 10 = 1.

Example 17.4.3

In the exercise in Example 6, you determined that the following reaction proceeds spontaneously under standard conditions because $E°_{cell} > 0$ (which you now know means that $\Delta G° < 0$):

$$2Ce^{4+}\ (aq) + 2Cl^-\ (aq) \rightarrow 2Ce^{3+}\ (aq) + Cl_2\ (g)$$

Calculate E for this reaction under the following nonstandard conditions and determine whether it will occur spontaneously: [Ce^{4+}] = 0.013 M, [Ce^{3+}] = 0.60 M, [Cl^-] = 0.0030 M, Cl_2= 1.0 atm, and T = 25°C.

Given: balanced redox reaction, standard cell potential, and nonstandard conditions

Asked for: cell potential

Strategy:

Determine the number of electrons transferred during the redox process. Then use the Nernst equation to find the cell potential under the nonstandard conditions.

Solution:

We can use the information given and the Nernst equation to calculate E_{cell}. Moreover, because the temperature is 25°C (298 K), we can use Equation 17.4.17 instead of 19.46. The overall reaction involves the net transfer of two electrons:

$2Ce^{4+}(aq) + 2e^- \rightarrow 2Ce^{3+}(aq)$

$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

so n = 2. Substituting the concentrations given in the problem, the partial pressure of Cl_2, and the value of $E°_{cell}$ into Equation 17.4.17,

$$E_{cell} = E^o_{cell} - \frac{0.0591\ V}{F}\ log\ Q$$

$$= 0.25\ V - \frac{0.0591\ V}{2}\ logn\ \left(\frac{[Ce^{3+}]^2\ P_{Cl_2}}{[Ce^{4+}]^2\ [Cl^-]^2}\right)$$

$$= 0.25\ V - [(0.0296\ V)\ (8.37)] = 0.00\ V$$

Thus the reaction will *not* occur spontaneously under these conditions (because E = 0 V and ΔG = 0). The composition specified is that of an equilibrium mixture.

Exercise

In the exercise in Example 6, you determined that molecular oxygen will not oxidize MnO_2 to permanganate via the reaction

$$4MnO_2\ (s) + 3O_2\ (g) + 4OH^-\ (aq) \rightarrow 4MnO_4^-\ (aq) + 2H_2O\ (l)\ \;\;\; E_{cell}^{o}=-0.20\;V$$

Calculate E_{cell} for the reaction under the following nonstandard conditions and decide whether the reaction will occur spontaneously: pH 10, $P(O_2)$ = 0.20 atm, $[MNO_4^-]$ = 1.0 × 10^{-4} M, and T = 25°C.

Answer: E_{cell} = −0.22 V; the reaction will not occur spontaneously.

Applying the Nernst equation to a simple electrochemical cell such as the Zn/Cu cell discussed in Section 17.1.4 allows us to see how the cell voltage varies as the reaction progresses and the concentrations of the dissolved ions change. Recall that the overall reaction for this cell is as follows:

$$Zn\ (s) + Cu^{2+}\ (aq) \rightarrow Zn^{2+}\ (aq) + Cu\ (s)\ \;\;\; E_{cell}^{o}=1.10\;V \tag{17.4.18}$$

The reaction quotient is therefore $Q = [Zn^{2+}]/[Cu^{2+}]$. Suppose that the cell initially contains 1.0 M Cu^{2+} and 1.0 × 10^{-6} M Zn^{2+}. The initial voltage measured when the cell is connected can then be calculated from Equation 17.4.17:

$$E_{cell} = E^o_{cell} - \frac{0.0591\ V}{n}\ log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E_{cell} = 1.10\ V - \frac{0.0591\ V}{2}\ log\frac{1.0 \times 10^{-6}}{1.0} = 1.28\ V$$

Thus the initial voltage is *greater* than $E°$ because Q < 1. As the reaction proceeds, $[Zn^{2+}]$ in the anode compartment increases as the zinc electrode dissolves, while $[Cu^{2+}]$ in the cathode compartment decreases as metallic copper is deposited on the electrode. During this process, the ratio $Q = [Zn^{2+}]/[Cu^{2+}]$ steadily increases, and the cell voltage therefore steadily decreases. Eventually, $[Zn^{2+}] = [Cu^{2+}]$, so Q = 1 and $E_{cell} = E°_{cell}$. Beyond this point, $[Zn^{2+}]$ will continue to increase in the anode compartment, and $[Cu^{2+}]$ will continue to decrease in the cathode compartment. Thus the value of Q will increase further, leading to a further decrease in E_{cell}. When the concentrations in the two compartments are the opposite of the initial concentrations (i.e., 1.0 M Zn^{2+} and 1.0 × 10^{-6} M Cu^{2+}), Q = 1.0 × 10^6, and the cell potential will be reduced to 0.92 V.

The variation of E_{cell} with log Q over this range is linear with a slope of −0.0591/n, as illustrated in Figure 17.4.2. As the reaction proceeds still further, Q continues to increase, and E_{cell} continues to decrease. If neither of the electrodes dissolves completely, thereby breaking the electrical circuit, the cell voltage will eventually reach zero. This is the situation that occurs when a battery is "dead." The value of Q when E_{cell} = 0 is calculated as follows:

$$E_{cell} = E^o_{cell} - \frac{0.0591\ V}{n}\ log\ Q = 0$$

$$E^o = \frac{0.0591\ V}{n}\ log\ Q$$

$$log\ Q) = \frac{E^o\ n}{0.0591\ V} = \frac{(1.10\ \cancel{V})\ (2)}{0.0591\ \cancel{V}} = 37.23$$

$$Q = 10^{37.23} = 1.7 \times 10^{37}$$

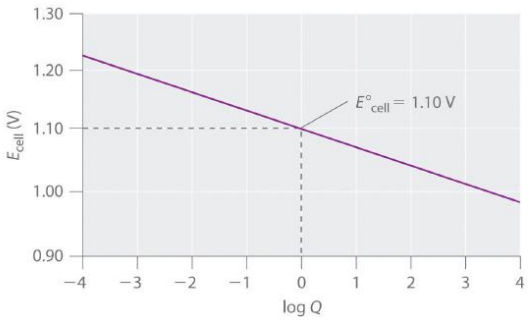


Figure 17.4.2 The Variation of E_{cell} with Log Q for a Zn/Cu Cell Initially, log Q < 0, and the voltage of the cell is greater than $E°_{cell}$. As the reaction progresses, log Q increases, and E_{cell} decreases. When $[Zn^{2+}] = [Cu^{2+}]$, log Q = 0 and $E_{cell} = E°_{cell}$ = 1.10 V. As long as the electrical circuit remains intact, the reaction will continue, and log Q will increase until $Q = K$ and the cell voltage reaches zero. At this point, the system will have reached equilibrium.

Recall that at equilibrium, $Q = K$. Thus the equilibrium constant for the reaction of Zn metal with Cu^{2+} to give Cu metal and Zn^{2+} is 1.7×10^{37} at 25°C.

Concentration Cells

A voltage can also be generated by constructing an electrochemical cell in which each compartment contains the same redox active solution but at different concentrations. The voltage is produced as the concentrations equilibrate. Suppose, for example, we have a cell with 0.010 M $AgNO_3$ in one compartment and 1.0 M $AgNO_3$ in the other. The cell diagram and corresponding half-reactions are as follows:

$$Ag\,(s)\mid Ag^{+}\,(aq,\ 0.010\ M)\parallel Ag^{+}\,(aq,\ 1.0\ M)\mid Ag\,(s)$$

$$cathode:\quad Ag^{+}\,(aq,\ 1.0\ M)+e^{-}\rightarrow Ag\,(s)$$

$$anode:\quad Ag\,(s)\rightarrow Ag^{+}\,(aq,\ 0.010\ M)+e^{-}$$

$$overall:\quad Ag^{+}\,(aq,\ 1.0\ M)\rightarrow Ag^{+}\,(aq,\ 0.010\ M)$$

As the reaction progresses, the concentration of Ag^+ will increase in the left (oxidation) compartment as the silver electrode dissolves, while the Ag^+ concentration in the right (reduction) compartment decreases as the electrode in that compartment gains mass. The *total* mass of Ag(s) in the cell will remain constant, however. We can calculate the potential of the cell using the Nernst equation, inserting 0 for $E°_{cell}$ because $E°_{cathode} = -E°_{anode}$:

$$E_{cell}=E^{o}_{cell}-\frac{0.0591\ V}{n}\,logQ=0-\left(\frac{0.0591\ V}{1}\right)log\frac{0.010}{1.0}=0.12$$

An electrochemical cell of this type, in which the anode and cathode compartments are identical except for the concentration of a reactant, is called a concentration cellAn electrochemical cell in which the anode and the cathode compartments are identical except for the concentration of a reactant.. As the reaction proceeds, the difference between the concentrations of Ag^+ in the two compartments will decrease, as will E_{cell}. Finally, when the concentration of Ag^+ is the same in both compartments, equilibrium will have been reached, and the measured potential difference between the two compartments will be zero (E_{cell} = 0).

Example 17.4.4

Calculate the voltage in a galvanic cell that contains a manganese electrode immersed in a 2.0 M solution of $MnCl_2$ as the cathode, and a manganese electrode immersed in a 5.2×10^{-2} M solution of $MnSO_4$ as the anode (T = 25°C).

Given: galvanic cell, identities of the electrodes, and solution concentrations

Asked for: voltage

Strategy:

A Write the overall reaction that occurs in the cell.

B Determine the number of electrons transferr

$$E_{cell} = E^{o}_{cell} - \frac{0.0591\ V}{n}\ log\ Q = 0 - \left(\frac{0.0591\ V}{2}\right) log \frac{5.2 \times 10^{-2}}{2.0} = 0.047$$

ed. Substitute this value into the Nernst equation to calculate the voltage.

Solution:

A This is a concentration cell, in which the electrode compartments contain the same redox active substance but at different concentrations. The anions (Cl^- and SO_4^{2-}) do not participate in the reaction, so their identity is not important. The overall reaction is as follows:

$Mn^{2+}(aq, 2.0\ M) \rightarrow Mn^{2+}(aq, 5.2 \times 10^{-2}\ M)$

B For the reduction of $Mn^{2+}(aq)$ to Mn(s), $n = 2$. We substitute this value and the given Mn^{2+} concentrations into Equation 17.4.17:

Thus manganese will dissolve from the electrode in the compartment that contains the more dilute solution and will be deposited on the electrode in the compartment that contains the more concentrated solution.

Exercise

Suppose we construct a galvanic cell by placing two identical platinum electrodes in two beakers that are connected by a salt bridge. One beaker contains 1.0 M HCl, and the other a 0.010 M solution of Na_2SO_4 at pH 7.00. Both cells are in contact with the atmosphere, with $P(O_2) = 0.20$ atm. If the relevant electrochemical reaction in both compartments is the four-electron reduction of oxygen to water, $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$, what will be the potential when the circuit is closed?

Answer: 0.41 V

Using Cell Potentials to Measure Solubility Products

Because voltages are relatively easy to measure accurately using a voltmeter, electrochemical methods provide a convenient way to determine the concentrations of very dilute solutions and the solubility products (K_{sp}) of sparingly soluble substances. As you learned in Chapter 16, solubility products can be very small, with values of less than or equal to 10^{-30}. Equilibrium constants of this magnitude are virtually impossible to measure accurately by direct methods, so we must use alternative methods that are more sensitive, such as electrochemical methods.

To understand how an electrochemical cell is used to measure a solubility product, consider the cell shown in Figure 17.4.3, which is designed to measure the solubility product of silver chloride: $K_{sp} = [Ag^+][Cl^-]$. In one compartment, the cell contains a silver wire inserted into a 1.0 M solution of Ag^+; the other compartment contains a silver wire inserted into a 1.0 M Cl^- solution saturated with AgCl. In this system, the Ag^+ ion concentration in the first compartment equals K_{sp}. We can see this by dividing both sides of the equation for K_{sp} by $[Cl^-]$ and substituting: $[Ag^+] = K_{sp}/[Cl^-] = K_{sp}/1.0 = K_{sp}$. The overall cell reaction is as follows:

$Ag^+(aq, concentrated) \rightarrow Ag^+(aq, dilute)$

Thus the voltage of the concentration cell due to the difference in $[Ag^+]$ between the two cells is as follows:

$$E_{cell} = 0 - \left(\frac{0.0591\ V}{1}\right) log \left(\frac{[Ag^+]_{dilute}}{[Ag^+]_{concentrated}}\right) = -0.0591\ V\ log \left(\frac{K_{sp}}{1.0}\right) = -0.0591\ V$$

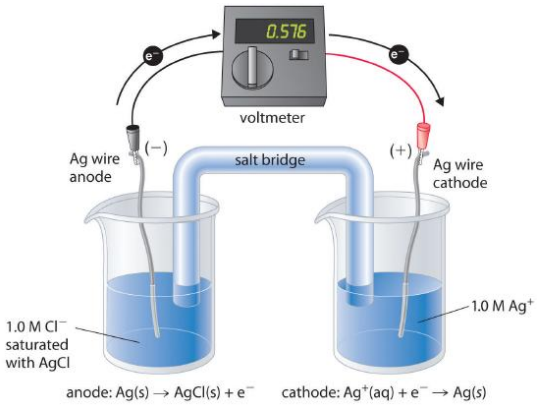


Figure 17.4.3. A Galvanic Cell for Measuring the Solubility Product of AgCl One compartment contains a silver wire inserted into a 1.0 M solution of Ag^+, and the other compartment contains a silver wire inserted into a 1.0 M Cl^- solution saturated with AgCl. The potential due to the difference in $[Ag^+]$ between the two cells can be used to determine K_{sp}.

By closing the circuit, we can measure the potential caused by the difference in $[Ag^+]$ in the two cells. In this case, the experimentally measured voltage of the concentration cell at 25°C is 0.580 V. Solving Equation 17.4.26 for K_{sp},

$$log\ K_{sp} = \frac{-E_{cell}}{0.0591\ V} = \frac{-0.580\ \cancel{V}}{0.0591\ \cancel{V}} = -9.81$$

$$K_{sp} = 1.5 \times 10^{-10}$$

Thus a single potential measurement can provide the information we need to determine the value of the solubility product of a sparingly soluble salt.

Example 17.4.5

To measure the solubility product of lead(II) sulfate ($PbSO_4$) at 25°C, you construct a galvanic cell like the one shown in Figure 17.4.3, which contains a 1.0 M solution of a very soluble Pb^{2+} salt [lead(II) acetate trihydrate] in one compartment that is connected by a salt bridge to a 1.0 M solution of Na_2SO_4 saturated with $PbSO_4$ in the other. You then insert a Pb electrode into each compartment and close the circuit. Your voltmeter shows a voltage of 230 mV. What is K_{sp} for $PbSO_4$? Report your answer to two significant figures.

Given: galvanic cell, solution concentrations, electrodes, and voltage

Asked for: K_{sp}

Strategy:

A From the information given, write the equation for K_{sp}. Express this equation in terms of the concentration of Pb^{2+}.

B Determine the number of electrons transferred in the electrochemical reaction. Substitute the appropriate values into Equation 17.4.26 and solve for K_{sp}.

Solution:

A You have constructed a concentration cell, with one compartment containing a 1.0 M solution of Pb^{2+} and the other containing a dilute solution of Pb^{2+} in 1.0 M Na_2SO_4. As for any concentration cell, the voltage between the two compartments can be calculated using the Nernst equation. The first step is to relate the concentration of Pb^{2+} in the dilute solution to K_{sp}:

$$[Pb^{2+}]\ [SO_4^{2-}] = K_{sp}$$

$$[Pb^{2+}] = \frac{K_{sp}}{[SO_4^{2-}]} = \frac{K_{sp}}{1.0\ M} = K_{sp}$$

B The reduction of Pb^{2+} to Pb is a two-electron process and proceeds according to the following reaction:

Pb^{2+}(aq, concentrated) → Pb^{2+}(aq, dilute)

so

$$E_{cell} = E^o_{cell} - \frac{0.0591\ V}{n}\ log\ Q$$

$$0.230\ V = 0 - \left(\frac{0.0591\ V}{2}\right) log\left(\frac{[Pb^{2+}]_{dilute}}{[Pb^{2+}]_{concentrated}}\right) = -0.0296\ V\ log\left(\frac{K_{sp}}{1.0}\right)$$

$$-7.77 = log\ K_{sp}$$

$$1.7 \times 10^{-8} = K_{sp}$$

Exercise

A concentration cell similar to the one described in Example 11 contains a 1.0 M solution of lanthanum nitrate $[La(NO_3)_3]$ in one compartment and a 1.0 M solution of sodium fluoride saturated with LaF_3 in the other. A metallic La strip is inserted into each

compartment, and the circuit is closed. The measured potential is 0.32 V. What is the K_{sp} for LaF_3? Report your answer to two significant figures.

Answer: 5.7×10^{-17}

Using Cell Potentials to Measure Concentrations

Another use for the Nernst equation is to calculate the concentration of a species given a measured potential and the concentrations of all the other species. We saw an example of this in Example 11, in which the experimental conditions were defined in such a way that the concentration of the metal ion was equal to K_{sp}. Potential measurements can be used to obtain the concentrations of dissolved species under other conditions as well, which explains the widespread use of electrochemical cells in many analytical devices. Perhaps the most common application is in the determination of $[H^+]$ using a pH meter, as illustrated in Example 12.

Example 17.4.6

Suppose a galvanic cell is constructed with a standard Zn/Zn^{2+} couple in one compartment and a modified hydrogen electrode in the second compartment (Figure 17.1.3). The pressure of hydrogen gas is 1.0 atm, but $[H^+]$ in the second compartment is unknown. The cell diagram is as follows:

$Zn(s)\,|\,Zn^{2+}(aq, 1.0\ M)\,\|\,H^+(aq, ?\ M)\,|\,H_2(g, 1.0\ atm)\,|\,Pt(s)$

What is the pH of the solution in the second compartment if the measured potential in the cell is 0.26 V at 25°C?

Given: galvanic cell, cell diagram, and cell potential

Asked for: pH of the solution

Strategy:

A Write the overall cell reaction.

B Substitute appropriate values into the Nernst equation and solve for $-\log[H^+]$ to obtain the pH.

Solution:

A Under standard conditions, the overall reaction that occurs is the reduction of protons by zinc to give H_2 (note that Zn lies below H_2 in Table 17.3.1):

$$Zn\,(s) + 2H^+\,(aq) \rightarrow Zn^{2+}\,(aq) + H_2\,(g) \quad E_o = 0.76\ V$$

B By substituting the given values into the simplified Nernst equation (Equation 17.4.17), we can calculate $[H^+]$ under nonstandard conditions:

\(E_{cell} =E_{cell}^{o}-\dfrac{0.0591\;V}{n}\;log \left (\dfrac{\left [Zn^{2+} \right]P_{H_{2}}}{\left [H^{+} \right]^{2}} \right)

$$0.26\ V = 0.76\ V - \left(\frac{0.0591\ V}{2}\right) log\left(\frac{(1.0)\,(1.0)}{[H^+]^2}\right) = -0.0296\ V\ log\left(\frac{K_{sp}}{1.0}\right)$$

$$16.9 = log\left(\frac{1}{[H^+]^2}\right) = log\,[H^+]^{-2} = -2\ log\,[H^+]$$

$$8.46 = -log\,[H^+]$$

$$8.5 = pH$$

Thus the potential of a galvanic cell can be used to measure the pH of a solution.

Exercise

Suppose you work for an environmental laboratory and you want to use an electrochemical method to measure the concentration of Pb^{2+} in groundwater. You construct a galvanic cell using a standard oxygen electrode in one compartment ($E°_{cathode}$ = 1.23 V). The other compartment contains a strip of lead in a sample of groundwater to which you have added sufficient acetic acid, a weak organic acid, to ensure electrical conductivity. The cell diagram is as follows"

$Pb(s)\,|\,Pb^{2+}(aq, ?\ M)\|H^+(aq), 1.0\ M\,|\,O_2(g, 1.0\ atm)\,|\,Pt(s)$

When the circuit is closed, the cell has a measured potential of 1.62 V. Use Table 17.7.1 and Standard Reduction Potentials at 25°C" to determine the concentration of Pb^{2+} in the groundwater.

Answer: 1.2×10^{-9} M

Summary

A **coulomb (C)** relates electrical potential, expressed in volts, and energy, expressed in joules. The current generated from a redox reaction is measured in **amperes (A)**, where 1 A is defined as the flow of 1 C/s past a given point. The **faraday (*F*)** is Avogadro's number multiplied by the charge on an electron and corresponds to the charge on 1 mol of electrons. The product of the cell potential and the total charge is the maximum amount of energy available to do work, which is related to the change in free energy that occurs during the chemical process. Adding together the ΔG values for the half-reactions gives ΔG for the overall reaction, which is proportional to *both* the potential *and* the number of electrons (n) transferred. Spontaneous redox reactions have a negative ΔG and therefore a positive E_{cell}. Because the equilibrium constant K is related to ΔG, $E°_{cell}$ and K are also related. Large equilibrium constants correspond to large positive values of $E°$. The **Nernst equation** allows us to determine the spontaneous direction of any redox reaction under any reaction conditions from values of the relevant standard electrode potentials. **Concentration cells** consist of anode and cathode compartments that are identical except for the concentrations of the reactant. Because $\Delta G = 0$ at equilibrium, the measured potential of a concentration cell is zero at equilibrium (the concentrations are equal). A galvanic cell can also be used to measure the solubility product of a sparingly soluble substance and calculate the concentration of a species given a measured potential and the concentrations of all the other species.

Key Takeaway

- The Nernst equation can be used to determine the direction of spontaneous reaction for any redox reaction in aqueous solution.

Key Equations

Charge on a mole of electrons (faraday)

Equation 17.4.2: $F \approx 96{,}486$ J/(V·mol)

Maximum work from an electrochemical cell

Equation 17.4.3: $w_{max} = -nFE_{cell}$

Relationship between Δ *G* ° and Δ *E* °

Equation 17.4.5: $\Delta G° = -nFE°_{cell}$

Relationship between Δ *G* ° and *K* for a redox reaction

Equation 17.4.10: $\Delta G° = -RT \ln K$

Relationship between Δ *E* ° and *K* for a redox reaction at 25°C

Equation 17.4.12: $E^o_{cell} = \left(\frac{RT}{nF}\right) ln\ K$

Equation 17.4.13: $E^o_{cell} = \left(\frac{0.0591}{n}\right) log\ K$

Relationship between Δ *G* ° and *Q*

Equation 17.4.14: $\Delta G = \Delta G° + RT \ln Q$

Relationship between E_{cell} and *Q* at 25°C

Equation 17.4.17: $E_{cell} = E^o_{cell} - \frac{0.0591\ V}{F}\ ln\ Q$

Conceptual Problems

1. State whether you agree or disagree with this reasoning and explain your answer: Standard electrode potentials arise from the number of electrons transferred. The greater the number of electrons transferred, the greater the measured potential difference. If 1 mol of a substance produces 0.76 V when 2 mol of electrons are transferred—as in $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$—then 0.5 mol of the substance will produce 0.76/2 V because only 1 mol of electrons is transferred.

2. What is the relationship between the *measured cell potential* and the *total charge* that passes through a cell? Which of these is dependent on concentration? Which is dependent on the identity of the oxidant or the reductant? Which is dependent on the number of electrons transferred?
3. In the equation $w_{max} = -nFE°_{cell}$, which quantities are extensive properties and which are intensive properties?
4. For any spontaneous redox reaction, E is positive. Use thermodynamic arguments to explain why this is true.
5. State whether you agree or disagree with this statement and explain your answer: Electrochemical methods are especially useful in determining the reversibility or irreversibility of reactions that take place in a cell.
6. Although the sum of two half-reactions gives another half-reaction, the sum of the potentials of the two half-reactions cannot be used to obtain the potential of the net half-reaction. Why? When does the sum of two half-reactions correspond to the overall reaction? Why?
7. Occasionally, you will find high-quality electronic equipment that has its electronic components plated in gold. What is the advantage of this?
8. Blood analyzers, which measure pH, $P(CO_2)$ and $P(O_2)$ are frequently used in clinical emergencies. For example, blood $P(CO_2)$ is measured with a pH electrode covered with a plastic membrane that is permeable to CO_2. Based on your knowledge of how electrodes function, explain how such an electrode might work. Hint: $CO_2(g) + H_2O(l) \rightarrow HCO_3^-(aq) + H^+(aq)$.
9. Concentration cells contain the same species in solution in two different compartments. Explain what produces a voltage in a concentration cell. When does V = 0 in such a cell?
10. Describe how an electrochemical cell can be used to measure the solubility of a sparingly soluble salt.

3. extensive: w_{max} and n; intensive: $E°_{cell}$

Answers

2.
4.
1.
5.
6.
7. Gold is highly resistant to corrosion because of its very positive reduction potential.
8.
9.
10.

Numerical Problems

1. The chemical equation for the combustion of butane is as follows:

$$C_4H10\,(g) + \frac{13}{2}O_2\,(g) \rightarrow 2CO_2\,(g) + 5H_2O\,(g)$$

This reaction has $\Delta H° = -2877$ kJ/mol. Calculate $E°_{cell}$ and then determine $\Delta G°$. Is this a spontaneous process? What is the change in entropy that accompanies this process at 298 K?

2. How many electrons are transferred during the reaction $Pb(s) + Hg_2Cl_2(s) \rightarrow PbCl_2(aq) + 2Hg(l)$? What is the standard cell potential? Is the oxidation of Pb by Hg_2Cl_2 spontaneous? Calculate $\Delta G°$ for this reaction.
3. For the cell represented as $Al(s)\,|\,Al^{3+}(aq)\,\|\,Sn^{2+}(aq),\ Sn^{4+}(aq)\,|\,Pt(s)$, how many electrons are transferred in the redox reaction? What is the standard cell potential? Is this a spontaneous process? What is $\Delta G°$?
4. Explain why the sum of the potentials for the half-reactions $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$ and $Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$ does not equal the potential for the reaction $Sn^{4+}(aq) + 4e^- \rightarrow Sn(s)$. What is the net cell potential? Compare the values of $\Delta G°$ for the sum of the potentials and the actual net cell potential.
5. Based on the Standard Reduction Potentials at 25°C", do you agree with the proposed potentials for the following half-reactions? Why or why not?
    1. $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$, $E° = 0.68$ V

2. $Ce^{4+}(aq) + 4e^- \rightarrow Ce(s)$, $E° = -0.62$ V

6. For each reaction, calculate $E°_{cell}$ and then determine $\Delta G°$. Indicate whether each reaction is spontaneous.

   1. $2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$
   2. $K_2S_2O_6(aq) + I_2(s) \rightarrow 2KI(aq) + 2K_2SO_4(aq)$
   3. $Sn(s) + CuSO_4(aq) \rightarrow Cu(s) + SnSO_4(aq)$

7. What is the standard change in free energy for the reaction between Ca^{2+} and Na(s) to give Ca(s) and Na^+? Do the sign and magnitude of $\Delta G°$ agree with what you would expect based on the positions of these elements in the periodic table? Why or why not?

8. In acidic solution, permanganate (MnO_4^-) oxidizes Cl^- to chlorine gas, and MnO_4^- is reduced to $Mn^{2+}(aq)$.

   1. Write the balanced chemical equation for this reaction.
   2. Determine $E°_{cell}$.
   3. Calculate the equilibrium constant.

9. Potentiometric titrations are an efficient method for determining the endpoint of a redox titration. In such a titration, the potential of the solution is monitored as measured volumes of an oxidant or a reductant are added. Data for a typical titration, the potentiometric titration of Fe(II) with a 0.1 M solution of Ce(IV), are given in the following table. The starting potential has been arbitrarily set equal to zero because it is the *change* in potential with the addition of the oxidant that is important.

Titrant (mL)	E (mV)
2.00	50
6.00	100
9.00	255
10.00	960
11.00	1325
12.00	1625
14.00	1875

   1. Write the balanced chemical equation for the oxidation of Fe^{2+} by Ce^{4+}.
   2. Plot the data and then locate the endpoint.
   3. How many millimoles of Fe^{2+} did the solution being titrated originally contain?

10. The standard electrode potential ($E°$) for the half-reaction $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ is -0.257 V. What pH is needed for this reaction to take place in the presence of 1.00 atm $H_2(g)$ as the reductant if $[Ni^{2+}]$ is 1.00 M?

11. The reduction of Mn(VII) to Mn(s) by $H_2(g)$ proceeds in five steps that can be readily followed by changes in the color of the solution. Here is the redox chemistry:

    1. $MnO_4^-(aq) + e^- \rightarrow MnO_4^{2-}(aq)$; $E° = +0.56$ V (purple → dark green)
    2. $MnO_4^{2-}(aq) + 2e^- + 4H^+(aq) \rightarrow MnO_2(s)$; $E° = +2.26$ V (dark green → dark brown solid)
    3. $MnO_2(s) + e^- + 4H^+(aq) \rightarrow Mn^{3+}(aq)$; $E° = +0.95$ V (dark brown solid → red-violet)
    4. $Mn^{3+}(aq) + e^- \rightarrow Mn^{2+}(aq)$; $E° = +1.51$ V (red-violet → pale pink)
    5. $Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$; $E° = -1.18$ V (pale pink → colorless)

    1. Is the reduction of MnO_4^- to $Mn^{3+}(aq)$ by $H_2(g)$ spontaneous under standard conditions? What is $E°_{cell}$?
    2. Is the reduction of $Mn^{3+}(aq)$ to Mn(s) by $H_2(g)$ spontaneous under standard conditions? What is $E°_{cell}$?

12. Mn(III) can disproportionate (both oxidize and reduce itself) by means of the following half-reactions:

$Mn^{3+}(aq) + e^- \rightarrow Mn^{2+}(aq)$; $E°$ = +1.51 V

$Mn^{3+}(aq) + 2H_2O(l) \rightarrow MnO_2(s) + 4H^+(aq) + e^-$; $E°$ = +0.95 V

1. What is $E°$ for the disproportionation reaction?
2. Is disproportionation more or less thermodynamically favored at low pH than at pH 7.0? Explain your answer.
3. How could you prevent the disproportionation reaction from occurring?

13. For the reduction of oxygen to water, $E°$ = 1.23 V. What is the potential for this half-reaction at pH 7.00? What is the potential in a 0.85 M solution of NaOH?

14. The biological molecule abbreviated as NADH (reduced nicotinamide adenine dinucleotide) can be formed by reduction of NAD^+ (nicotinamide adenine dinucleotide) via the half-reaction $NAD^+ + H^+ + 2e^- \rightarrow NADH$; $E°$ = −0.32 V.

    1. Would NADH be able to reduce acetate to pyruvate?
    2. Would NADH be able to reduce pyruvate to lactate?
    3. What potential is needed to convert acetate to lactate?

    acetate + CO_2 + $2H^+$ + $2e^- \rightarrow$ pyruvate + H_2O; $E°$ = +0.70 V

    pyruvare + $2H^+$ + $2e^- \rightarrow$ lactate; $E°$ = -0.185 V

15. Given the following biologically relevant half-reactions, will FAD (flavin adenine dinucleotide), a molecule used to transfer electrons whose reduced form is $FADH_2$, be an effective oxidant for the conversion of acetaldehyde to acetate at pH 4.00?

    acetate + $2H^+$ + $2e^- \rightarrow$ acetaldehyde + H_2O; $E°$ = -0.58 V

    FAD + $2H^+$ + $2e^- \rightarrow$ $FADH_2$; $E°$ = -0.18 V

16. Ideally, any half-reaction with $E° > 1.23$ V will oxidize water as a result of the half-reaction $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$.

    1. Will FeO_4^{2-} oxidize water if the half-reaction for the reduction of Fe(VI) → Fe(III) is $FeO_4^{2-}(aq) + 8H^+(aq) + 3e^- \rightarrow Fe^{3+}(aq) + 4H_2O$; $E°$ = 1.9 V?
    2. What is the highest pH at which this reaction will proceed spontaneously if $[Fe^{3+}] = [FeO_4^{2-}]$ = 1.0 M and <math display="inline" xml:id="av_1.0-19_m077"><semantics><mrow><msub><mi>P</mi><mrow><msub><mtext>O</mtext><mn>2</mn></msub></mrow></msub></mrow></semantics></math> = 1.0 atm?

17. Under acidic conditions, ideally any half-reaction with $E° > 1.23$ V will oxidize water via the reaction $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$.

    1. Will aqueous acidic $KMnO_4$ evolve oxygen with the formation of MnO_2?
    2. At pH 14.00, what is $E°$ for the oxidation of water by aqueous $KMnO_4$ (1 M) with the formation of MnO_2?
    3. At pH 14.00, will water be oxidized if you are trying to form MnO_2 from MnO_4^{2-} via the reactio $2MnO_4^{2-}(aq) + 2H_2O(l) \rightarrow 2MnO_2(s) + O_2(g) + 4OH^-(aq)$?

18. Complexing agents can bind to metals and result in the net stabilization of the complexed species. What is the net thermodynamic stabilization energy that results from using CN^- as a complexing agent for Mn^{3+}/Mn^{2+}?

    $Mn^{3+}(aq) + e^- \rightarrow Mn^{2+}(aq)$; $E°$ = +1.51 V

    $Mn(CN)_6^{3-}(aq) + e^- \rightarrow Mn(CN)_6^{4-}(aq)$; $E°$ = -0.24V

19. You have constructed a cell with zinc and lead amalgam electrodes described by the cell diagram $Zn(Hg)(s)|Zn(NO_3)_2(aq)‖Pb(NO_3)_2(aq)|Pb(Hg)(s)$. If you vary the concentration of $Zn(NO_3)_2$ and measure the potential at different concentrations, you obtain the following data:

$Zn(NO_3)_2$ (M)	E_{cell} (V)
0.0005	0.7398
0.002	0.7221
0.01	0.7014

1. Write the half-reactions that occur in this cell.
2. What is the overall redox reaction?
3. What is $E°_{cell}$? What is $\Delta G°$ for the overall reaction?
4. What is the equilibrium constant for this redox reaction?

20. Hydrogen gas reduces Ni^{2+} according to the following reaction: $Ni^{2+}(aq) + H_2(g) \rightarrow Ni(s) + 2H^+(aq)$; $E°_{cell} = -0.25$ V; $\Delta H = 54$ kJ/mol.

    1. What is K for this redox reaction?
    2. Is this reaction likely to occur?
    3. What conditions can be changed to increase the likelihood that the reaction will occur as written?
    4. Is the reaction more likely to occur at higher or lower pH?

21. The silver–silver bromide electrode has a standard potential of 0.07133 V. What is K_{sp} of AgBr?

3. $6e^-$; $E°_{cell} = 1.813$ V; the reaction is spontaneous; $\Delta G° = -525$ kJ/mol Al.

Answers

2.
4.
1.
5.
6.
7.
8.
9.
10.
11.
12.
13.
14.
15. yes; $E° = 0.40$ V
16.
17. 1. yes; $E° = 0.45$ V
    2. 0.194 V
    3. yes; $E° = 0.20$ V
18.
19.
20.
21.

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Chapter 17.5: Commercial Galvanic Cells

Template:HideTOC

Learning Objective

To learn how commercial galvanic cells work.

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Because galvanic cells can be self-contained and portable, they can be used as batteries and fuel cells. A battery (storage cell) is a galvanic cell (or a series of galvanic cells) that contains all the reactants needed to produce electricity. In contrast, a fuel cell is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. In this section, we describe the chemistry behind some of the more common types of batteries and fuel cells.

Batteries

There are two basic kinds of batteries: *disposable*, or *primary*, batteries, in which the electrode reactions are effectively irreversible and which cannot be recharged; and *rechargeable*, or *secondary*, batteries, which form an insoluble product that adheres to the electrodes. These batteries can be recharged by applying an electrical potential in the reverse direction. The recharging process temporarily converts a rechargeable battery from a galvanic cell to an electrolytic cell.

Batteries are cleverly engineered devices that are based on the same fundamental laws as galvanic cells. The major difference between batteries and the galvanic cells we have previously described is that commercial batteries use solids or pastes rather than solutions as reactants to maximize the electrical output per unit mass. The use of highly concentrated or solid reactants has another beneficial effect: the concentrations of the reactants and the products do not change greatly as the battery is discharged; consequently, the output voltage remains remarkably constant during the discharge process. This behavior is in contrast to that of the Zn/Cu cell, whose output decreases logarithmically as the reaction proceeds (Figure 17.4.3). When a battery consists of more than one galvanic cell, the cells are usually connected in series—that is, with the positive (+) terminal of one cell connected to the negative (−) terminal of the next, and so forth. The overall voltage of the battery is therefore the sum of the voltages of the individual cells.

Leclanché Dry Cell

The dry cell, by far the most common type of battery, is used in flashlights, electronic devices such as the Walkman and Game Boy, and many other devices. Although the dry cell was patented in 1866 by the French chemist Georges Leclanché and more than 5 billion such cells are sold every year, the details of its electrode chemistry are still not completely understood. In spite of its name, the Leclanché dry cell is actually a “wet cell”: the electrolyte is an acidic water-based paste containing MnO_2, NH_4Cl, $ZnCl_2$, graphite, and starch (part (a) in Figure 17.5.1). The half-reactions at the anode and the cathode can be summarized as follows:

$$cathode: \; 2MnO_2(s) + 2NH_4^+(aq) + 2e^- \rightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$$

$$anode: \; Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

The Zn^{2+} ions formed by the oxidation of Zn(s) at the anode react with NH_3 formed at the cathode and Cl^- ions present in solution, so the overall cell reaction is as follows:

$$overall: \; 2MnO_2(s) + 2NH_4Cl(aq) + Zn(s) \rightarrow Mn_2O_3(s) + Zn(NH_3)_2Cl_2(s) + H_2O(l)$$

The dry cell produces about 1.55 V and is inexpensive to manufacture. It is not, however, very efficient in producing electrical energy because only the relatively small fraction of the MnO_2 that is near the cathode is actually reduced and only a small fraction of the zinc cathode is actually consumed as the cell discharges. In addition, dry cells have a limited shelf life because the Zn anode reacts spontaneously with NH_4Cl in the electrolyte, causing the case to corrode and allowing the contents to leak out.

The alkaline battery is essentially a Leclanché cell adapted to operate under alkaline, or basic, conditions. The half-reactions that occur in an alkaline battery are as follows:

$$cathode: \ 2MnO_2(s) + H_2O(l) + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq)$$

$$anode: \ Zn(s) + 2OH^-(aq) \rightarrow ZnO(S) + H_2O(l) + 2e^-$$

$$overall: \ 2MnO_2(s) + Zn(s) \rightarrow Mn_2O_3(s) + ZnO(s)$$

This battery also produces about 1.5 V, but it has a longer shelf life and more constant output voltage as the cell is discharged than the Leclanché dry cell. Although the alkaline battery is more expensive to produce than the Leclanché dry cell, the improved performance makes this battery more cost-effective.

Button Batteries

Although some of the small *button* batteries used to power watches, calculators, and cameras are miniature alkaline cells, most are based on a completely different chemistry. In these batteries, the anode is a zinc–mercury amalgam rather than pure zinc, and the cathode uses either HgO or Ag_2O as the oxidant rather than MnO_2 (part (b) in Figure 17.5.1). The cathode and overall reactions and cell output for these two types of button batteries are as follows:

$$cathode\,(Hg): \ HgO(s) + H_2O(l) + 2e^- \rightarrow Hg(l) + 2OH^-(aq)$$

$$overall\,(Hg): \ HgO(s) + Zn(s) \rightarrow Hg(l) + ZnO(s) \quad E_{cell} = 1.35\ V$$

$$cathode\,(Ag): \ Ag_2O(s) + H_2O(l) + 2e^- \rightarrow 2Ag(s) + 2OH^-(aq)$$

$$overall\,(Ag): \ Ag_2O(s) + Zn(s) \rightarrow 2Ag(s) + ZnO(s) \quad E_{cell} = 1.6\ V$$

The major advantages of the mercury and silver cells are their reliability and their high output-to-mass ratio. These factors make them ideal for applications where small size is crucial, as in cameras and hearing aids. The disadvantages are the expense and the environmental problems caused by the disposal of heavy metals, such as Hg and Ag.

Lithium–Iodine Battery

None of the batteries described above is actually "dry." They all contain small amounts of liquid water, which adds significant mass and causes potential corrosion problems. Consequently, substantial effort has been expended to develop water-free batteries.

One of the few commercially successful water-free batteries is the lithium–iodine battery The anode is lithium metal, and the cathode is a solid complex of I_2. Separating them is a layer of solid LiI, which acts as the electrolyte by allowing the diffusion of Li^+ ions. The electrode reactions are as follows:

$$cathode: \ I_2(s) + 2e^- \rightarrow 2I^-(LiI)$$

$$anode: \ 2Li(s) \rightarrow 2Li^+(LiI) + 2e^-$$

$$overall: \ 2Li(s) + I_2(s) \rightarrow 2LiI(s) \quad E_{cell} = 3.5\ V$$

As shown in part (c) in Figure 17.5.1, a typical lithium–iodine battery consists of two cells separated by a nickel metal mesh that collects charge from the anode. Because of the high internal resistance caused by the solid electrolyte, only a low current can be drawn. Nonetheless, such batteries have proven to be long-lived (up to 10 yr) and reliable. They are therefore used in applications where frequent replacement is difficult or undesirable, such as in cardiac pacemakers and other medical implants and in computers for memory protection. These batteries are also used in security transmitters and smoke alarms. Other batteries based on lithium anodes and solid electrolytes are under development, using TiS_2, for example, for the cathode.



Cardiac pacemaker. *An x-ray of a patient showing the location and size of a pacemaker powered by a lithium–iodine battery.*

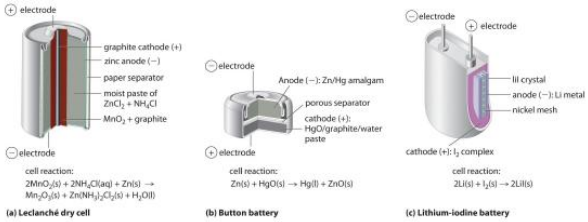


Figure 17.5.1 Three Kinds of Primary (Nonrechargeable) Batteries *(a) A Leclanché dry cell is actually a "wet cell," in which the electrolyte is an acidic water-based paste containing MnO_2, NH_4Cl, $ZnCl_2$, graphite, and starch. Though inexpensive to manufacture, the cell is not very efficient in producing electrical energy and has a limited shelf life. (b) In a button battery, the anode is a zinc–mercury amalgam, and the cathode can be either HgO (shown here) or Ag_2O as the oxidant. Button batteries are reliable and have a high output-to-mass ratio, which allows them to be used in applications such as calculators and watches, where their small size is crucial. (c) A lithium–iodine battery consists of two cells separated by a metallic nickel mesh that collects charge from the anodes. The anode is lithium metal, and the cathode is a solid complex of I_2. The electrolyte is a layer of solid LiI that allows Li^+ ions to diffuse from the cathode to the anode. Although this type of battery produces only a relatively small current, it is highly reliable and long-lived.*

Dry cells, button batteries, and lithium–iodine batteries are disposable and cannot be recharged once they are discharged. Rechargeable batteries, in contrast, offer significant economic and environmental advantages because they can be recharged and discharged numerous times. As a result, manufacturing and disposal costs drop dramatically for a given number of hours of battery usage. Two common rechargeable batteries are the nickel–cadmium battery and the lead–acid battery, which we describe next.

Nickel–Cadmium (NiCad) Battery

The nickel–cadmium, or *NiCad*, battery is used in small electrical appliances and devices like drills, portable vacuum cleaners, and AM/FM digital tuners. It is a water-based cell with a cadmium anode and a highly oxidized nickel cathode that is usually described as the nickel(III) oxo-hydroxide, NiO(OH). As shown in Figure 17.5.2, the design maximizes the surface area of the electrodes and minimizes the distance between them, which decreases internal resistance and makes a rather high discharge current possible.



Figure 17.5.2 The Nickel–Cadmium (NiCad) Battery, a Rechargeable Battery *NiCad batteries contain a cadmium anode and a highly oxidized nickel cathode. This design maximizes the surface area of the electrodes and minimizes the distance between them, which gives the battery both a high discharge current and a high capacity.*

The electrode reactions during the discharge of a NiCad battery are as follows:

$$cathode: \ 2NiO(OH)(s) + 2H_2O(l) + 2e^- \rightarrow 2Ni(OH)_2(s) + 2OH^-(aq)$$

$$anode:\ Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$$

$$overall:\ Cd(s) + 2NiO(OH)(s) + 2H_2O(l) \rightarrow Cd(OH)_2(s) + 2Ni(OH)_2(s) \quad E_{cell} = 1.4\ V$$

Because the products of the discharge half-reactions are solids that adhere to the electrodes [$Cd(OH)_2$ and $2Ni(OH)_2$], the overall reaction is readily reversed when the cell is recharged. Although NiCad cells are lightweight, rechargeable, and high capacity, they have certain disadvantages. For example, they tend to lose capacity quickly if not allowed to discharge fully before recharging, they do not store well for long periods when fully charged, and they present significant environmental and disposal problems because of the toxicity of cadmium.

A variation on the NiCad battery is the nickel–metal hydride battery (NiMH) used in hybrid automobiles, wireless communication devices, and mobile computing. The overall chemical equation for this type of battery is as follows:

\(NiO\left (OH \right)\left (s \right)+MH \rightarrow Ni\left (OH \right)_{2}\left (s \right) + M\left (s \right))

The NiMH battery has a 30%–40% improvement in capacity over the NiCad battery; it is more environmentally friendly so storage, transportation, and disposal are not subject to environmental control; and it is not as sensitive to recharging memory. It is, however, subject to a 50% greater self-discharge rate, a limited service life, and higher maintenance, and it is more expensive than the NiCad battery.

Lead–Acid (Lead Storage) Battery

The lead–acid battery is used to provide the starting power in virtually every automobile and marine engine on the market. Marine and car batteries typically consist of multiple cells connected in series. The total voltage generated by the battery is the potential per cell ($E°_{cell}$) times the number of cells. As shown in Figure 17.5.3, the anode of each cell in a lead storage battery is a plate or grid of spongy lead metal, and the cathode is a similar grid containing powdered lead dioxide (PbO_2). The electrolyte is usually an approximately 37% solution (by mass) of sulfuric acid in water, with a density of 1.28 g/mL (about 4.5 M H_2SO_4). Because the redox active species are solids, there is no need to separate the electrodes. The electrode reactions in each cell during discharge are as follows:

$$cathode:\ 2PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l) \quad E_{cathode} = 1.685\ V$$

$$anode:\ PbS(s) + HSO_4^-(aq) \rightarrow PbSO_4(s) + H^+(aq) + 2e^- \quad E_{anode} = -0.356\ V$$

$$overall:\ 2PbO_2(s) + 2HSO_4^-(aq) + 2H^+(aq) \rightarrow 2bSO_4(s) + 2H_2O(l) \quad E_{cell} = 2.041\ V$$

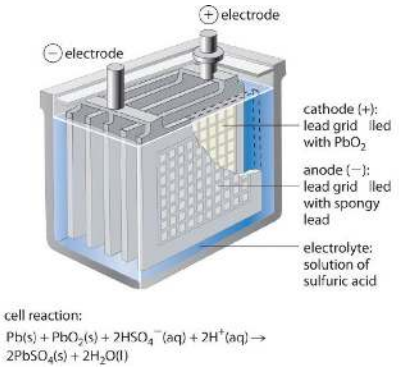


Figure 17.5.3 One Cell of a Lead–Acid Battery *The anodes in each cell of a rechargeable battery are plates or grids of lead containing spongy lead metal, while the cathodes are similar grids containing powdered lead dioxide (PbO_2). The electrolyte is an aqueous solution of sulfuric acid. The value of E° for such a cell is about 2 V. Connecting three such cells in series produces a 6 V battery, whereas a typical 12 V car battery contains six cells in series. When treated properly, this type of high-capacity battery can be discharged and recharged many times over.*

As the cell is discharged, a powder of $PbSO_4$ forms on the electrodes. Moreover, sulfuric acid is consumed and water is produced, decreasing the density of the electrolyte and providing a convenient way of monitoring the status of a battery by simply measuring the density of the electrolyte.

When an external voltage in excess of 2.04 V per cell is applied to a lead–acid battery, the electrode reactions reverse, and $PbSO_4$ is converted back to metallic lead and PbO_2. If the battery is recharged too vigorously, however, electrolysis of water can occur, resulting in the evolution of potentially explosive hydrogen gas. (For more information on electrolysis, see Section 17.7.) The gas bubbles formed in this way can dislodge some of the $PbSO_4$ or PbO_2 particles from the grids, allowing them to fall to the bottom of the cell, where they can build up and cause an internal short circuit. Thus the recharging process must be carefully monitored to optimize the life of the battery. With proper care, however, a lead–acid battery can be discharged and recharged thousands of times. In automobiles, the alternator supplies the electric current that causes the discharge reaction to reverse.



Source: Photo courtesy of Mitchclanky2008, http://www.flickr.com/photos/25597837@N05/2422765479/.

Fuel Cells

A fuel cell is a galvanic cell that requires a constant external supply of reactants because the products of the reaction are continuously removed. Unlike a battery, it does not store chemical or electrical energy; a fuel cell allows electrical energy to be extracted directly from a chemical reaction. In principle, this should be a more efficient process than, for example, burning the fuel to drive an internal combustion engine that turns a generator, which is typically less than 40% efficient, and in fact, the efficiency of a fuel cell is generally between 40% and 60%. Unfortunately, significant cost and reliability problems have hindered the wide-scale adoption of fuel cells. In practice, their use has been restricted to applications in which mass may be a significant cost factor, such as US manned space vehicles.

These space vehicles use a hydrogen/oxygen fuel cell that requires a continuous input of $H_2(g)$ and $O_2(g)$, as illustrated in Figure 17.5.4 . The electrode reactions are as follows:

$$cathode: \ O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O(g)$$

$$anode: \ 2H_2(g) \rightarrow 4H^+ + 4e^-$$

$$overall: \ 2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

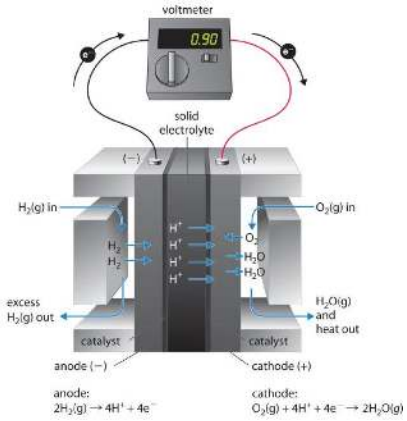


Figure 17.5.4 A Hydrogen Fuel Cell Produces Electrical Energy Directly from a Chemical Reaction *Hydrogen is oxidized to protons at the anode, and the electrons are transferred through an external circuit to the cathode, where oxygen is reduced and combines with H^+ to form water. A solid electrolyte allows the protons to diffuse from the anode to the cathode. Although fuel cells are an essentially pollution-free means of obtaining electrical energy, their expense and technological complexity have thus far limited their applications.*

The overall reaction represents an essentially pollution-free conversion of hydrogen and oxygen to water, which in space vehicles is then collected and used. Although this type of fuel cell should produce 1.23 V under standard conditions, in practice the device achieves only about 0.9 V. One of the major barriers to achieving greater efficiency is the fact that the four-electron reduction of $O_2(g)$ at the cathode is intrinsically rather slow, which limits current that can be achieved. All major automobile manufacturers have major research programs involving fuel cells: one of the most important goals is the development of a better catalyst for the reduction of O_2.

Summary

A **battery** is a contained unit that produces electricity, whereas a **fuel cell** is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. One type of battery is the **Leclanché dry cell**, which contains an electrolyte in an acidic water-based paste. This battery is called an **alkaline battery** when adapted to operate under alkaline conditions. Button batteries have a high output-to-mass ratio; **lithium–iodine batteries** consist of a solid electrolyte; the **nickel–cadmium** (NiCad) battery is rechargeable; and the **lead–acid battery**, which is also rechargeable, does not require the electrodes to be in separate compartments. A fuel cell requires an external supply of reactants as the products of the reaction are continuously removed. In a fuel cell, energy is not stored; electrical energy is provided by a chemical reaction.

Key Takeaway

- Commercial batteries are galvanic cells that use solids or pastes as reactants to maximize the electrical output per unit mass.

Conceptual Problems

1. What advantage is there to using an alkaline battery rather than a Leclanché dry cell?
2. Why does the density of the fluid in lead–acid batteries drop when the battery is discharged?
3. What type of battery would you use for each application and why?
   a. powering an electric motor scooter
   b. a backup battery for a smartphone
   c. powering an iPod
4. Why are galvanic cells used as batteries and fuel cells? What is the difference between a battery and a fuel cell? What is the advantage to using highly concentrated or solid reactants in a battery?

Answer

3. a. lead storage battery
   b. lithium–iodine battery
   c. NiCad, NiMH, or lithium ion battery (rechargeable)
4.

Numerical Problem

1. This reaction is characteristic of a lead storage battery:
   $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$
   If you have a battery with an electrolyte that has a density of 1.15 g/cm^3 and contains 30.0% sulfuric acid by mass, is the potential greater than or less than that of the standard cell?

Answer

1. $[H_2SO_4] = 3.52$ M; $E > E°$

Contributors

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Chapter 17.6: Corrosion

Learning Objective

- To understand the process of corrosion.

CorrosionA galvanic process by which metals deteriorate through oxidation—usually but not always to their oxides. is a galvanic process by which metals deteriorate through oxidation—usually but not always to their oxides. For example, when exposed to air, iron rusts, silver tarnishes, and copper and brass acquire a bluish-green surface called a *patina*. Of the various metals subject to corrosion, iron is by far the most important commercially. An estimated $100 billion per year is spent in the United States alone to replace iron-containing objects destroyed by corrosion. Consequently, the development of methods for protecting metal surfaces from corrosion constitutes a very active area of industrial research. In this section, we describe some of the chemical and electrochemical processes responsible for corrosion. We also examine the chemical basis for some common methods for preventing corrosion and treating corroded metals.

Note the Pattern

Corrosion is a galvanic process.

Under ambient conditions, the oxidation of most metals is thermodynamically spontaneous, with the notable exception of gold and platinum. Hence it is actually somewhat surprising that any metals are useful at all in Earth's moist, oxygen-rich atmosphere. Some metals, however, are resistant to corrosion for kinetic reasons. For example, aluminum in soft-drink cans and airplanes is protected by a thin coating of metal oxide that forms on the surface of the metal and acts as an impenetrable barrier that prevents further destruction. Aluminum cans also have a thin plastic layer to prevent reaction of the oxide with acid in the soft drink. Chromium, magnesium, and nickel also form protective oxide films. Stainless steels are remarkably resistant to corrosion because they usually contain a significant proportion of chromium, nickel, or both.

In contrast to these metals, when iron corrodes, it forms a red-brown hydrated metal oxide ($Fe_2O_3{\cdot}xH_2O$), commonly known as *rust*, that does not provide a tight protective film (Figure 17.6.1). Instead, the rust continually flakes off to expose a fresh metal surface vulnerable to reaction with oxygen and water. Because both oxygen and water are required for rust to form, an iron nail immersed in deoxygenated water will not rust—even over a period of several weeks. Similarly, a nail immersed in an organic solvent such as kerosene or mineral oil saturated with oxygen will not rust because of the absence of water.

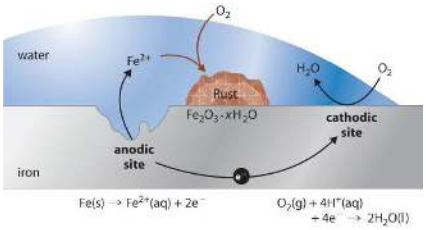


Figure 17.6.1 Rust, the Result of Corrosion of Metallic Iron Iron is oxidized to Fe^{2+}(aq) at an anodic site on the surface of the iron, which is often an impurity or a lattice defect. Oxygen is reduced to water at a different site on the surface of the iron, which acts as the cathode. Electrons are transferred from the anode to the cathode through the electrically conductive metal. Water is a solvent for the Fe^{2+} that is produced initially and acts as a salt bridge. Rust ($Fe_2O_3{\cdot}xH_2O$) is formed by the subsequent oxidation of Fe^{2+} by atmospheric oxygen.

In the corrosion process, iron metal acts as the anode in a galvanic cell and is oxidized to Fe^{2+}; oxygen is reduced to water at the cathode. The relevant reactions are as follows:

$$cathode:\ O_2\,(g) + 4H^+\,(aq) + 4e^- \rightarrow 2H_2O\,(l) \quad E^o = 1.23\ V$$

$$anode:\ Fe\,(s) \rightarrow Fe^{2+}\,(aq) + 2e^- \quad E^o = -0.24\ V$$

$$overall:\ 2Fe\,(s) + O_2\,(g) + 4H^+\,(aq) \rightarrow 2Fe^{2+}\,(aq) + 2H_2O\,(l) \quad E^o = 1.68\ V$$

The Fe^{2+} ions produced in the initial reaction are then oxidized by atmospheric oxygen to produce the insoluble hydrated oxide containing Fe^{3+}, as represented in the following equation:

$$4Fe^{2+}\,(aq) + O_2\,(g) + (2 + 4x)\,H_2O\,(l) \rightarrow 2Fe_2O_3 \cdot xH_2O + 4H^+$$

The sign and magnitude of $E°$ for the corrosion process (Equation 17.6.3) indicate that there is a strong driving force for the oxidation of iron by O_2 under standard conditions (1 M H^+). Under neutral conditions, the driving force is somewhat less but still appreciable (E = 1.25 V at pH 7.0). Normally, the reaction of atmospheric CO_2 with water to form H^+ and HCO_3^- provides a low enough pH to enhance the reaction rate, as does acid rain. Automobile manufacturers spend a great deal of time and money developing paints that adhere tightly to the car's metal surface to prevent oxygenated water, acid, and salt from coming into contact with the underlying metal. Unfortunately, even the best paint is subject to scratching or denting, and the electrochemical nature of the corrosion process means that two scratches relatively remote from each other can operate together as anode and cathode, leading to sudden mechanical failure (Figure 17.6.2).

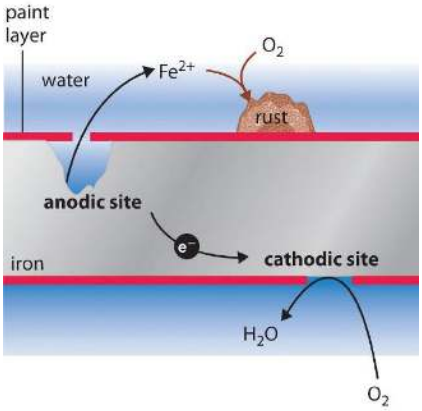


Figure 17.6.2 Small Scratches in a Protective Paint Coating Can Lead to the Rapid Corrosion of Iron Holes in a protective coating allow oxygen to be reduced at the surface with the greater exposure to air (the cathode), while metallic iron is oxidized to Fe^{2+}(aq) at the less exposed site (the anode). Rust is formed when Fe^{2+}(aq) diffuses to a location where it can react with atmospheric oxygen, which is often remote from the anode. The electrochemical interaction between cathodic and anodic sites can cause a large pit to form *under* a painted surface, eventually resulting in sudden failure with little visible warning that corrosion has occurred.

One of the most common techniques used to prevent the corrosion of iron is applying a protective coating of another metal that is more difficult to oxidize. Faucets and some external parts of automobiles, for example, are often coated with a thin layer of chromium using an electrolytic process that will be discussed in Section 19.7. With the increased use of polymeric materials in cars, however, the use of chrome-plated steel has diminished in recent years. Similarly, the "tin cans" that hold soups and other foods are actually made of steel coated with a thin layer of tin. Neither chromium nor tin is intrinsically resistant to corrosion, but both form protective oxide coatings.

As with a protective paint, scratching a protective metal coating will allow corrosion to occur. In this case, however, the presence of the second metal can actually increase the rat that Fe is more easily oxidized than Sn. As a result, the more corrosion-resistant metal (in this case, tin) accelerates the corrosion of iron by acting as the cathode and providing a large surface area for the reduction of oxygen (Figure 17.6.3). This process is seen in some older homes where copper and iron pipes have been directly connected to each other. The less easily oxidized copper acts as the cathode, causing iron to dissolve rapidly near the connection and occasionally resulting in a catastrophic plumbing failure.

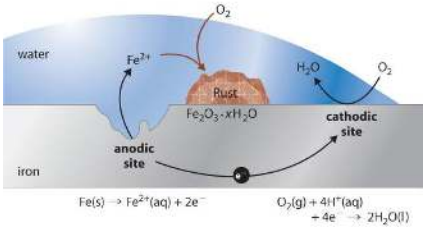


Figure 17.6.3 Galvanic Corrosion If iron is in contact with a more corrosion-resistant metal such as tin, copper, or lead, the other metal can act as a large cathode that greatly increases the rate of reduction of oxygen. Because the reduction of oxygen is coupled to the oxidation of iron, this can result in a dramatic increase in the rate at which iron is oxidized at the anode. Galvanic corrosion is likely to occur whenever two dissimilar metals are connected directly, allowing electrons to be transferred from one to the other.

One way to avoid these problems is to use a more easily oxidized metal to protect iron from corrosion. In this approach, called *cathodic protection*, a more reactive metal such as Zn ($E°$ = −0.76 V for $Zn^{2+} + 2e^- \rightarrow Zn$) becomes the anode, and iron becomes the cathode. This prevents oxidation of the iron and protects the iron object from corrosion. The reactions that occur under these conditions are as follows:

$$cathode: \ O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$$

$$anode: \ Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \quad E° = -0.24\ V$$

$$overall: \ 2Zn(s) + O_2(g) + 4H^+(aq) \rightarrow 2Zn^{2+}(aq) + 2H_2O(l)$$

The more reactive metal reacts with oxygen and will eventually dissolve, “sacrificing” itself to protect the iron object. Cathodic protection is the principle underlying *galvanized steel*, which is steel protected by a thin layer of zinc. Galvanized steel is used in objects ranging from nails to garbage cans. In a similar strategy, sacrificial electrodesAn electrode containing a more reactive metal that is attached to a metal object to inhibit that object’s corrosion. using magnesium, for example, are used to protect underground tanks or pipes (Figure 17.6.4). Replacing the sacrificial electrodes is more cost-effective than replacing the iron objects they are protecting.

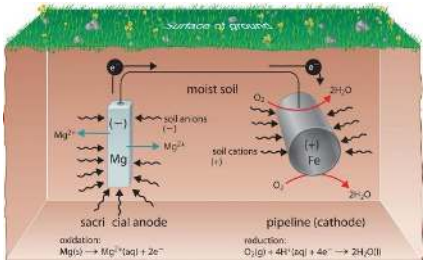


Figure 17.6.4 The Use of a Sacrificial Electrode to Protect Against Corrosion Connecting a magnesium rod to an underground steel pipeline protects the pipeline from corrosion. Because magnesium ($E°$ = −2.37 V) is much more easily oxidized than iron ($E°$ = −0.45 V), the Mg rod acts as the anode in a galvanic cell. The pipeline is therefore forced to act as the cathode at which oxygen is reduced. The soil between the anode and the cathode acts as a salt bridge that completes the electrical circuit and maintains electrical neutrality. As Mg(s) is oxidized to Mg^{2+} at the anode, anions in the soil, such as nitrate, diffuse toward the anode to neutralize the positive charge. Simultaneously, cations in the soil, such as H^+ or NH_4^+, diffuse toward the cathode, where they replenish the protons that are consumed as oxygen is reduced. A similar strategy uses many miles of somewhat less reactive zinc wire to protect the Alaska oil pipeline.

Example 17.6.1

Suppose an old wooden sailboat, held together with iron screws, has a bronze propeller (recall that bronze is an alloy of copper containing about 7%–10% tin).

1. If the boat is immersed in seawater, what corrosion reaction will occur? What is $E°_{cell}$?
2. How could you prevent this corrosion from occurring?

Given: identity of metals

Asked for: corrosion reaction, $E°_{cell}$, and preventive measures

Strategy:

A Write the reactions that occur at the anode and the cathode. From these, write the overall cell reaction and calculate $E°_{cell}$.

B Based on the relative redox activity of various substances, suggest possible preventive measures.

Solution:

1. **A** According to Table 17.3.1, both copper and tin are less active metals than iron (i.e., they have higher positive values of $E°$ than iron). Thus if tin or copper is brought into electrical contact by seawater with iron in the presence of oxygen, corrosion will occur. We therefore anticipate that the bronze propeller will act as the cathode at which O_2 is reduced, and the iron screws will act as anodes at which iron dissolves:

$$cathode: \ O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l) \quad E°_{cathode} = 1.23\ V$$

$$anode: \ Fe(s) \rightarrow Fe^{2+}(aq) + 2e^- \quad E°_{anode} = -0.45\ V$$

$$overall: \ 2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l) \quad E°_{cell} = 1.68\ V$$

   Over time, the iron screws will dissolve, and the boat will fall apart.

2. **B** Possible ways to prevent corrosion, in order of decreasing cost and inconvenience, are as follows: disassembling the boat and rebuilding it with bronze screws; removing the boat from the water and storing it in a dry place; or attaching an inexpensive piece of zinc metal to the propeller shaft to act as a sacrificial electrode and replacing it once or twice a year. Because zinc is a more active metal than iron, it will act as the sacrificial anode in the electrochemical cell and dissolve (Equation 17.6.6).

Exercise

Suppose the water pipes leading into your house are made of lead, while the rest of the plumbing in your house is iron. To eliminate the possibility of lead poisoning, you call a plumber to replace the lead pipes. He quotes you a very low price if he can use up his existing supply of copper pipe to do the job.

1. Do you accept his proposal?
2. What else should you have the plumber do while at your home?

Answer:

1. Not unless you plan to sell the house very soon because the Cu/Fe pipe joints will lead to rapid corrosion.
2. Any existing Pb/Fe joints should be examined carefully for corrosion of the iron pipes due to the Pb–Fe junction; the less active Pb will have served as the cathode for the reduction of O_2, promoting oxidation of the more active Fe nearby.

Summary

The deterioration of metals through oxidation is a galvanic process called **corrosion**. Protective coatings consist of a second metal that is more difficult to oxidize than the metal being protected. Alternatively, a more easily oxidized metal can be applied to a metal surface, thus providing cathodic protection of the surface. A thin layer of zinc protects galvanized steel. **Sacrificial electrodes** can also be attached to an object to protect it.

Key Takeaway

- Corrosion is a galvanic process that can be prevented using cathodic protection.

Conceptual Problems

1. Do you expect a bent nail to corrode more or less rapidly than a straight nail? Why?
2. What does it mean when a metal is described as being coated with a sacrificial layer? Is this different from galvanic protection?
3. Why is it important for automobile manufacturers to apply paint to the metal surface of a car? Why is this process particularly important for vehicles in northern climates, where salt is used on icy roads?
3. Paint keeps oxygen and water from coming into direct contact with the metal, which prevents corrosion. Paint is more necessary

Answer

2. because salt is an electrolyte that increases the conductivity of water and facilitates the flow of electric current between anodic
1. and cathodic sites.

Contributors

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Chapter 17.7: Electrolysis

Learning Objective

- To understand electrolysis and describe it quantitatively.

In this chapter, we have described various galvanic cells in which a spontaneous chemical reaction is used to generate electrical energy. In an electrolytic cell, however, the opposite process, called electrolysisAn electrochemical process in which an external voltage is applied to an electrolytic cell to drive a nonspontaneous reaction., occurs: an external voltage is applied to drive a nonspontaneous reaction (Figure 17.1.1). In this section, we look at how electrolytic cells are constructed and explore some of their many commercial applications.

Note the Pattern

In an electrolytic cell, an external voltage is applied to drive a nonspontaneous reaction.

Electrolytic Cells

If we construct an electrochemical cell in which one electrode is copper metal immersed in a 1 M Cu^{2+} solution and the other electrode is cadmium metal immersed in a 1 M Cd^{2+} solution and then close the circuit, the potential difference between the two compartments will be 0.74 V. The cadmium electrode will begin to dissolve (Cd is oxidized to Cd^{2+}) and is the anode, while metallic copper will be deposited on the copper electrode (Cu^{2+} is reduced to Cu), which is the cathode (part (a) in Figure 17.7.1). The overall reaction is as follows:

$$Cd\,(s) + Cu^{2+}\,(aq) \rightarrow Cu\,(s) + Cd^{2+}\,(aq)$$

This reaction is thermodynamically spntaneous as written (

$$\Delta G^o = nFE^o_{cell} = \left(2\ \cancel{mol\ e^-}\right)\left[96,486\ J/\left(\cancel{V}\cdot\cancel{mol}\right)\right]\left(0.74\ \cancel{V}\right) = -140\ kJ/mol$$

In this direction, the system is acting as a galvanic cell.

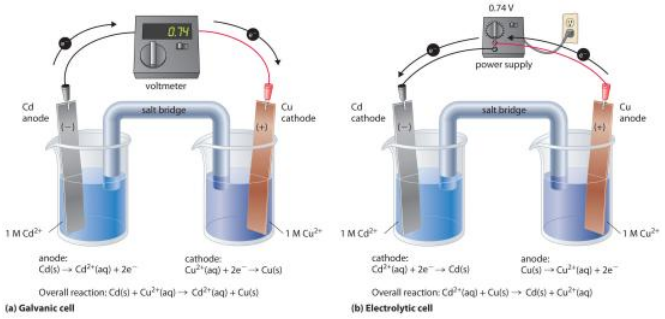


Figure 17.7.1 An Applied Voltage Can Reverse the Flow of Electrons in a Galvanic Cd/Cu Cell (a) When compartments that contain a Cd electrode immersed in 1 M Cd^{2+}(aq) and a Cu electrode immersed in 1 M Cu^{2+}(aq) are connected to create a galvanic cell, Cd(s) is spontaneously oxidized to Cd^{2+}(aq) at the anode, and Cu^{2+}(aq) is spontaneously reduced to Cu(s) at the cathode. The potential of the galvanic cell is 0.74 V. (b) Applying an external potential greater than 0.74 V in the reverse direction forces electrons to flow from the Cu electrode [which is now the anode, at which metallic Cu(s) is oxidized to Cu^{2+}(aq)] and into the Cd electrode [which is now the cathode, at which Cd^{2+}(aq) is reduced to Cd(s)]. The anode in an electrolytic cell is *positive* because electrons are flowing from it, whereas the cathode is *negative* because electrons are flowing into it.

The reverse reaction, the reduction of Cd^{2+} by Cu, is thermodynamically nonspontaneous and will occur only with an *input* of 140 kJ. We can force the reaction to proceed in the reverse direction by applying an electrical potential greater than 0.74 V from an external power supply. The applied voltage forces electrons through the circuit in the reverse direction, converting a galvanic cell to an electrolytic cell. Thus the copper electrode is now the anode (Cu is oxidized), and the cadmium electrode is now the cathode (Cd^{2+} is reduced) (part (b) in Figure 17.7.1). The signs of the cathode and the anode have switched to reflect the flow of electrons in the circuit. The half-reactions that occur at the cathode and the anode are as follows:

$$cathode:\ Cd^{2+}\,(aq) + 2e^- \rightarrow Cd\,(s) \quad E^o_{cathode} = -0.40\ V$$

$$anode: \ Cu(s) \rightarrow Cu^{2+}(aq) + 2e^- \quad E^o_{anode} = 0.34\ V$$

$$overall: \ Cd^{2+}(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + Cd(s) \quad E^o_{cell} = -0.74\ V$$

Because $E°_{cell} < 0$, the overall reaction—the reduction of Cd^{2+} by Cu—clearly cannot occur spontaneously and proceeds only when sufficient electrical energy is applied. The differences between galvanic and electrolytic cells are summarized in Table 17.7.1.

Table 17.7.1 Comparison of Galvanic and Electrolytic Cells

Property	Galvanic Cell	Electrolytic Cell
ΔG	< 0	> 0
E_{cell}	> 0	< 0
Electrode Process		
anode	oxidation	oxidation
cathode	reduction	reduction
Sign of Electrode		
anode	−	+
cathode	+	−

Electrolytic Reactions

At sufficiently high temperatures, ionic solids melt to form liquids that conduct electricity extremely well due to the high concentrations of ions. If two inert electrodes are inserted into molten NaCl, for example, and an electrical potential is applied, Cl^- is oxidized at the anode, and Na^+ is reduced at the cathode. The overall reaction is as follows:

$$2NaCl(l) \rightarrow Na(l) + Cl_2(g)$$

This is the reverse of the formation of NaCl from its elements. The product of the reduction reaction is *liquid* sodium because the melting point of sodium metal is 97.8°C, well below that of NaCl (801°C). Approximately 20,000 tons of sodium metal are produced commercially in the United States each year by the electrolysis of molten NaCl in a *Downs cell* (Figure 17.7.2). In this specialized cell, $CaCl_2$ (melting point = 772°C) is first added to the NaCl to lower the melting point of the mixture to about 600°C, thereby lowering operating costs.

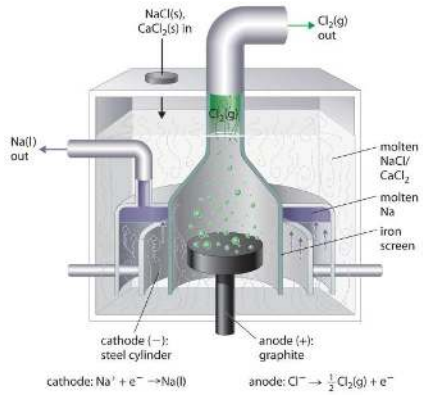


Figure 17.7.2 A Downs Cell for the Electrolysis of Molten NaCl The electrolysis of a molten mixture of NaCl and $CaCl_2$ results in the formation of elemental sodium and chlorine gas. Because sodium is a liquid under these conditions and liquid sodium is less dense than molten sodium chloride, the sodium floats to the top of the melt and is collected in concentric capped iron cylinders surrounding the cathode. Gaseous chlorine collects in the inverted cone over the anode. An iron screen separating the cathode and anode compartments ensures that the molten sodium and gaseous chlorine do not come into contact.

Similarly, in the *Hall–Heroult process* used to produce aluminum commercially, a molten mixture of about 5% aluminum oxide (Al_2O_3; melting point = 2054°C) and 95% cryolite (Na_3AlF_6; melting point = 1012°C) is electrolyzed at about 1000°C, producing molten aluminum at the cathode and CO_2 gas at the carbon anode. The overall reaction is as follows:

$$2Al_2O_3\,(l) + 3C\,(s) \rightarrow 4Al\,(l) + 3CO_2\,(g)$$

Oxide ions react with oxidized carbon at the anode, producing CO_2(g).

There are two important points to make about these two commercial processes and about the electrolysis of molten salts in general.

1. The electrode potentials for molten salts are likely to be very different from the standard cell potentials listed in Table 17.3.1 and Standard Reduction Potentials at 25°C", which are compiled for the reduction of the hydrated ions in aqueous solutions under standard conditions.
2. Using a mixed salt system means there is a possibility of competition between different electrolytic reactions. When a mixture of NaCl and $CaCl_2$ is electrolyzed, Cl^- is oxidized because it is the only anion present, but either Na^+ or Ca^{2+} can be reduced. Conversely, in the Hall–Heroult process, only one cation is present that can be reduced (Al^{3+}), but there are three species that can be oxidized: C, O^{2-}, and F^-.

In the Hall–Heroult process, C is oxidized instead of O^{2-} or F^- because oxygen and fluorine are more electronegative than carbon, which means that C is a weaker oxidant than either O_2 or F_2. Similarly, in the Downs cell, we might expect electrolysis of a NaCl/$CaCl_2$ mixture to produce calcium rather than sodium because Na is slightly less electronegative than Ca (χ = 0.93 versus 1.00, respectively), making Na easier to oxidize and, conversely, Na^+ more difficult to reduce. In fact, the reduction of Na^+ to Na is the observed reaction. In cases where the electronegativities of two species are similar, other factors, such as the formation of complex ions, become important and may determine the outcome.

Example 17.7.1

If a molten mixture of $MgCl_2$ and KBr is electrolyzed, what products will form at the cathode and the anode, respectively?

Given: identity of salts

Asked for: electrolysis products

Strategy:

A List all the possible reduction and oxidation products. Based on the electronegativity values shown in Figure 3.1.2, determine which species will be reduced and which species will be oxidized.

B Identify the products that will form at each electrode.

Solution:

A The possible reduction products are Mg and K, and the possible oxidation products are Cl_2 and Br_2. Because Mg is more electronegative than K (χ = 1.31 versus 0.82), it is likely that Mg will be reduced rather than K. Because Cl is more electronegative than Br (3.16 versus 2.96), Cl_2 is a stronger oxidant than Br_2.

B Electrolysis will therefore produce Br_2 at the anode and Mg at the cathode.

Exercise

Predict the products if a molten mixture of $AlBr_3$ and LiF is electrolyzed.

Answer: Br_2 and Al

Electrolysis can also be used to drive the thermodynamically nonspontaneous decomposition of water into its constituent elements: H_2 and O_2. However, because pure water is a very poor electrical conductor, a small amount of an ionic solute (such as H_2SO_4 or Na_2SO_4) must first be added to increase its electrical conductivity. Inserting inert electrodes into the solution and applying a voltage between them will result in the rapid evolution of bubbles of H_2 and O_2 (Figure 17.7.3). The reactions that occur are as follows:

$$cathode:\ 2H^+\,(aq) + 2e^- \rightarrow H_2\,(g) \quad E^o_{cathode} = 0\ V$$

$$anode:\ 2H_2O\,(l) \rightarrow O_2\,(g) + 4H^+\,(g) + 4e^- \quad E^o_{anode} = 1.23\ V$$

$$overall: \ 2H_2O\,(l) \rightarrow O_2\,(g) + 2H_2\,(g) \quad E^o_{cell} = -1.23\ V$$



Figure 17.7.3 The Electrolysis of Water Applying an external potential of about 1.7–1.9 V to two inert electrodes immersed in an aqueous solution of an electrolyte such as H_2SO_4 or Na_2SO_4 drives the thermodynamically nonspontaneous decomposition of water into H_2 at the cathode and O_2 at the anode.

For a system that contains an electrolyte such as Na_2SO_4, which has a negligible effect on the ionization equilibrium of liquid water, the pH of the solution will be 7.00 and $[H^+] = [OH^-] = 1.0 \times 10^{-7}$. Assuming that $P(O_2) = P(H_2) = 1$ atm, we can use the standard potentials and Equation 19.64 to calculate E for the overall reaction:

$$E_{cell} = E^o_{cell} - \left(\frac{0.0591\ V}{n}\right) log\ \left(P_{O_2}P^2_{H_2}\right)$$

$$E_{cell} = -1.23\ V - \left(\frac{0.0591\ V}{4}\right) log\ (1) = -1.23\ V$$

Thus E_{cell} is −1.23 V, which is the value of $E°_{cell}$ if the reaction is carried out in the presence of 1 M H^+ rather than at pH 7.0.

In practice, a voltage about 0.4–0.6 V greater than the calculated value is needed to electrolyze water. This added voltage, called an overvoltageThe voltage that must be applied in electrolysis in addition to the calculated (theoretical) value to overcome factors such as a high activation energy and the formation of bubbles on a surface., represents the additional driving force required to overcome barriers such as the large activation energy for the formation of a gas at a metal surface. Overvoltages are needed in all electrolytic processes, which explain why, for example, approximately 14 V must be applied to recharge the 12 V battery in your car.

In general, any metal that does *not* react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation. The *p*-block metals and most of the transition metals are in this category, but metals in high oxidation states, which form oxoanions, cannot be reduced to the metal by simple electrolysis. Active metals, such as aluminum and those of groups 1 and 2, react so readily with water that they can be prepared only by the electrolysis of molten salts. Similarly, any nonmetallic element that does not readily oxidize water to O_2 can be prepared by the electrolytic oxidation of an aqueous solution that contains an appropriate anion. In practice, among the nonmetals, only F_2 cannot be prepared using this method. Oxoanions of nonmetals in their highest oxidation states, such as NO_3^-, SO_4^{2-}, PO_4^{3-}, are usually difficult to reduce electrochemically and usually behave like spectator ions that remain in solution during electrolysis.

Note the Pattern

In general, any metal that does not react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation.

Electroplating

In a process called electroplatingA process in which a layer of a second metal is deposited on the metal electrode that acts as the cathode during electrolysis., a layer of a second metal is deposited on the metal electrode that acts as the cathode during electrolysis. Electroplating is used to enhance the appearance of metal objects and protect them from corrosion. Examples of electroplating include the chromium layer found on many bathroom fixtures or (in earlier days) on the bumpers and hubcaps of

cars, as well as the thin layer of precious metal that coats silver-plated dinnerware or jewelry. In all cases, the basic concept is the same. A schematic view of an apparatus for electroplating silverware and a photograph of a commercial electroplating cell are shown in Figure 17.7.4.

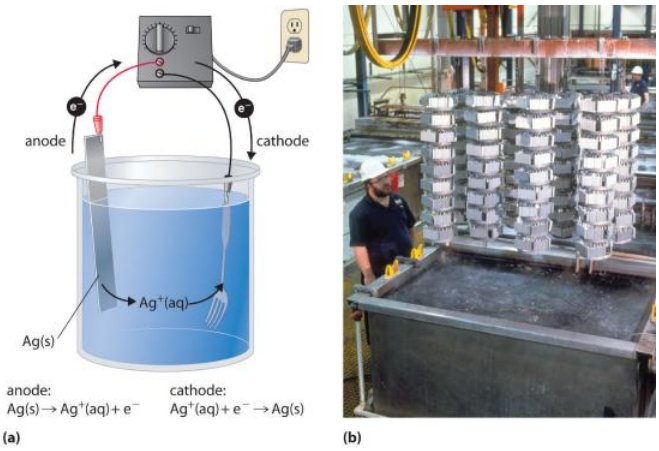


Figure 17.7.4 Electroplating (a) Electroplating uses an electrolytic cell in which the object to be plated, such as a fork, is immersed in a solution of the metal to be deposited. The object being plated acts as the cathode, on which the desired metal is deposited in a thin layer, while the anode usually consists of the metal that is being deposited (in this case, silver) that maintains the solution concentration as it dissolves. (b) In this commercial electroplating apparatus, a large number of objects can be plated simultaneously by lowering the rack into the Ag^+ solution and applying the correct potential.

The half-reactions in electroplating a fork, for example, with silver are as follows:

$$cathode\,(fork):\ Ag^+(aq) + e^- \rightarrow Ag(s) \quad E^o_{cathode} = 0.80\ V$$

$$anode\,(silverbar):\ Ag(s) \rightarrow Ag^+(aq) + e^- \quad E^o_{anode} = 0.80\ V$$

The overall reaction is the transfer of silver metal from one electrode (a silver bar acting as the anode) to another (a fork acting as the cathode). Because $E°_{cell}$ = 0 V, it takes only a small applied voltage to drive the electroplating process. In practice, various other substances may be added to the plating solution to control its electrical conductivity and regulate the concentration of free metal ions, thus ensuring a smooth, even coating.

Quantitative Considerations

If we know the stoichiometry of an electrolysis reaction, the amount of current passed, and the length of time, we can calculate the amount of material consumed or produced in a reaction. Conversely, we can use stoichiometry to determine the combination of current and time needed to produce a given amount of material.

The quantity of material that is oxidized or reduced at an electrode during an electrochemical reaction is determined by the stoichiometry of the reaction and the amount of charge that is transferred. For example, in the reaction $Ag^+(aq) + e^- \rightarrow Ag(s)$, 1 mol of electrons reduces 1 mol of Ag^+ to Ag metal. In contrast, in the reaction $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$, 1 mol of electrons reduces only 0.5 mol of Cu^{2+} to Cu metal. Recall that the charge on 1 mol of electrons is 1 faraday (1 *F*), which is equal to 96,486 C. We can therefore calculate the number of moles of electrons transferred when a known current is passed through a cell for a given period of time. The total charge (C) transferred is the product of the current (A) and the time (*t*, in seconds):

$$C = A \times t$$

The stoichiometry of the reaction and the total charge transferred enable us to calculate the amount of product formed during an electrolysis reaction or the amount of metal deposited in an electroplating process.

For example, if a current of 0.60 A passes through an aqueous solution of $CuSO_4$ for 6.0 min, the total number of coulombs of charge that passes through the cell is as follows:

$$charge = (0.60\ A)\left(6.0\ \cancel{min}\right)\left(60\ s/\cancel{min}\right) = 220 A \cdot s$$

The number of moles of electrons transferred to Cu^{2+} is therefore

$$moles\ e^- = \frac{220\ \cancel{C}}{96,486\ \cancel{C}/mol} = 2.3 \times 10^{-3}\ mol\ e^-$$

Because two electrons are required to reduce a single Cu^{2+} ion, the total number of moles of Cu produced is half the number of moles of electrons transferred, or 1.2×10^{-3} mol. This corresponds to 76 mg of Cu. In commercial electrorefining processes, much higher currents (greater than or equal to 50,000 A) are used, corresponding to approximately 0.5 *F*/s, and reaction times are on the order of 3–4 weeks.

Example 17.7.2

A silver-plated spoon typically contains about 2.00 g of Ag. If 12.0 h are required to achieve the desired thickness of the Ag coating, what is the average current per spoon that must flow during the electroplating process, assuming an efficiency of 100%?

Given: mass of metal, time, and efficiency

Asked for: current required

Strategy:

A Calculate the number of moles of metal corresponding to the given mass transferred.

B Write the reaction and determine the number of moles of electrons required for the electroplating process.

C Use the definition of the faraday to calculate the number of coulombs required. Then convert coulombs to current in amperes.

Solution:

A We must first determine the number of moles of Ag corresponding to 2.00 g of Ag:

$$moles\ Ag = \frac{2.0\ \cancel{g}}{107.868\ \cancel{g}/mol} = 1.85 \times 10^{-2}\ mol\ Ag$$

B The reduction reaction is $Ag^+(aq) + e^- \rightarrow Ag(s)$, so 1 mol of electrons produces 1 mol of silver.

C Using the definition of the faraday,

$$Coulombs = \left(1.85 \times 10^{-2}\ \cancel{mol}\right)\left(96,486\ C/\cancel{mol}\right) = 1.78 \times 10^3\ C$$

The current in amperes needed to deliver this amount of charge in 12.0 h is therefore

$$amperes = \frac{1.78 \times 10^3\ C}{\left(12.0\ \cancel{h}\right)\left(60\ \cancel{min}/\cancel{h}\right)\left(60\ s/\cancel{min}\right)}$$
$$= 4.12 \times 10^{-2}\ C/s = 4.12 \times 10^{-2}\ A$$

Because the electroplating process is usually much less than 100% efficient (typical values are closer to 30%), the actual current necessary is greater than 0.1 A.

Exercise

A typical aluminum soft-drink can weighs about 29 g. How much time is needed to produce this amount of Al(s) in the Hall–Heroult process, using a current of 15 A to reduce a molten Al_2O_3/Na_3AlF_6 mixture?

Answer: 5.8 h

Summary

In **electrolysis**, an external voltage is applied to drive a nonspontaneous reaction. A Downs cell is used to produce sodium metal from a mixture of salts, and the Hall–Heroult process is used to produce aluminum commercially. Electrolysis can also be used to produce H_2 and O_2 from water. In practice, an additional voltage, called an **overvoltage**, must be applied to overcome factors such as a large activation energy and a junction potential. **Electroplating** is the process by which a second metal is deposited on a metal surface, thereby enhancing an object's appearance or providing protection from corrosion. The amount of material consumed or produced in a reaction can be calculated from the stoichiometry of an electrolysis reaction, the amount of current passed, and the duration of the electrolytic reaction.

Key Takeaways

- In electrolysis, an external voltage is applied to drive a nonspontaneous reaction.
- The quantity of material oxidized or reduced can be calculated from the stoichiometry of the reaction and the amount of charge transferred.

Key Equation

Relationship of charge, current and time

Equation 17.7.14: $C = A \times t$

Conceptual Problems

1. Why might an electrochemical reaction that is thermodynamically favored require an overvoltage to occur?
2. How could you use an electrolytic cell to make quantitative comparisons of the strengths of various oxidants and reductants?
3. Why are mixtures of molten salts, rather than a pure salt, generally used during electrolysis?
4. Two solutions, one containing $Fe(NO_3)_2 \cdot 6H_2O$ and the other containing the same molar concentration of $Fe(NO_3)_3 \cdot 6H_2O$, were electrolyzed under identical conditions. Which solution produced the most metal? Justify your answer.

Numerical Problems

1. The electrolysis of molten salts is frequently used in industry to obtain pure metals. How many grams of metal are deposited from these salts for each mole of electrons?
    1. $AlCl_3$
    2. $MgCl_2$
    3. $FeCl_3$
2. Electrolysis is the most direct way of recovering a metal from its ores. However, the $Na^+(aq)/Na(s)$, $Mg^{2+}(aq)/Mg(s)$, and $Al^{3+}(aq)/Al(s)$ couples all have standard electrode potentials ($E°$) more negative than the reduction potential of water at pH 7.0 (−0.42 V), indicating that these metals can never be obtained by electrolysis of aqueous solutions of their salts. Why? What reaction would occur instead?
3. What volume of chlorine gas at standard temperature and pressure is evolved when a solution of $MgCl_2$ is electrolyzed using a current of 12.4 A for 1.0 h?
4. What mass of copper metal is deposited if a 5.12 A current is passed through a $Cu(NO_3)_2$ solution for 1.5 h.
5. What mass of PbO_2 is reduced when a current of 5.0 A is withdrawn over a period of 2.0 h from a lead storage battery?
6. Electrolysis of $Cr^{3+}(aq)$ produces $Cr^{2+}(aq)$. If you had 500 mL of a 0.15 M solution of $Cr^{3+}(aq)$, how long would it take to reduce the Cr^{3+} to Cr^{2+} using a 0.158 A current?
7. Predict the products obtained at each electrode when aqueous solutions of the following are electrolyzed.
    1. $AgNO_3$
    2. RbI
8. Predict the products obtained at each electrode when aqueous solutions of the following are electrolyzed.
    1. $MgBr_2$
    2. $Hg(CH_3CO_2)_2$
    3. $Al_2(SO_4)_3$

3. 5.2 L

Answers

2.

1.

5.

6.

7. 1. cathode: Ag(s); anode: $O_2(g)$;

2. cathode: $H_2(g)$; anode: $I_2(s)$

8.

Contributors

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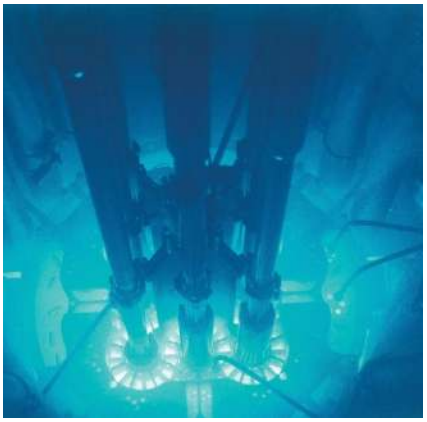
Chapter 18.0: Introduction

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Until now, you have studied chemical processes in which atoms share or transfer electrons to form new compounds, leaving the atomic nuclei largely unaffected. In this chapter, we examine some properties of the atomic nucleus and the changes that can occur in atomic nuclei.

Nuclear reactions differ from other chemical processes in one critical way: in a nuclear reaction, the identities of the elements change. In addition, nuclear reactions are often accompanied by the release of enormous amounts of energy, as much as a *billion* times more than the energy released by chemical reactions. Moreover, the yields and rates of a nuclear reaction are generally unaffected by changes in temperature, pressure, or the presence of a catalyst.

We begin by examining the structure of the atomic nucleus and the factors that determine whether a particular nucleus is stable or decays spontaneously to another element. We then discuss the major kinds of nuclear decay reactions, as well as the properties and uses of the radiation emitted when nuclei decay. You will learn how radioactive emissions can be used to study the mechanisms of chemical reactions and biological processes and how to calculate the amount of energy released during a nuclear reaction. You will also discover why houses are tested for radon gas, how radiation is used to probe organs such as the brain, and how the energy from nuclear reactions can be harnessed to produce electricity. Last, we explore the nuclear chemistry that takes place in stars, and we describe the role that stars play in producing most of the elements in the universe.



The glow caused by intense radiation. *The high-energy particles ejected into the surrounding water or air by an intense radioactive source such as this nuclear reactor core produce a ghostly bluish glow.*

Contributors

- Anonymous

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Chapter 18.1: The Components of the Nucleus

Learning Objective

- To understand the factors that affect nuclear stability.

Although most of the known elements have at least one isotope whose atomic nucleus is stable indefinitely, all elements have isotopes that are unstable and disintegrate, or *decay*, at measurable rates by emitting radiation. Some elements have no stable isotopes and eventually decay to other elements. In contrast to the chemical reactions that were the main focus of earlier chapters and are due to changes in the arrangements of the valence electrons of atoms, the process of nuclear decay results in changes inside an atomic nucleus. We begin our discussion of nuclear reactions by reviewing the conventions used to describe the components of the nucleus.

The Atomic Nucleus

As you learned in Chapter 1, each element can be represented by the notation

$$^{A}_{Z}X \qquad \text{(Chapter 18.1.1)}$$

where *A*, the mass number, is the sum of the number of protons and the number of neutrons, and *Z*, the atomic number, is the number of protons. The protons and neutrons that make up the nucleus of an atom are called nucleonsThe protons and neutrons that make up the nucleus of an atom., and an atom with a particular number of protons and neutrons is called a nuclideAn atom with a particular number of nucleons.. Nuclides with the same number of protons but different numbers of neutrons are called **isotopes**. Isotopes can also be represented by an alternative notation that uses the name of the element followed by the mass number, such as carbon-12. The stable isotopes of oxygen, for example, can be represented in any of the following ways:

$$\begin{array}{lcccc} ^{A}_{Z}X: & ^{16}_{8}O & ^{17}_{8}O & ^{18}_{8}O & \\ ^{A}X: & ^{16}O & ^{17}O & ^{18}O & \\ element-A & oxygen-16 & oxygen-17 & oxygen-18 & \end{array} \qquad \text{(Chapter 18.1.2)}$$

Because the number of neutrons is equal to $A - Z$, we see that the first isotope of oxygen has 8 neutrons, the second isotope 9 neutrons, and the third isotope 10 neutrons. Isotopes of all naturally occurring elements on Earth are present in nearly fixed proportions, with each proportion constituting an isotope's *natural abundance*. For example, in a typical terrestrial sample of oxygen, 99.76% of the O atoms is oxygen-16, 0.20% is oxygen-18, and 0.04% is oxygen-17.

Any nucleus that is unstable and decays spontaneously is said to be radioactiveAny nucleus that is unstable and decays spontaneously, emitting particles and electromagnetic radiation., emitting subatomic particles and electromagnetic radiation. The emissions are collectively called *radioactivity* and can be measured. Isotopes that emit radiation are called radioisotopesAn isotope that emits radiation.. As you learned in Chapter 13, the rate at which radioactive decay occurs is characteristic of the isotope and is generally reported as a **half-life** ($t_{1/2}$), the amount of time required for half of the initial number of nuclei present to decay in a first-order reaction. (For more information on half-life, see Section 13.5) An isotope's half-life can range from fractions of a second to billions of years and, among other applications, can be used to measure the age of ancient objects. Example 1 and its corresponding exercise review the calculations involving radioactive decay rates and half-lives.

Example 18.1.1

Fort Rock Cave in Oregon is the site where archaeologists discovered several Indian sandals, the oldest ever found in Oregon. Analysis of the ^{14}C content of the sagebrush used to make the sandals gave an average decay rate of 5.1 disintegrations per minute (dpm) per gram of carbon. The current $^{14}C/^{12}C$ ratio in living organisms is 1.3×10^{-12}, with a decay rate of 15 dpm/g C. How long ago was the sagebrush in the sandals cut? The half-life of ^{14}C is 5730 yr.

Given: radioisotope, current $^{14}C/^{12}C$ ratio, initial decay rate, final decay rate, and half-life

Asked for: age

Strategy:

A Use Equation 13.5.7 to calculate N_0/N, the ratio of the number of atoms of ^{14}C originally present in the sample to the number of atoms now present.

B Substitute the value for the half-life of ^{14}C into Equation 13.5.3 to obtain the rate constant for the reaction.

C Substitute the calculated values for N_0/N and the rate constant into Equation 13.5.8 to obtain the elapsed time t.

Solution:

We can use the integrated rate law for a first-order nuclear reaction (Equation 13.5.8) to calculate the amount of time that has passed since the sagebrush was cut to make the sandals:

$$ln\frac{N}{N_o} = -kt \tag{Chapter 18.1.3}$$

A From Equation 13.5.5, we know that $A = kN$. We can therefore use the initial and final activities (A_0 = 15 and A = 5.1) to calculate N_0/N:

$$\frac{A_o}{A} = \frac{kN_o}{kN} = \frac{N_o}{N} = \frac{1.5}{5.1} \tag{Chapter 18.1.4}$$

B Now we can calculate the rate constant k from the half-life of the reaction (5730 yr) using Equation 13.5.5:

$$t_{1/2} = \frac{0.693}{k} \tag{Chapter 18.1.5}$$

Rearranging this equation to solve for k,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730\ yr} = 1.21 \times 10^{-4}\ yr^{-1} \tag{Chapter 18.1.6}$$

C Substituting the calculated values into the equation for t,

$$t = \frac{ln\,(N/N_o)}{k} = \frac{ln\,(15/5.1)}{1.21 \times 10^{-4}\ yr^{-1}} = 8900\ yr \tag{Chapter 18.1.7}$$

Thus the sagebrush in the sandals is about 8900 yr old.

Exercise

While trying to find a suitable way to protect his own burial chamber, the ancient Egyptian pharaoh Sneferu developed the pyramid, a burial structure that protected desert graves from thieves and exposure to wind. Analysis of the ^{14}C content of several items in pyramids built during his reign gave an average decay rate of 8.6 dpm/g C. When were the objects in the chamber created?

Answer: about 4600 yr ago, or about 2600 BC

Nuclear Stability

As discussed in Chapter 1, the nucleus of an atom occupies a tiny fraction of the volume of an atom and contains the number of protons and neutrons that is characteristic of a given isotope. Electrostatic repulsions would normally cause the positively charged protons to repel each other, but the nucleus does not fly apart because of the strong nuclear forceAn extremely powerful but very short-range attractive force between nucleons that keeps the nucleus of an atom from flying apart (due to electrostatic repulsions between protons)., an extremely powerful but very short-range attractive force between nucleons (Figure 18.1.1). All stable nuclei except the hydrogen-1 nucleus (^1H) contain at least one neutron to overcome the electrostatic repulsion between protons. As the number of protons in the nucleus increases, the number of neutrons needed for a stable nucleus increases even more rapidly. Too many protons (or too few neutrons) in the nucleus result in an imbalance between forces, which leads to nuclear instability.

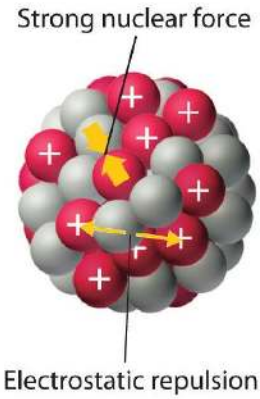


Figure 18.1.1 Competing Interactions within the Atomic Nucleus Eectrostatic repulsions between positively charged protons would normally cause the nuclei of atoms (except H) to fly apart. In stable atomic nuclei, these repulsions are overcome by the strong nuclear force, a short-range but powerful attractive interaction between nucleons. If the attractive interactions due to the strong nuclear force are weaker than the electrostatic repulsions between protons, the nucleus is unstable, and it will eventually decay.

The relationship between the number of protons and the number of neutrons in stable nuclei, arbitrarily defined as having a half-life longer than 10 times the age of Earth, is shown graphically in Figure 18.1.2. The stable isotopes form a “peninsula of stability” in a “sea of instability.” Only two stable isotopes, ^{1}H and ^{3}He, have a neutron-to-proton ratio less than 1. Several stable isotopes of light atoms have a neutron-to-proton ratio equal to 1 (e.g., ^{4}He, ^{10}B, ^{40}Ca. All other stable nuclei have a higher neutron-to-proton ratio, which increases steadily to about 1.5 for the heaviest nuclei. Regardless of the number of neutrons, however, all elements with $Z >$ 83 are unstable and radioactive.

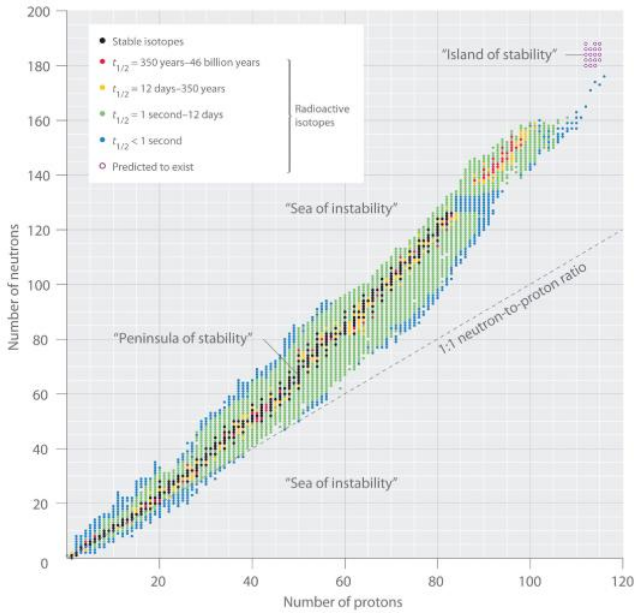


Figure 18.1.2 The Relationship between Nuclear Stability and the Neutron-to-Proton Ratio In this plot of the number of neutrons versus the number of protons, each black point corresponds to a stable nucleus. In this classification, a stable nucleus is arbitrarily defined as one with a half-life longer than 46 billion years (10 times the age of Earth). As the number of protons (the atomic number) increases, the number of neutrons required for a stable nucleus increases even more rapidly. Isotopes shown in red, yellow, green, and blue are progressively less stable and more radioactive; the farther an isotope is from the diagonal band of stable isotopes, the shorter its half-life. The purple dots indicate superheavy nuclei that are predicted to be relatively stable, meaning that they are expected to be radioactive but to have relatively long half-lives. In most cases, these elements have not yet been observed or synthesized.

Data source: National Nuclear Data Center, Brookhaven National Laboratory, Evaluated Nuclear Structure Data File (ENSDF), Chart of Nuclides, http://www.nndc.bnl.gov/chart.

As shown in Figure 18.1.3, more than half of the stable nuclei (166 out of 279) have *even* numbers of both neutrons and protons; only 6 of the 279 stable nuclei do not have odd numbers of both. Moreover, certain numbers of neutrons or protons result in especially stable nuclei; these are the so-called *magic numbers* 2, 8, 20, 50, 82, and 126. For example, tin (Z = 50) has 10 stable isotopes, but the elements on either side of tin in the periodic table, indium (Z = 49) and antimony (Z = 51), have only 2 stable isotopes each. Nuclei with magic numbers of *both* protons *and* neutrons are said to be "doubly magic" and are even more stable. Examples of elements with doubly magic nuclei are ^{4}He with 2 protons and 2 neutrons, and ^{208}Pb with 82 protons and 126 neutrons, which is the heaviest known stable isotope of any element.

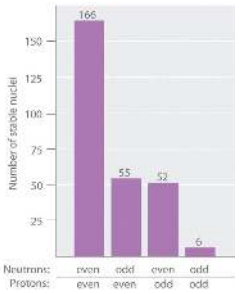


Figure 18.1.3 The Relationship between the Number of Protons and the Number of Neutrons and Nuclear Stability Most stable nuclei contain even numbers of both neutrons and protons.

The pattern of stability suggested by the magic numbers of nucleons is reminiscent of the stability associated with the closed-shell electron configurations of the noble gases in group 18 and has led to the hypothesis that the nucleus contains shells of nucleons that are in some ways analogous to the shells occupied by electrons in an atom. As shown in Figure 18.1.2, the "peninsula" of stable isotopes is surrounded by a "reef" of radioactive isotopes, which are stable enough to exist for varying lengths of time before they eventually decay to produce other nuclei.

Example 18.1.2

Classify each nuclide as stable or radioactive.

1. $^{30}_{15}P$
2. $^{98}_{43}Tc$
3. tin-118
4. $^{239}_{94}Pu$

Given: mass number and atomic number

Asked for: predicted nuclear stability

Strategy:

Use the number of protons, the neutron-to-proton ratio, and the presence of even or odd numbers of neutrons and protons to predict the stability or radioactivity of each nuclide.

Solution:

1. This isotope of phosphorus has 15 neutrons and 15 protons, giving a neutron-to-proton ratio of 1.0. Although the atomic number, 15, is much less than the value of 83 above which all nuclides are unstable, the neutron-to-proton ratio is less than that expected for stability for an element with this mass. As shown in Figure 18.1.2, its neutron-to-proton ratio should be greater than 1. Moreover, this isotope has an odd number of both neutrons and protons, which also tends to make a nuclide unstable. Consequently, $^{30}_{15}P$ is predicted to be radioactive, and it is.
2. This isotope of technetium has 55 neutrons and 43 protons, giving a neutron-to-proton ratio of 1.28, which places $^{98}_{43}Tc$ near the edge of the band of stability. The atomic number, 55, is much less than the value of 83 above which all isotopes are unstable. These facts suggest that $^{98}_{43}Tc$ might be stable. However, $^{98}_{43}Tc$ has an odd number of both neutrons and protons, a combination that seldom gives a stable nucleus. Consequently, $^{98}_{43}Tc$ is predicted to be radioactive, and it is.
3. Tin-118 has 68 neutrons and 50 protons, for a neutron-to-proton ratio of 1.36. As in part b, this value and the atomic number both suggest stability. In addition, the isotope has an *even* number of both neutrons and protons, which tends to increase nuclear stability. Most important, the nucleus has 50 protons, and 50 is one of the magic numbers associated with especially stable nuclei. Thus $^{118}_{50}Sn$ should be particularly stable.
4. This nuclide has an atomic number of 94. Because all nuclei with Z > 83 are unstable, $^{239}_{94}Sn$must be radioactive.

Exercise

Classify each nuclide as stable or radioactive.

1. $^{232}_{90}Th$
2. $^{40}_{20}Ca$
3. $^{15}_{8}O$
4. $^{139}_{57}La$

Answer:

1. radioactive
2. stable
3. radioactive
4. stable

Superheavy Elements

In addition to the "peninsula of stability," Figure 18.1.2 shows a small "island of stability" that is predicted to exist in the upper right corner. This island corresponds to the superheavy elementsAn element with an atomic number near the magic number of 126., with atomic numbers near the magic number 126. Because the next magic number for neutrons should be 184, it was suggested that an element with 114 protons and 184 neutrons might be stable enough to exist in nature. Although these claims were met with skepticism for many years, since 1999 a few atoms of isotopes with Z = 114 and Z = 116 have been prepared and found to be surprisingly stable. One isotope of element 114 lasts 2.7 seconds before decaying, described as an "eternity" by nuclear chemists. Moreover, there is recent evidence for the existence of a nucleus with A = 292 that was found in ^{232}Th. With an estimated half-life greater than 10^8 years, the isotope is particularly stable. Its measured mass is consistent with predictions for the mass of an isotope with Z = 122. Thus a number of relatively long-lived nuclei may well be accessible among the superheavy elements.

Summary

Subatomic particles of the nucleus (protons and neutrons) are called **nucleons**. A **nuclide** is an atom with a particular number of protons and neutrons. An unstable nucleus that decays spontaneously is **radioactive**, and its emissions are collectively called *radioactivity*. Isotopes that emit radiation are called **radioisotopes**. Each nucleon is attracted to other nucleons by the **strong nuclear force**. Stable nuclei generally have even numbers of both protons and neutrons and a neutron-to-proton ratio of at least 1. Nuclei that contain *magic numbers* of protons and neutrons are often especially stable. **Superheavy elements**, with atomic numbers near 126, may even be stable enough to exist in nature.

Key Takeaway

- Nuclei with magic numbers of neutrons or protons are especially stable, as are those nuclei that are doubly magic.

Conceptual Problems

1. What distinguishes a nuclear reaction from a chemical reaction? Use an example of each to illustrate the differences.
2. What do chemists mean when they say a substance is *radioactive*?
3. What characterizes an isotope? How is the mass of an isotope of an element related to the atomic mass of the element shown in the periodic table?
4. In a typical nucleus, why does electrostatic repulsion between protons not destabilize the nucleus? How does the neutron-to-proton ratio affect the stability of an isotope? Why are all isotopes with Z > 83 unstable?
5. What is the significance of a *magic number* of protons or neutrons? What is the relationship between the number of stable isotopes of an element and whether the element has a magic number of protons?
6. Do you expect Bi to have a large number of stable isotopes? Ca? Explain your answers.
7. Potassium has three common isotopes, ^{39}K, ^{40}K, and ^{41}K, but only potassium-40 is radioactive (a beta emitter). Suggest a reason for the instability of ^{40}K.
8. Samarium has 11 relatively stable isotopes, but only 4 are nonradioactive. One of these 4 isotopes is ^{144}Sm, which has a lower neutron-to-proton ratio than lighter, radioactive isotopes of samarium. Why is ^{144}Sm more stable?

5. Isotopes with magic numbers of protons and/or neutrons tend to be especially stable. Elements with magic numbers of protons
4. tend to have more stable isotopes than elements that do not.
3.

Answers

7. Potassium-40 has 19 protons and 21 neutrons. Nuclei with odd numbers of both protons and neutrons tend to be unstable. In addition, the neutron-to-proton ratio is very low for an element with this mass, which decreases nuclear stability.

8.

Numerical Problems

1. Write the nuclear symbol for each isotope using notation.
    1. chlorine-39
    2. lithium-8
    3. osmium-183
    4. zinc-71
2. Write the nuclear symbol for each isotope using $^{A}_{Z}X$ notation.
    1. lead-212
    2. helium-5
    3. oxygen-19
    4. plutonium-242
3. Give the number of protons, the number of neutrons, and the neutron-to-proton ratio for each isotope.
    1. iron-57
    2. ^{185}W
    3. potassium-39
    4. ^{131}Xe
4. Give the number of protons, the number of neutrons, and the neutron-to-proton ratio for each isotope.
    1. technetium-99m
    2. ^{140}La
    3. radium-227
    4. ^{208}Bi
5. Which of these nuclides do you expect to be radioactive? Explain your reasoning.
    1. ^{20}ne
    2. tungsten-184
    3. ^{106}Ti
6. Which of these nuclides do you expect to be radioactive? Explain your reasoning.
    1. ^{107}Ag
    2. ^{50}V
    3. lutetium-176

Answers

1. 1. $^{39}_{17}Cl$
    2. $^{8}_{3}Li$
    3. $^{183}_{76}Os$
    4. $^{71}_{30}Zn$
2.
3. 1. 26 protons; 31 neutrons; 1.19
    2. 74 protons; 111 neutrons; 1.50
    3. 19 protons; 20 neutrons; 1.05
    4. 54 protons; 77 neutrons; 1.43

4.
5.
6.

Contributors

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Chapter 18.2: Nuclear Reactions

Learning Objective

- To understand the different kinds of radioactive decay.

The two general kinds of nuclear reactions are nuclear decay reactions and nuclear transmutation reactions. In a nuclear decay reactionA nuclear reaction that occurs when an unstable nucleus emits radiation and is transformed into the nucleus of one or more other elements., also called *radioactive decay*, an unstable nucleus emits radiation and is transformed into the nucleus of one or more other elements. The resulting *daughter nuclei* have a lower mass and are lower in energy (more stable) than the *parent nucleus* that decayed. In contrast, in a nuclear transmutation reactionA nuclear reaction in which a nucleus reacts with a subatomic particle or another nuleus to give a product nucleus that is more massive than the starting material., a nucleus reacts with a subatomic particle or another nucleus to form a product nucleus that is *more massive* than the starting material. As we shall see, nuclear decay reactions occur spontaneously under all conditions, but nuclear transmutation reactions occur only under very special conditions, such as the collision of a beam of highly energetic particles with a target nucleus or in the interior of stars. We begin this section by considering the different classes of radioactive nuclei, along with their characteristic nuclear decay reactions and the radiation they emit.

Note the Pattern

Nuclear decay reactions occur spontaneously under all conditions, whereas nuclear transmutation reactions are induced.

Classes of Radioactive Nuclei

The three general classes of radioactive nuclei are characterized by a different decay process or set of processes:

1. **Neutron-rich nuclei.** The nuclei on the upper left side of the band of stable nuclei in Figure 18.1.2 have a neutron-to-proton ratio that is too high to give a stable nucleus. These nuclei decay by a process that *converts a neutron to a proton*, thereby *decreasing* the neutron-to-proton ratio.
2. **Neutron-poor nuclei.** Nuclei on the lower right side of the band of stable nuclei have a neutron-to-proton ratio that is too low to give a stable nucleus. These nuclei decay by processes that have the net effect of *converting a proton to a neutron*, thereby *increasing* the neutron-to-proton ratio.
3. **Heavy nuclei.** With very few exceptions, heavy nuclei (those with $A \geq 200$) are intrinsically unstable regardless of the neutron-to-proton ratio, and all nuclei with $Z > 83$ are unstable. This is presumably due to the cumulative effects of electrostatic repulsions between the large number of positively charged protons, which cannot be totally overcome by the strong nuclear force, regardless of the number of neutrons present. Such nuclei tend to decay by emitting an α particle (a helium nucleus, ^4_2He), which decreases the number of protons and neutrons in the original nucleus by 2. Because the neutron-to-proton ratio in an α particle is 1, the net result of alpha emission is an increase in the neutron-to-proton ratio.

Note the Pattern

Nuclear decay reactions always produce daughter nuclei that have a more favorable neutron-to- proton ratio and hence are more stable than the parent nucleus.

Nuclear Decay Reactions

Just as we use the number and type of *atoms* present to balance a chemical equation, we can use the number and type of *nucleons* present to write a balanced nuclear equation for a nuclear decay reaction. This procedure also allows us to predict the identity of either the parent or the daughter nucleus if the identity of only one is known. Regardless of the mode of decay, *the total number of nucleons is conserved* in all nuclear reactions.

To describe nuclear decay reactions, chemists have extended the $^A_Z X$ notation for nuclides to include radioactive emissions. Table 18.2.1 " lists the name and symbol for each type of emitted radiation. We introduced the most common of these, α and β particles and γ rays, in Chapter 1 and Chapter 13. The most notable addition is the positron, a particle that has the same mass as an electron but a *positive* charge rather than a negative charge.

Table 18.2.1 Nuclear Decay Emissions and Their Symbols

Identity	Symbol	Charge	Mass (amu)
helium nucleus	$^{4}_{2}\alpha$	+2	4.001506
electron	$^{0}_{-1}\beta$ *or* β^{-}	−1	0.000549
photon	$^{0}_{0}\gamma$	—	—
neutron	$^{1}_{0}n$	0	1.008665
proton	$^{1}_{1}p$	+1	1.007276
positron	$^{0}_{+1}\beta$ *or* β^{+}	+1	0.000549

Like the notation used to indicate isotopes, the upper left superscript in the symbol for a particle gives the mass number, which is the total number of protons and neutrons. For a proton or a neutron, $A = 1$. Because neither an electron nor a positron contains protons or neutrons, its mass number is 0. The numbers should not be taken literally, however, as meaning that these particles have zero mass; ejection of a beta particle (an electron) simply has a negligible effect on the mass of a nucleus.

Similarly, the lower left subscript gives the charge of the particle. Because protons carry a positive charge, $Z = +1$ for a proton. In contrast, a neutron contains no protons and is electrically neutral, so $Z = 0$. In the case of an electron, $Z = −1$, and for a positron, $Z = +1$. Because γ rays are high-energy photons, both A and Z are 0. In some cases, two different symbols are used for particles that are identical but produced in different ways. For example, the symbol $^{0}_{-1}e$ which is usually simplified to e^{-}, represents a free electron or an electron associated with an *atom*, whereas the symbol $^{0}_{-1}\beta$ which is often simplified to β^{-}, denotes an electron that originates from within the *nucleus*, which is a β particle. Similarly, $^{4}_{2}He^{2+}$ refers to the nucleus of a helium atom, and $^{4}_{2}\alpha$ denotes an identical particle that has been ejected from a heavier nucleus.

There are six fundamentally different kinds of nuclear decay reactions, and each releases a different kind of particle or energy. The essential features of each reaction are shown in Figure 18.2.1. The most common are *alpha* and *beta decay* and *gamma emission*, but the others are essential to an understanding of nuclear decay reactions.

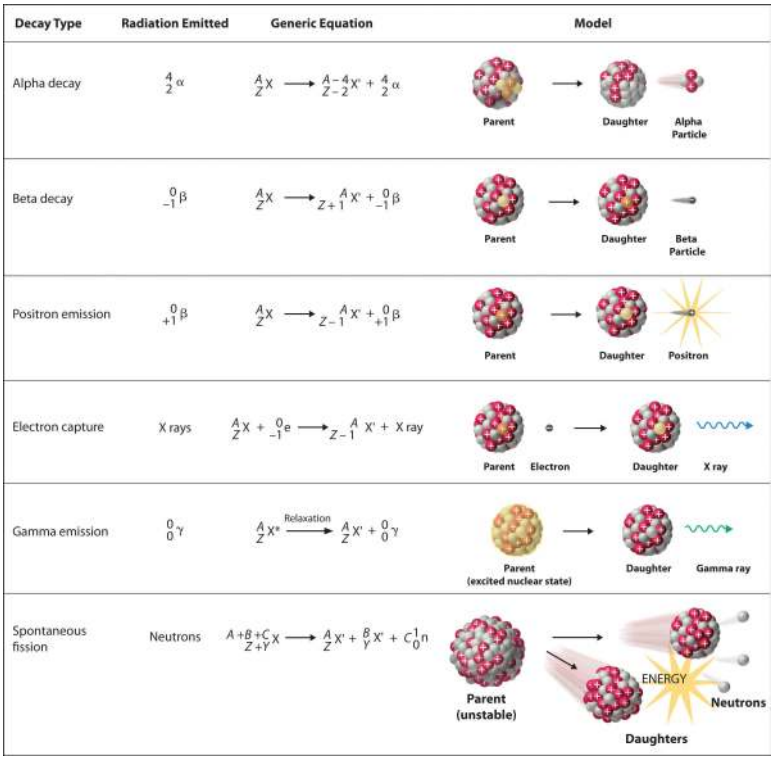


Figure 18.2.1 Common Modes of Nuclear Decay

Alpha Decay

Many nuclei with mass numbers greater than 200 undergo alpha (α) decayA nuclear decay reaction that results in the emission of a helium-4 nucleus as an α particle., which results in the emission of a helium-4 nucleus as an alpha (α) particleA helium nucleus: ${}^{4}_{2}\alpha$ The general reaction is as follows:

$$\underset{\text{parent}}{{}^{A}_{Z}X} \rightarrow \underset{\text{daughter}}{{}^{A-4}_{Z-2}X} + \underset{\text{alpha particle}}{{}^{4}_{2}\alpha}$$

The daughter nuclide contains two fewer protons and two fewer neutrons than the parent. Thus α-particle emission produces a daughter nucleus with a mass number $A - 4$ and a nuclear charge $Z - 2$ compared to the parent nucleus. Radium-226, for example, undergoes alpha decay to form radon-222:

$$^{226}_{88}Ra \rightarrow ^{222}_{86}Rn + ^{4}_{2}\alpha$$

Because nucleons are conserved in this and all other nuclear reactions, the sum of the mass numbers of the products, 222 + 4 = 226, equals the mass number of the parent. Similarly, the sum of the atomic numbers of the products, 86 + 2 = 88, equals the atomic number of the parent. Thus the nuclear equation is balanced.

Note the Pattern

Just as the total number of atoms is conserved in a chemical reaction, the total number of nucleons is conserved in a nuclear reaction.

Beta Decay

Nuclei that contain too many neutrons often undergo beta (β) decayA nuclear decay reaction in which a neutron is converted to a proton and a high-energy electron that is ejected from the nucleus as a β particle., in which a neutron is converted to a proton and a high-energy electron that is ejected from the nucleus as a β particle:

$$\underset{\text{unstable neutron}}{{}^{1}_{0}n} \rightarrow \underset{\text{retained proton}}{{}^{1}_{1}p} + \underset{\text{emitted } \beta \text{ particle}}{{}^{0}_{-1}\beta}$$

The general reaction for beta decay is therefore

$$\underset{\text{parent}}{{}^{A}_{Z}X} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z+1}X'} + \underset{\text{beta}}{{}^{0}_{-1}\beta}$$

Although beta decay does *not* change the mass number of the nucleus, it does result in an increase of +1 in the atomic number because of the addition of a proton in the daughter nucleus. Thus beta decay decreases the neutron-to-proton ratio, moving the nucleus toward the band of stable nuclei. For example, carbon-14 undergoes beta decay to form nitrogen-14:

$$^{14}_{6}C \rightarrow ^{14}_{7}N + ^{0}_{-1}\beta$$

Once again, the number of nucleons is conserved, and the charges are balanced. The parent and the daughter nuclei have the same mass number, 14, and the sum of the atomic numbers of the products is 6, which is the same as the atomic number of the carbon-14 parent.

Positron Emission

Because a positron has the same mass as an electron but opposite charge, positron emissionA nuclear decay reaction in which a proton is transformed into a neutron, and a high-energy positron is emitted. is the opposite of beta decay. Thus positron emission is characteristic of neutron-poor nuclei, which decay by transforming a proton to a neutron and emitting a high-energy positron:

$$^{1}_{1}p \rightarrow ^{1}_{0}n + ^{0}_{+1}\beta$$

The general reaction for positron emission is therefore

$$\underset{\text{parent}}{{}^{A}_{Z}X} \rightarrow \underset{\text{daughter}}{{}^{A}_{Z-1}X'} + \underset{\text{positron}}{{}^{0}_{+1}\beta}$$

Like beta decay, positron emission does not change the mass number of the nucleus. In this case, however, the atomic number of the daughter nucleus is *lower* by 1 than that of the parent. Thus the neutron-to-proton ratio has increased, again moving the nucleus closer to the band of stable nuclei. For example, carbon-11 undergoes positron emission to form boron-11:

$$^{11}_{6}C \rightarrow ^{11}_{5}N + ^{0}_{+1}\beta$$

Nucleons are conserved, and the charges balance. The mass number, 11, does not change, and the sum of the atomic numbers of the products is 6, the same as the atomic number of the parent carbon-11 nuclide.

Electron Capture

A neutron-poor nucleus can decay by either positron emission or electron capture (EC)A nuclear decay reaction in which an electron in an inner shell reacts with a proton to produce a neutron., in which an electron in an inner shell reacts with a proton to produce a neutron:

$$^{1}_{1}p + ^{-1}_{0}e \rightarrow \ ^{1}_{0}n$$

When a second electron moves from an outer shell to take the place of the lower-energy electron that was absorbed by the nucleus, an x-ray is emitted. The overall reaction for electron capture is thus

$$\underset{parent}{^{A}_{Z}X} + \underset{electron}{^{0}_{-1}e} \rightarrow \underset{daughter}{^{A}_{Z-1}X'} + x-ray$$

Electron capture does not change the mass number of the nucleus because both the proton that is lost and the neutron that is formed have a mass number of 1. As with positron emission, however, the atomic number of the daughter nucleus is *lower* by 1 than that of the parent. Once again, the neutron-to-proton ratio has increased, moving the nucleus toward the band of stable nuclei. For example, iron-55 decays by electron capture to form manganese-55, which is often written as follows:

$$^{55}_{26}Fe \xrightarrow{EC} \ ^{55}_{25}Mn + x-ray$$

The atomic numbers of the parent and daughter nuclides differ in Equation 18.2.11, although the mass numbers are the same. To write a balanced nuclear equation for this reaction, we must explicitly include the captured electron in the equation:

$$^{55}_{26}Fe_{-1}^{0}e \ \rightarrow \ ^{55}_{25}Mn + x-ray$$

Both positron emission and electron capture are usually observed for nuclides with low neutron-to-proton ratios, but the decay rates for the two processes can be very different.

Gamma Emission

Many nuclear decay reactions produce daughter nuclei that are in a nuclear excited state, which is similar to an atom in which an electron has been excited to a higher-energy orbital to give an electronic excited state. Just as an electron in an electronic excited state emits energy in the form of a photon when it returns to the ground state, a nucleus in an excited state releases energy in the form of a photon when it returns to the ground state. (For more information on electron ground states, see Chapter 2) These high-energy photons are γ rays. Gamma (γ) emissionA nuclear decay reaction that results when a nucleus in an excited state releases energy in the form of a high-energy photon (a γ ray) when it returns to the ground state. can occur virtually instantaneously, as it does in the alpha decay of uranium-238 to thorium-234, where the asterisk denotes an excited state:

$$^{238}_{92}U \rightarrow \underset{excited\ state}{^{234}_{90}Th^{*}} + ^{4}_{2}\alpha \xrightarrow{relaxation} ^{234}_{90}Th + ^{0}_{0}\gamma$$

If we disregard the decay event that created the excited nucleus, then

$$^{234}_{90}Th^{*} \rightarrow \ ^{234}_{90}Th + ^{0}_{0}\gamma$$

or more generally,

$$^{A}_{Z}X^{*} \rightarrow \ ^{A}_{Z}X + ^{0}_{0}\gamma$$

Gamma emission can also occur after a significant delay. For example, technetium-99*m* has a half-life of about 6 hours before emitting a γ ray to form technetium-99. (The *m* is for metastable, which is explained in Section 13.5.)

Because γ rays are energy, their emission does not affect either the mass number or the atomic number of the daughter nuclide. Gamma-ray emission is therefore the only kind of radiation that does not necessarily involve the conversion of one element to another, although it is almost always observed in conjunction with some other nuclear decay reaction.

Spontaneous Fission

Only very massive nuclei with high neutron-to-proton ratios can undergo spontaneous fissionA nuclear decay reaction in which the nucleus breaks into two pieces with different atomic numbers and atomic masses., in which the nucleus breaks into two pieces that have different atomic numbers and atomic masses. This process is most important for the transactinide elements, with $Z \geq 104$. Spontaneous fission is invariably accompanied by the release of large amounts of energy, and it is usually accompanied by the emission of several neutrons as well. An example is the spontaneous fission of ${}^{254}_{98}Cf$ which gives a distribution of fission products; one possible set of products is shown in the following equation:

$$ {}^{254}_{98}Cf \rightarrow {}^{118}_{46}Pd + {}^{132}_{52}Te + 4{}^{1}_{0}n $$

Once again, the number of nucleons is conserved. Thus the sum of the mass numbers of the products (118 + 132 + 4 = 254) equals the mass number of the reactant. Similarly, the sum of the atomic numbers of the products [46 + 52 + (4 × 0) = 98] is the same as the atomic number of the parent nuclide.

Example 18.2.1

Write a balanced nuclear equation to describe each reaction.

1. the beta decay of ${}^{35}_{16}S$
2. the decay of ${}^{201}_{80}Hg$ by electron capture
3. the decay of ${}^{30}_{15}P$ by positron emission

Given: radioactive nuclide and mode of decay

Asked for: balanced nuclear equation

Strategy:

A Identify the reactants and the products from the information given.

B Use the values of *A* and *Z* to identify any missing components needed to balance the equation.

Solution:

A We know the identities of the reactant and one of the products (a β particle). We can therefore begin by writing an equation that shows the reactant and one of the products and indicates the unknown product as ${}^{A}_{Z}X$

$$ {}^{35}_{16}S \rightarrow {}^{A}_{Z}X + {}^{-1}_{0}\beta $$

B Because both protons and neutrons must be conserved in a nuclear reaction, the unknown product must have a mass number of $A = 35 - 0 = 35$ and an atomic number of $Z = 16 - (-1) = 17$. The element with $Z = 17$ is chlorine, so the balanced nuclear equation is as follows:

$$ {}^{35}_{16}S \rightarrow {}^{35}_{16}Cl + {}^{-1}_{0}\beta $$

A We know the identities of both reactants: ${}^{201}_{80}Hg$. The reaction is as follows:

$$ {}^{201}_{80}Hg + {}^{-1}_{0}e \rightarrow {}^{A}_{Z}X $$

B Both protons and neutrons are conserved, so the mass number of the product must be $A = 201 + 0 = 201$, and the atomic number of the product must be $Z = 80 + (-1) = 79$, which corresponds to the element gold. The balanced nuclear equation is thus

$$ {}^{201}_{80}Hg + {}^{-1}_{0}e \rightarrow {}^{201}_{79}Au $$

1. **A** As in part (a), we are given the identities of the reactant and one of the products—in this case, a positron. The unbalanced nuclear equation is therefore

   $$ {}^{30}_{15}P + \rightarrow {}^{A}_{Z}X + {}^{0}_{+1}\beta $$

   B The mass number of the second product is $A = 30 - 0 = 30$, and its atomic number is $Z = 15 - 1 = 14$, which corresponds to silicon. The balanced nuclear equation for the reaction is as follows:

   $$ {}^{30}_{15}P + \rightarrow {}^{30}_{14}Si + {}^{0}_{+1}\beta $$

Exercise

Write a balanced nuclear equation to describe each reaction.

1. $^{11}_{6}C$ by positron emission
2. the beta decay of molybdenum-99
3. the emission of an α particle followed by gamma emission from
4. $^{185}_{74}C$

Answer:

1. $^{11}_{6}C \rightarrow {}^{11}_{5}B + {}^{0}_{+1}\beta$
2. $^{99}_{42}C \rightarrow {}^{90m}_{43}Tc + {}^{0}_{-1}\beta$
3. $^{185}_{74}W \rightarrow {}^{181}_{72}Hf + {}^{0}_{0}\gamma\beta + {}^{4}_{2}\alpha$

Example 18.2.2

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

1. $^{45}_{22}Ti$
2. $^{292}_{94}Pu$
3. $^{12}_{5}B$
4. $^{256}_{100}Fm$

Given: nuclide

Asked for: type of nuclear decay

Strategy:

Based on the neutron-to-proton ratio and the value of *Z*, predict the type of nuclear decay reaction that will produce a more stable nuclide.

Solution:

1. This nuclide has a neutron-to-proton ratio of only 1.05, which is much less than the requirement for stability for an element with an atomic number in this range. Nuclei that have low neutron-to-proton ratios decay by converting a proton to a neutron. The two possibilities are positron emission, which converts a proton to a neutron and a positron, and electron capture, which converts a proton and a core electron to a neutron. In this case, both are observed, with positron emission occurring about 86% of the time and electron capture about 14% of the time.
2. Nuclei with $Z > 83$ are too heavy to be stable and usually undergo alpha decay, which decreases both the mass number and the atomic number. Thus $^{292}_{94}Pu$ is expected to decay by alpha emission.
3. This nuclide has a neutron-to-proton ratio of 1.4, which is very high for a light element. Nuclei with high neutron-to-proton ratios decay by converting a neutron to a proton and an electron. The electron is emitted as a β particle, and the proton remains in the nucleus, causing an increase in the atomic number with no change in the mass number. We therefore predict that $^{12}_{5}B$ will undergo beta decay.
4. This is a massive nuclide, with an atomic number of 100 and a mass number much greater than 200. Nuclides with $A \geq 200$ tend to decay by alpha emission, and even heavier nuclei tend to undergo spontaneous fission. We therefore predict that $^{256}_{100}Fm$ will decay by either or both of these two processes. In fact, it decays by both spontaneous fission and alpha emission, in a 97:3 ratio.

Exercise

Predict the kind of nuclear change each unstable nuclide undergoes when it decays.

1. $^{32}_{14}Si$
2. $^{43}_{21}Sc$
3. $^{231}_{91}Pa$

Answer:

1. beta decay
2. positron emission or electron capture

3. alpha decay

Radioactive Decay Series

The nuclei of all elements with atomic numbers greater than 83 are unstable. Thus all isotopes of all elements beyond bismuth in the periodic table are radioactive. Because alpha decay decreases Z by only 2, and positron emission or electron capture decreases Z by only 1, it is impossible for any nuclide with $Z > 85$ to decay to a stable daughter nuclide in a single step, except via nuclear fission. Consequently, radioactive isotopes with $Z > 85$ usually decay to a daughter nucleus that is radiaoctive, which in turn decays to a second radioactive daughter nucleus, and so forth, until a stable nucleus finally results. This series of sequential alpha- and beta-decay reactions is called a radioactive decay seriesA series of sequential alpha- and beta-decay reactions that occur until a stable nucleus is finally obtained.. The most common is the uranium-238 decay series, which produces lead-206 in a series of 14 sequential alpha- and beta-decay reactions (Figure 18.2.2). Although a radioactive decay series can be written for almost any isotope with $Z > 85$, only two others occur naturally: the decay of uranium-235 to lead-207 (in 11 steps) and thorium-232 to lead-208 (in 10 steps). A fourth series, the decay of neptunium-237 to bismuth-209 in 11 steps, is known to have occurred on the primitive Earth. With a half-life of “only” 2.14 million years, all the neptunium-237 present when Earth was formed decayed long ago, and today all the neptunium on Earth is synthetic.

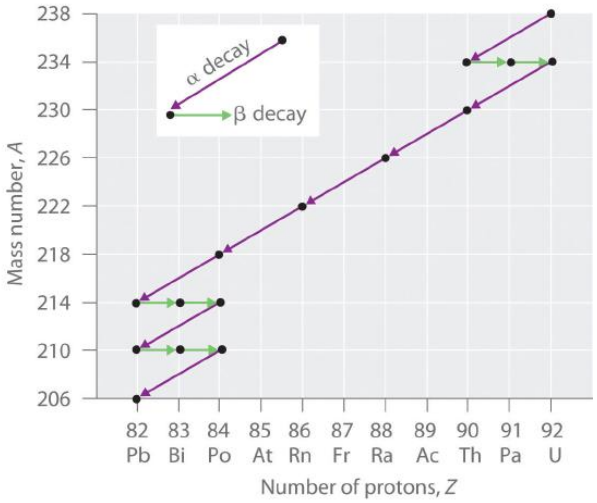


Figure 18.2.2 A Radioactive Decay Series *Three naturally occurring radioactive decay series are known to occur currently: the uranium-238 decay series, the decay of uranium-235 to lead-207, and the decay of thorium-232 to lead-208.*

Due to these radioactive decay series, small amounts of very unstable isotopes are found in ores that contain uranium or thorium. These rare, unstable isotopes should have decayed long ago to stable nuclei with a lower atomic number, and they would no longer be found on Earth. Because they are generated continuously by the decay of uranium or thorium, however, their amounts have reached a steady state, in which their rate of formation is equal to their rate of decay. In some cases, the abundance of the daughter isotopes can be used to date a material or identify its origin, as described in Section 13.5.

Induced Nuclear Reactions

The discovery of radioactivity in the late 19th century showed that some nuclei spontaneously transform into nuclei with a different number of protons, thereby producing a different element. When scientists realized that these naturally occurring radioactive isotopes decayed by emitting subatomic particles, they realized that—in principle—it should be possible to carry out the reverse reaction, converting a stable nucleus to another more massive nucleus by bombarding it with subatomic particles in a nuclear transmutation reaction.

The first successful nuclear transmutation reaction was carried out in 1919 by Ernest Rutherford, who showed that α particles emitted by radium could react with nitrogen nuclei to form oxygen nuclei. As shown in the following equation, a proton is emitted in the process:

$$ {}^{4}_{2}\alpha + {}^{14}_{7}N \rightarrow {}^{17}_{8}O + {}^{1}_{1}p $$

Rutherford's nuclear transmutation experiments led to the discovery of the neutron. He found that bombarding the nucleus of a light target element with an α particle usually converted the target nucleus to a product that had an atomic number higher by 1 and a mass number higher by 3 than the target nucleus. Such behavior is consistent with the emission of a proton after reaction with the α particle. Very light targets such as Li, Be, and B reacted differently, however, emitting a new kind of highly penetrating radiation rather than a proton. Because neither a magnetic field nor an electrical field could deflect these high-energy particles, Rutherford concluded that they were electrically neutral. (For more information on high-energy particles, see Chapter 1.) Other observations suggested that the mass of the neutral particle was similar to the mass of the proton. In 1932, James Chadwick (Nobel Prize in Physics, 1935), who was a student of Rutherford's at the time, named these neutral particles *neutrons* and proposed that they were fundamental building blocks of the atom. The reaction that Chadwick initially used to explain the production of neutrons was as follows:

$$^{4}_{2}\alpha + ^{9}_{4}Be \rightarrow ^{12}_{6}C + ^{1}_{0}n$$

Because α particles and atomic nuclei are both positively charged, electrostatic forces cause them to repel each other. Only α particles with very high kinetic energy can overcome this repulsion and collide with a nucleus (Figure 18.2.3). Neutrons have no electrical charge, however, so they are not repelled by the nucleus. Hence bombardment with neutrons is a much easier way to prepare new isotopes of the lighter elements. In fact, carbon-14 is formed naturally in the atmosphere by bombarding nitrogen-14 with neutrons generated by cosmic rays:

$$^{1}_{0}n + ^{14}_{7}N \rightarrow ^{14}_{6}C + ^{1}_{1}p$$

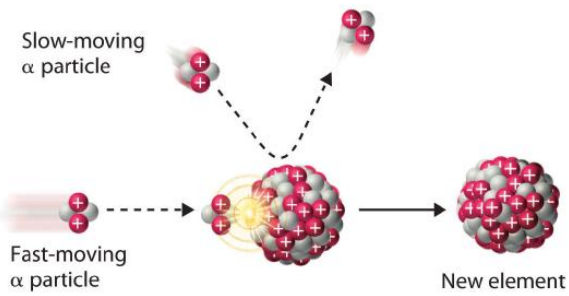


Figure 18.2.3 A Nuclear Transmutation Reaction *Bombarding a target of one element with high-energy nuclei or subatomic particles can create new elements. Electrostatic repulsions normally prevent a positively charged particle from colliding and reacting with a positively charged nucleus. If the positively charged particle is moving at a very high speed, however, its kinetic energy may be great enough to overcome the electrostatic repulsions, and it may collide with the target nucleus. Such collisions can result in a nuclear transmutation reaction.*

Example 18.2.3

In 1933, Frédéric Joliot and Iréne Joliot-Curie (daughter of Marie and Pierre Curie) prepared the first artificial radioactive isotope by bombarding aluminum-27 with α particles. For each ^{27}Al that reacted, one neutron was released. Identify the product nuclide and write a balanced nuclear equation for this transmutation reaction.

Given: reactants in a nuclear transmutation reaction

Asked for: product nuclide and balanced nuclear equation

Strategy:

A Based on the reactants and one product, identify the other product of the reaction. Use conservation of mass and charge to determine the values of Z and A of the product nuclide and thus its identity.

B Write the balanced nuclear equation for the reaction.

Solution:

A Bombarding an element with α particles usually produces an element with an atomic number that is 2 greater than the atomic number of the target nucleus. Thus we expect that aluminum (Z = 13) will be converted to phosphorus (Z = 15). With one neutron released, conservation of mass requires that the mass number of the other product be 3 greater than the mass number of the target.

In this case, the mass number of the target is 27, so the mass number of the product will be 30. The second product is therefore phosphorus-30, $^{30}_{15}P$

B The balanced nuclear equation for the reaction is as follows:

$$^{4}_{2}\alpha + ^{27}_{13}Al \rightarrow ^{30}_{15}P + ^{1}_{0}n$$

Exercise

Because all isotopes of technetium are radioactive and have short half-lives, it does not exist in nature. Technetium can, however, be prepared by nuclear transmutation reactions. For example, bombarding a molybdenum-96 target with deuterium nuclei $^{2}_{1}H$ produces technetium-97. Identify the other product of the reaction and write a balanced nuclear equation for this transmutation reaction.

Answer: neutron, $^{1}_{0}n; ^{96}_{42}Mo + ^{2}_{1}H \rightarrow ^{97}_{43}Tc + ^{1}_{0}n$

We noted earlier in this section that very heavy nuclides, corresponding to $Z \geq 104$, tend to decay by spontaneous fission. Nuclides with slightly lower values of Z, such as the isotopes of uranium (Z = 92) and plutonium (Z = 94), do not undergo spontaneous fission at any significant rate. Some isotopes of these elements, however, such as $^{235}_{92}U$ and $^{239}_{94}Pu$ undergo *induced nuclear fission* when they are bombarded with relatively low-energy neutrons, as shown in the following equation for uranium-235 and in Figure 18.2.4:

$$^{1}_{0}n + ^{235}_{92}U \rightarrow ^{236}_{92}U \rightarrow ^{141}_{56}Ba + ^{92}_{36}Kr + 3^{1}_{0}n$$

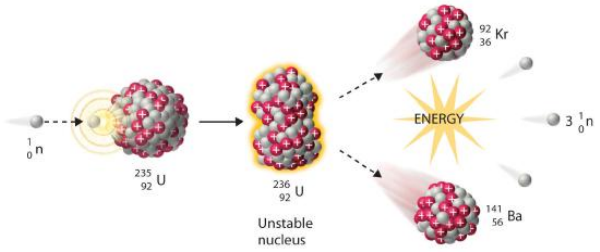


Figure 18.2.4 Neutron-Induced Nuclear Fission *Collision of a relatively slow-moving neutron with a fissile nucleus can split it into two smaller nuclei with the same or different masses. Neutrons are also released in the process, along with a great deal of energy.*

Any isotope that can undergo a nuclear fission reaction when bombarded with neutrons is called a *fissile isotope*.

During nuclear fission, the nucleus usually divides asymmetrically rather than into two equal parts, as shown in Figure 18.2.4. Moreover, every fission event of a given nuclide does not give the same products; more than 50 different fission modes have been identified for uranium-235, for example. Consequently, nuclear fission of a fissile nuclide can never be described by a single equation. Instead, as shown in Figure 18.2.5 , a distribution of many pairs of fission products with different yields is obtained, but the mass ratio of each pair of fission products produced by a single fission event is always roughly 3:2.

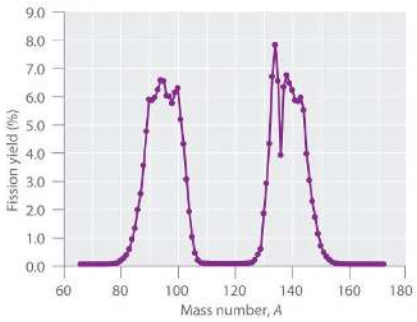


Figure 18.2.5 Mass Distribution of Nuclear Fission Products of ^{235}U *Nuclear fission usually produces a range of products with different masses and yields, although the mass ratio of each pair of fission products from a fission event is approximately 3:2. As shown in this plot, more than 50 different fission products are known for ^{235}U.*

Data source: T. R. England and B. F. Rider, Los Alamos National Laboratory, LA-UR-94-3106, ENDF-349 (1993).

Synthesis of Transuranium Elements

Uranium (Z = 92) is the heaviest naturally occurring element. Consequently, all the elements with Z > 92, the transuranium elementsAn artificial element that has been prepared by bombarding suitable target nuclei with smaller particles., are artificial and have been prepared by bombarding suitable target nuclei with smaller particles. The first of the transuranium elements to be prepared was neptunium (Z = 93), which was synthesized in 1940 by bombarding a ^{238}U target with neutrons. As shown in Equation 18.2.21, this reaction occurs in two steps. Initially, a neutron combines with a ^{238}U nucleus to form ^{239}U, which is unstable and undergoes beta decay to produce ^{239}Np:

$$ {}^{1}_{0}n + {}^{238}_{92}U \rightarrow {}^{239}_{92}U \rightarrow {}^{239}_{93}Np + {}^{0}_{-1}\beta $$

Subsequent beta decay of ^{239}Np produces the second transuranium element, plutonium (Z = 94):

$$ {}^{239}_{93}Np \rightarrow {}^{239}_{94}Pu + {}^{0}_{-1}\beta $$

Bombarding the target with more massive nuclei creates elements that have atomic numbers significantly greater than that of the target nucleus (Table 20.2.2). Such techniques have resulted in the creation of the superheavy elements 114 and 116, both of which lie in or near the “island of stability” discussed in Section 18.1 .

Table 20.2.2 Some Reactions Used to Synthesize Transuranium Elements

$ {}^{239}_{94}Pu + {}^{4}_{2}\alpha \rightarrow {}^{242}_{96}Cm + {}^{1}_{0}n $
$ {}^{239}_{94}Pu + {}^{4}_{2}\alpha \rightarrow {}^{241}_{95}Am + {}^{1}_{1}p + {}^{1}_{0}n $
$ {}^{242}_{96}Cm + {}^{4}_{2}\alpha \rightarrow {}^{243}_{97}Bk + {}^{1}_{1}p + 2{}^{1}_{0}n $
$ {}^{253}_{99}Es + {}^{4}_{2}\alpha \rightarrow {}^{256}_{101}Md + {}^{1}_{0}n $
$ {}^{238}_{92}U + {}^{12}_{6}C \rightarrow {}^{246}_{98}Cf + 4{}^{1}_{0}n $
$ {}^{252}_{98}Cf + {}^{10}_{5}B \rightarrow {}^{256}_{103}Lr + 6{}^{1}_{0}n $

A device called a *particle accelerator* is used to accelerate positively charged particles to the speeds needed to overcome the electrostatic repulsions between them and the target nuclei by using electrical and magnetic fields. Operationally, the simplest particle accelerator is the linear accelerator (Figure 18.2.6), in which a beam of particles is injected at one end of a long evacuated tube. Rapid alternation of the polarity of the electrodes along the tube causes the particles to be alternately accelerated toward a region of opposite charge and repelled by a region with the same charge, resulting in a tremendous acceleration as the particle travels down the tube. A modern linear accelerator such as the Stanford Linear Accelerator (SLAC) at Stanford University is about 2 miles long.

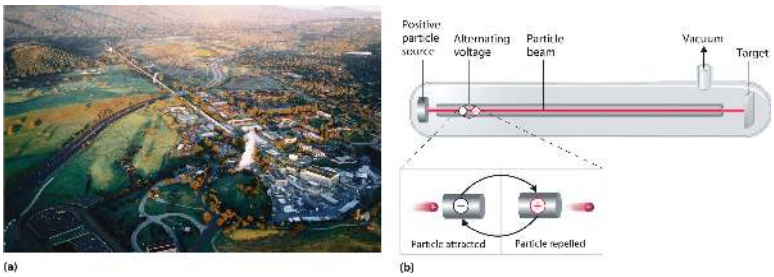


Figure 18.2.6 A Linear Particle Accelerator *(a) An aerial view of the SLAC, the longest linear particle accelerator in the world; the overall length of the tunnel is 2 miles. (b) Rapidly reversing the polarity of the electrodes in the tube causes the charged particles to be alternately attracted as they enter one section of the tube and repelled as they leave that section. As a result, the particles are continuously accelerated along the length of the tube.*

To achieve the same outcome in less space, a particle accelerator called a *cyclotron* forces the charged particles to travel in a circular path rather than a linear one. The particles are injected into the center of a ring and accelerated by rapidly alternating the polarity of two large D-shaped electrodes above and below the ring, which accelerates the particles outward along a spiral path toward the target.

The length of a linear accelerator and the size of the D-shaped electrodes in a cyclotron severely limit the kinetic energy that particles can attain in these devices. These limitations can be overcome by using a *synchrotron*, a hybrid of the two designs. A synchrotron contains an evacuated tube similar to that of a linear accelerator, but the tube is circular and can be more than a mile in diameter (Figure 19.2.7). Charged particles are accelerated around the circle by a series of magnets whose polarities rapidly alternate.



Figure 18.2.7 A Synchrotron *An aerial photograph of what is currently the world's most powerful particle accelerator, the Tevatron at the Fermi National Accelerator Laboratory (Fermilab) in Illinois. The large tube characteristic of a synchrotron is 4 miles in circumference, contains 1000 superconducting magnets cooled by liquid helium, and can accelerate a beam of protons to almost the speed of light, giving them an energy greater than 1 TeV (teraelectronvolt = 10^3 GeV = 10^{12} eV) for collisions with other particles.*

Summary

In **nuclear decay reactions (or radioactive decay)**, the *parent nucleus* is converted to a more stable *daughter nucleus*. Nuclei with too many neutrons decay by converting a neutron to a proton, whereas nuclei with too few neutrons decay by converting a proton to a neutron. Very heavy nuclei (with $A \geq 200$ and $Z > 83$) are unstable and tend to decay by emitting an **α particle**. When an unstable nuclide undergoes radioactive decay, the total number of nucleons is conserved, as is the total positive charge. Six different kinds of nuclear decay reactions are known. **Alpha decay** results in the emission of an α particle, $^4_2\alpha$ and produces a daughter nucleus with a mass number that is lower by 4 and an atomic number that is lower by 2 than the parent nucleus. **Beta decay** converts a neutron to a proton and emits a high-energy electron, producing a daughter nucleus with the same mass number as the parent and an atomic number that is higher by 1. **Positron emission** is the opposite of beta decay and converts a proton to a neutron plus a positron. Positron emission does not change the mass number of the nucleus, but the atomic number of the daughter nucleus is lower by 1 than the parent. In **electron capture (EC)**, an electron in an inner shell reacts with a proton to produce a neutron, with emission of an x-ray. The mass number does not change, but the atomic number of the daughter is lower by 1 than the parent. In **gamma emission**, a daughter nucleus in a *nuclear excited state* undergoes a transition to a lower-energy state by emitting a γ ray. Very heavy nuclei with high neutron-to-proton ratios can undergo **spontaneous fission**, in which the nucleus breaks into two pieces that can have different atomic numbers and atomic masses with the release of neutrons. Many very heavy nuclei decay via a **radioactive decay series**—a succession of some combination of alpha- and beta-decay reactions. In **nuclear transmutation reactions**, a target nucleus is bombarded with energetic subatomic particles to give a product nucleus that is more massive than the original. All **transuranium elements**—elements with $Z > 92$—are artificial and must be prepared by nuclear transmutation reactions. These reactions are carried out in *particle accelerators* such as *linear accelerators*, *cyclotrons*, and *synchrotrons*.

Key Takeaway

- Nuclear decay reactions occur spontaneously under all conditions and produce more stable daughter nuclei, whereas nuclear transmutation reactions are induced and form a product nucleus that is more massive than the starting material.

Key Equations

alpha decay

Equation 18.2.1: $^{A}_{Z}X \rightarrow ^{A-4}_{Z-2}X' + ^{4}_{2}\alpha$

beta decay

Equation 18.2.4: $^{A}_{Z}X \rightarrow ^{A}_{Z+1}X' + ^{0}_{-1}\beta$

positron emission

Equation 18.2.7: $^{A}_{Z}X \rightarrow ^{A}_{Z-1}X' + ^{0}_{+1}\beta$

electron capture

Equation 18.2.10: $^{A}_{Z}X + ^{0}_{-1}e \rightarrow ^{A}_{Z-1}X' + x-ray$

gamma emission

Equation 18.2.15: $^{A}_{Z}X^{*} \rightarrow ^{A}_{Z}X' + ^{0}_{0}\gamma$

Conceptual Problems

1. Describe the six classifications of nuclear decay reactions. What is the most common mode of decay for elements that have heavy nuclei? Why?
2. Complete the following table for these five nuclear reactions.

	Alpha Decay	Beta Decay	Gamma Emission	Positron Emission	Electron Capture
identity of particle or radiation	helium-4 nucleus				
mass number of parent − mass number of daughter	4				
atomic number of parent − atomic number of daughter		−1			
effect on neutron-to-proton ratio		decreases			

3. What is the most common decay process for elements in row 5 of the periodic table that contain too few neutrons for the number of protons present? Why?
4. Explain the difference between the symbols e^{-} and β^{-}. What is the difference in meaning between the symbols $^{4}_{2}He$ and $^{4}_{2}\alpha$
5. What is a mass number? Which particles have a mass number of zero?
6. What are the key differences between the equations written for chemical reactions and for nuclear reactions? How are they similar?
7. Can all the kinds of nuclear decay reactions discussed be characterized by the general equation: parent → daughter + particle? Explain your answer.
8. Which types of nuclear decay reactions conserve both mass number and atomic number? In which do the parent and daughter nuclei have the same mass number but different atomic numbers? Which do not convert one element to another?
9. Describe a radioactive decay series. How many series occur naturally? Of these, which one no longer occurs in nature? Why?
10. Only nine naturally occurring elements have an atomic number greater than 83, and all of them are radioactive. Except for some isotopes of uranium that have a very long half-life, the half-lives of the heavy elements are so short that these elements should have been completely converted to lighter, more stable elements long ago. Why are these elements still present in nature?

11. Why are neutrons preferred to protons when preparing new isotopes of the lighter elements?
12. Why are particle accelerators and cyclotrons needed to create the transuranium elements?

Answers

3. Both positron decay and electron capture increase the neutron-to-proton ratio; electron capture is more common for heavier elements such those of row 5.
2.
1.
4.
5. The mass number is the sum of the numbers of protons and neutrons present. Particles with a mass number of zero include β particles (electrons) and positrons; gamma rays and x-rays also have a mass number of zero.
6.
7.
8.
9.
10.
11. Unlike protons, neutrons have no charge, which minimizes the electrostatic barrier to colliding and reacting with a positively charged nucleus.
12.

Numerical Problems

1. What type of particle is emitted in each nuclear reaction?
    1. $^{238}Pu \rightarrow {}^{234}U$
    2. $^{32}Si \rightarrow {}^{32}P$
    3. $^{18}F \rightarrow {}^{18}O$
    4. $^{206}Tl \rightarrow {}^{206}Pb$
2. What type of particle is emitted in each nuclear reaction?
    1. $^{230}Th \rightarrow {}^{226}Ra$
    2. $^{224}Rn \rightarrow {}^{224}Fr$
    3. $^{210}Bi \rightarrow {}^{206}Tl$
    4. $^{36}Cl \rightarrow {}^{36}S$
3. Predict the mode of decay and write a balanced nuclear reaction for each isotope.
    1. ^{235}U
    2. ^{254}Es
    3. ^{36}S
    4. ^{99}Mo
4. Predict the mode of decay and write a balanced nuclear reaction for each isotope.
    1. ^{13}N
    2. ^{231}Pa
    3. ^{7}Be
    4. ^{77}Ge
5. Balance each nuclear reaction.
    1. $^{208}Po \rightarrow \alpha + Pb$
    2. $^{226}Ra \rightarrow \alpha + Rn$
    3. $^{228}Th \rightarrow Ra + \alpha + \gamma$
    4. $^{231}Pa \rightarrow Ac + \alpha + \gamma$
    5. $Ho \rightarrow {}^{166}Er + \beta^{-} + \gamma$

6. Ac → ^{226}Th + β^- + γ

6. Complete each nuclear reaction.

1. $^{210}_{84}Po \rightarrow ^{206} Pb$
2. $^{217}_{85}At \rightarrow Bi + \alpha$
3. $Ra \rightarrow ^{220}_{86} Rn + \alpha$
4. $^{208}Tl \rightarrow_{82} Pb + \beta^-$
5. $Np \rightarrow ^{239} Pu + \beta^-$
6. $Fe \rightarrow ^{52} Mn + \beta^+ + \gamma$

7. Write a balanced nuclear equation for each reaction.

1. β^- decay of ^{87}Rb
2. β^+ decay of ^{20}Mg
3. α decay of ^{268}Mt

8. Write a balanced nuclear equation for each reaction.

1. β^- decay of ^{45}K
2. β^+ decay of ^{41}Sc
3. α decay of ^{146}Sm

9. The decay products of several isotopes are listed here. Identify the type of radiation emitted and write a balanced nuclear equation for each.

1. ^{218}Po → ^{214}Pb
2. ^{32}Si → ^{32}P
3. an excited state of an iron-57 nucleus decaying to its ground state
4. conversion of thallium-204 to lead-204

10. The decay products of several isotopes are listed here. Identify the type of radiation emitted and write a balanced nuclear equation for each.

1. ^{218}Po → ^{218}At
2. ^{216}Po → ^{212}Pb
3. bismuth-211 converted to thallium-207
4. americium-242 converted to rhodium-107 with the emission of four neutrons

11. Predict the most likely mode of decay and write a balanced nuclear reaction for each isotope.

1. ^{238}U
2. ^{208}Po
3. ^{40}S
4. molybdenum-93*m*

12. Predict the most likely mode of decay and write a balanced nuclear reaction for each isotope.

1. ^{16}N
2. ^{224}Th
3. ^{118}In
4. ^{64}Ge

13. For each nuclear reaction, identify the type(s) of decay and write a balanced nuclear equation.

1. ^{216}Po → ? + At
2. ? → α + ^{231}Pa
3. ^{228}Th → ? + α + γ
4. ^{231}Pa → ? + β^- + γ

14. For each nuclear reaction, identify the type(s) of decay and write a balanced nuclear equation.

1. $^{212}Po \rightarrow {}^{208}Pb + ?$
2. $^{192}Ir \rightarrow Pt + ?$
3. $^{241}Am \rightarrow {}^{57}Fe + {}^{184}? + ?$
4. $Ge \rightarrow {}^{77}Ge + ?$

15. Identify the parent isotope and write a balanced nuclear reaction for each process.
    1. Lead-205 is formed via an alpha emission.
    2. Titanium-46 is formed via beta and gamma emission.
    3. Argon-36 is formed via a beta decay and a gamma emission.
16. Identify the parent isotope and write a balanced nuclear reaction for each process.
    1. Iodine-130 is formed by ejecting an electron and a gamma ray from a nucleus.
    2. Uranium-240 is formed by alpha decay.
    3. Curium-247 is formed by releasing a helium dication and a gamma ray.
17. Write a balanced nuclear equation for each process.
    1. Bromine undergoes a decay and produces a gas with an atomic mass of 80 amu.
    2. An element emits two neutrons while decaying into two metals, each of which can be extracted and converted to chlorides with the formula MCl_2. The masses of the two salts are 162.9 and 210.9 g/mol, respectively.
18. Write a balanced nuclear equation for each process.
    1. An unknown element emits γ rays plus particles that are readily blocked by paper. The sample also contains a substantial quantity of tin-104.
    2. An unstable element undergoes two different decay reactions: beta decay to produce a material with a mass of 222 amu and alpha decay to astatine.
19. Bombarding ^{249}Cf with ^{12}C produced a transuranium element with a mass of 257 amu, plus several neutral subatomic particles. Identify the element and write a nuclear reaction for this transmutation.
20. One transuranium element, ^{253}Es, is prepared by bombarding ^{238}U with 15 neutrons. What is the other product of this reaction? Write a balanced transmutation reaction for this conversion.
21. Complete this radioactive decay series:

$$^{223}_{88}Rn \xrightarrow{\alpha} Rn \xrightarrow{\alpha} Po \xrightarrow{\alpha} Pb \xrightarrow{\beta} Bi \xrightarrow{\alpha} Tl \xrightarrow{\beta} Pb$$

22. Complete each nuclear fission reaction.
    1. $^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{90}_{36}Kr + ? + 2{}^{1}_{0}n$
    2. $? + {}^{1}_{0}n \rightarrow {}^{140}Cs + {}^{96}Y + 4{}^{1}_{0}n$
23. Complete each nuclear fission reaction.
    1. $^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{145}_{57}La + ? + 3{}^{1}_{0}n$
    2. $? + {}^{1}_{0}n \rightarrow {}^{95}_{42}Mo + {}^{145}_{57}La + 2{}^{1}_{0}n + 7\,{}^{0}_{-1}\beta$
24. A stable nuclide absorbs a neutron, emits an electron, and then splits into two α particles. Identify the nuclide.
25. Using ^{18}O, how would you synthesize an element with atomic number 106 from ^{249}Cf? Write a balanced nuclear equation for the reaction.
26. Using ^{10}B and ^{252}Cf, how would you synthesize an element with atomic number 103? Write a balanced nuclear equation for the reaction.

3. 1. α decay; $^{235}_{92}U \rightarrow {}^{4}_{2}\alpha + {}^{231}_{90}Th$
   2. α decay; $^{254}_{99}Es \rightarrow {}^{4}_{2}\alpha + {}^{250}_{97}Bk$

Answers

1. 3. β decay; $^{36}_{16}S \rightarrow {}^{0}_{-1}\beta + {}^{36}_{17}Cl$
   4. β decay; $^{99}_{42}Mo \rightarrow {}^{0}_{-1}\beta + {}^{99m}_{43}Tc$

4.

5. 1. $^{208}_{84}Po \rightarrow ^{4}_{2}\alpha + ^{204}_{82}Pb$
   2. $^{226}_{88}Ra \rightarrow ^{4}_{2}\alpha + ^{222}_{86}Rn$
   3. $^{228}_{90}Th \rightarrow ^{4}_{2}\alpha + \gamma + ^{224}_{88}Ra$
   4. $^{231}_{91}Pa \rightarrow ^{4}_{2}\alpha + \gamma + ^{227}_{89}Ac$
   5. $^{166}_{67}Ho \rightarrow ^{0}_{-1}\beta + \gamma + ^{166}_{68}Er$
   6. $^{226}_{89}Ac \rightarrow ^{0}_{-1}\beta + \gamma + ^{226}_{90}Th$
6.
7. 1. $^{87}_{37}Rb \rightarrow ^{0}_{-1}\beta + ^{87}_{38}Sr$
   2. $^{20}_{12}Mg \rightarrow ^{0}_{+1}\beta + ^{20}_{11}Na$
   3. $^{268}_{109}Mt \rightarrow ^{4}_{2}\alpha + ^{264}_{107}Bh$
8.
9. 1. α particle; $^{218}_{84}Po \rightarrow ^{4}_{2}\alpha + ^{214}_{82}Pb$
   2. β particle; $^{32}_{14}Si \rightarrow ^{0}_{-1}\beta + ^{32}_{15}P$
   3. γ ray; $^{57m}_{26}Fe \rightarrow \gamma + ^{57}_{26}Fe$
   4. β particle; $^{204}_{81}Tl \rightarrow ^{0}_{-1}\beta + ^{204}_{82}Pb$
10.
11. 1. α emission; $^{238}_{92}U \rightarrow ^{4}_{2}\alpha + ^{234}_{90}Th$
    2. α emission; $^{208}_{84}Po \rightarrow ^{4}_{2}\alpha + ^{204}_{82}Pb$
    3. β emission; $^{40}_{16}S \rightarrow ^{0}_{-1}\beta + ^{40}_{17}Cl$
    4. γ emission; $^{93m}_{42}Mo \rightarrow \gamma + ^{93}_{42}Mo$
12.
13. 1. β decay; $^{216}_{84}Po \rightarrow ^{0}_{-1}\beta + ^{216}_{85}At$
    2. α decay; $^{235}_{93}Np \rightarrow ^{4}_{2}\alpha + ^{231}_{91}Pa$
    3. α decay; γ emission; $^{228}_{90}Th \rightarrow ^{4}_{2}\alpha + \gamma + ^{224}_{88}Ra$
    4. β decay, γ emission; $^{231}_{91}Pa \rightarrow ^{0}_{-1}\beta + \gamma + ^{231}_{92}U$
14.
15.
16.
17. 1. $^{80}_{35}Br \rightarrow ^{0}_{-1}\beta + ^{80}_{36}Kr$
    2. $^{234}_{94}Pu \rightarrow 2^{1}_{0}n + ^{140}_{56}Ba + ^{92}_{38}Sr>$
18.
19. $^{249}_{98}Cf + ^{12}_{6}C \rightarrow 4^{1}_{0}n + ^{257}_{104}Rf$
20.
21.
22.
23. 1. $^{235}_{92}U + ^{1}_{0}n \rightarrow 3^{1}_{0}n + ^{145}_{57}La + ^{88}_{35}Br$
    2. $^{235}_{92}U + ^{1}_{0}n \rightarrow 2^{1}_{0}n + 7\,^{0}_{-1}\beta + ^{95}_{43}Mo + ^{139}_{57}La$
24.
25.
26.

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Chapter 18.3: The Interaction of Nuclear Radiation with Matter

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Learning Objectives

To know the differences between ionizing and nonionizing radiation and their effects on matter.

To identify natural and artificial sources of radiation.

Learning Objective

- To know the differences between ionizing and nonionizing radiation and their effects on matter.

Because nuclear reactions do not typically affect the valence electrons of the atom (although electron capture draws an electron from an orbital of the lowest energy level), they do not directly cause chemical changes. Nonetheless, the particles and the photons emitted during nuclear decay are very energetic, and they can indirectly produce chemical changes in the matter surrounding the nucleus that has decayed. For instance, an α particle is an ionized helium nucleus (He^{2+}) that can act as a powerful oxidant. In this section, we describe how radiation interacts with matter and the some of the chemical and biological effects of radiation.

Ionizing versus Nonionizing Radiation

The effects of radiation on matter are determined primarily by the energy of the radiation, which depends on the nuclear decay reaction that produced it. Nonionizing radiation is relatively low in energy; when it collides with an atom in a molecule or an ion, most or all of its energy can be absorbed without causing a structural or a chemical change. Instead, the kinetic energy of the radiation is transferred to the atom or molecule with which it collides, causing it to rotate, vibrate, or move more rapidly. Because this energy can be transferred to adjacent molecules or ions in the form of heat, many radioactive substances are warm to the touch. Highly radioactive elements such as polonium, for example, have been used as heat sources in the US space program. As long as the intensity of the nonionizing radiation is not great enough to cause overheating, it is relatively harmless, and its effects can be neutralized by cooling.

In contrast, ionizing radiation is higher in energy, and some of its energy can be transferred to one or more atoms with which it collides as it passes through matter. If enough energy is transferred, electrons can be excited to very high energy levels, resulting in the formation of positively charged ions:

$$atom + ionizing\ radiation \rightarrow ion^{+} + e^{-}$$

Molecules that have been ionized in this way are often highly reactive, and they can decompose or undergo other chemical changes that create a cascade of reactive molecules that can damage biological tissues and other materials (Figure 18.3.1). Because the energy of ionizing radiation is very high, we often report its energy in units such as megaelectronvolts (MeV) per particle: 1 MeV/particle = 96 billion J/mol.

The Effects of Ionizing Radiation on Matter

The effects of ionizing radiation depend on four factors:

1. The type of radiation, which dictates how far it can penetrate into matter
2. The energy of the individual particles or photons
3. The number of particles or photons that strike a given area per unit time
4. The chemical nature of the substance exposed to the radiation

The relative abilities of the various forms of ionizing radiation to penetrate biological tissues are illustrated in Figure 18.3.2. Because of its high charge and mass, α radiation interacts strongly with matter. Consequently, it does not penetrate deeply into an object, and it can be stopped by a piece of paper, clothing, or skin. In contrast, γ rays, with no charge and essentially no mass, do not interact strongly with matter and penetrate deeply into most objects, including the human body.



Figure 18.3.1 Radiation Damage

When high-energy particles emitted by radioactive decay interact with matter, they can break bonds or ionize molecules, resulting in changes in physical properties such as ductility or color. The glass electrical

Several inches of lead or more than 12 inches of special concrete are needed to completely stop γ rays. Because β particles are intermediate in mass and charge between α particles and γ rays, their interaction with matter is also intermediate. Beta particles readily penetrate paper or skin, but they can be stopped by a piece of wood or a relatively thin sheet of metal.

insulator on the left has not been exposed to radiation, but the insulator on the right has received intense radiation doses over a long period of time. Radiation damage changed the chemical structure of the glass, causing it to become bright blue.

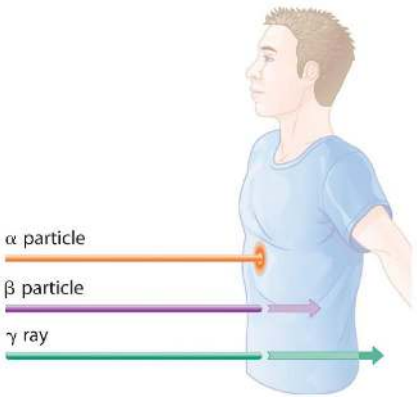


Figure 18.3.2 Depth of Penetration of Ionizing Radiation*The depth of penetration of alpha, beta, and gamma radiation varies with the particle. Because α particles interact strongly with matter, they do not penetrate deeply into the human body. In contrast, β particles do not interact as strongly with matter and penetrate more deeply. Gamma rays, which have no charge, are stopped by only very dense materials and can pass right through the human body without being absorbed.*

Because of their great penetrating ability, γ rays are by far the most dangerous type of radiation when they come from a source *outside* the body. Alpha particles, however, are the most damaging if their source is *inside* the body because internal tissues absorb all of their energy. Thus danger from radiation depends strongly on the type of radiation emitted and the extent of exposure, which allows scientists to safely handle many radioactive materials if they take precautions to avoid, for example, inhaling fine particulate dust that contains alpha emitters. Some properties of ionizing radiation are summarized in Table 18.3.1

Table 18.3.1 Some Properties of Ionizing Radiation

Type	Energy Range (MeV)	Penetration Distance in Water*	Penetration Distance in Air*
α particles	3–9	< 0.05 mm	< 10 cm
β particles	≤ 3	< 4 mm	1 m
x-rays	$<10^{-2}$	< 1 cm	< 3 m
γ rays	10^{-2}–10^{1}	< 20 cm	> 3 m

***Distance at which half of the radiation has been absorbed.**

Wilhelm Röntgen

Born in the Lower Rhine Province of Germany, Röntgen was the only child of a cloth manufacturer and merchant. His family moved to the Netherlands where he showed no particular aptitude in school, but where he was fond of roaming the countryside. Röntgen was expelled from technical school in Utrecht after being unjustly accused of drawing a caricature of one of the teachers. He began studying mechanical engineering in Zurich, which he could enter without having the credentials of a regular student, and received a PhD at the University of Zurich in 1869. In 1876 he became professor of physics.

There are many different ways to measure radiation exposure, or the *dose*. The roentgen (R), which measures the amount of energy absorbed by dry air, can be used to describe quantitative exposure.Named after the German physicist Wilhelm Röntgen (1845–1923; Nobel Prize in Physics, 1901), who discovered x-rays. The roentgen is actually defined as the amount of radiation needed to produce an electrical charge of 2.58×10^{-4} C in 1 kg of dry air. Damage to biological tissues, however, is proportional to the amount of energy absorbed by *tissues*, not air. The most common unit used to measure the effects of radiation on biological tissue is the rad (radiation absorbed dose); the SI equivalent is the *gray* (Gy). The rad is defined as the amount of radiation that causes 0.01 J of energy to be absorbed by 1 kg of matter, and the gray is defined as the amount of radiation that causes 1 J of energy to be absorbed per kilogram:

$$1\ rad = 0.010\ J/kg \quad 1\ Gy = 1\ J/kg$$

Thus a 70 kg human who receives a dose of 1.0 rad over his or her entire body absorbs 0.010 J/70 kg = 1.4×10^{-4} J, or 0.14 mJ. To put this in perspective, 0.14 mJ is the amount of energy transferred to your skin by a 3.8×10^{-5} g droplet of boiling water. Because the energy of the droplet of water is transferred to a relatively large area of tissue, it is harmless. A radioactive particle, however, transfers its energy to a single molecule, which makes it the atomic equivalent of a bullet fired from a high-powered rifle.

Because α particles have a much higher mass and charge than β particles or γ rays, the difference in mass between α and β particles is analogous to being hit by a bowling ball instead of a table tennis ball traveling at the same speed. Thus the amount of tissue damage caused by 1 rad of α particles is much greater than the damage caused by 1 rad of β particles or γ rays. Thus a unit called the rem (roentgen equivalent in man) was devised to describe the *actual* amount of tissue damage caused by a given amount of radiation. The number of rems of radiation is equal to the number of rads multiplied by the *RBE* (relative biological effectiveness) factor, which is 1 for β particles, γ rays, and x-rays and about 20 for α particles. Because actual radiation doses tend to be very small, most measurements are reported in *millirems* (1 mrem = 10^{-3} rem).

Natural Sources of Radiation

We are continuously exposed to measurable background radiation from a variety of natural sources, which, on average, is equal to about 150–600 mrem/yr (Figure 18.3.3). One component of background radiation is *cosmic rays*, high-energy particles and γ rays emitted by the sun and other stars, which bombard Earth continuously. Because cosmic rays are partially absorbed by the atmosphere before they reach Earth's surface, the exposure of people living at sea level (about 30 mrem/yr) is significantly less than the exposure of people living at higher altitudes (about 50 mrem/yr in Denver, Colorado). Every 4 hours spent in an airplane at greater than 30,000 ft adds about 1 mrem to a person's annual radiation exposure.

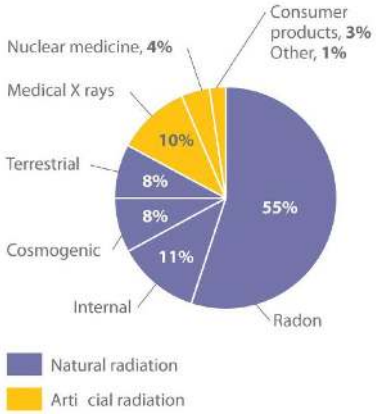


Figure 18.3.3 The Radiation Exposure of a Typical Adult in the United States *The average radiation dose from natural sources for an adult in the United States is about 150–600 mrem/yr. Radon accounts for more than half of an adult's total radiation exposure, whereas background radiation (terrestrial and cosmogenic) and exposure from medical sources account for about 15% each.*

Data source: Office of Civilian Radioactive Waste Management

A second component of background radiation is *cosmogenic radiation*, produced by the interaction of cosmic rays with gases in the upper atmosphere. When high-energy cosmic rays collide with oxygen and nitrogen atoms, neutrons and protons are released. These, in turn, react with other atoms to produce radioactive isotopes, such as ^{14}C:

$$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{14}_{6}C + ^{1}_{1}p$$

The carbon atoms react with oxygen atoms to form CO_2, which is eventually washed to Earth's surface in rain and taken up by plants. About 1 atom in 1×10^{12} of the carbon atoms in our bodies is radioactive ^{14}C, which decays by beta emission. About 5000 ^{14}C nuclei disintegrate in your body during the 15 s or so that it takes you to read this paragraph. Tritium (^{3}H) is also produced in the upper atmosphere and falls to Earth in precipitation. The total radiation dose attributable to ^{14}C is estimated to be 1 mrem/yr, while that due to ^{3}H is about 1000 times less.

The third major component of background radiation is *terrestrial radiation*, which is due to the remnants of radioactive elements that were present on primordial Earth and their decay products. For example, many rocks and minerals in the soil contain small amounts of radioactive isotopes, such as ^{232}Th and ^{238}U, as well as radioactive daughter isotopes, such as ^{226}Ra. The amount of background radiation from these sources is about the same as that from cosmic rays (approximately 30 mrem/yr). These isotopes are also found in small amounts in building materials derived from rocks and minerals, which significantly increases the radiation exposure for people who live in brick or concrete-block houses (60–160 mrem/yr) instead of houses made of wood (10–20 mrem/yr). Our tissues also absorb radiation (about 40 mrem/yr) from naturally occurring radioactive elements that are present in our bodies. For example, the average adult contains about 140 g of potassium as the K^+ ion. Naturally occurring potassium contains 0.0117% ^{40}K, which decays by emitting both a β particle and a γ ray. In the last 20 seconds, about the time it took you to read this paragraph, approximately 40,000 ^{40}K nuclei disintegrated in your body.

By far the most important source of background radiation is *radon*, the heaviest of the noble gases (group 18). Radon-222 is produced during the decay of ^{238}U, and other isotopes of radon are produced by the decay of other heavy elements. Even though radon is chemically inert, all its isotopes are radioactive. For example, ^{222}Rn undergoes two successive alpha-decay events to give ^{214}Pb:

$$^{222}_{86}Rn \rightarrow ^{218}_{84}Po + ^{4}_{2}\alpha \rightarrow ^{214}_{82}Pb + ^{4}_{2}\alpha$$

Because radon is a dense gas, it tends to accumulate in enclosed spaces such as basements, especially in locations where the soil contains greater-than-average amounts of naturally occurring uranium minerals. Under most conditions, radioactive decay of radon poses no problems because of the very short range of the emitted α particle. If an atom of radon happens to be in your lungs when it decays, however, the chemically reactive daughter isotope polonium-218 can become irreversibly bound to molecules in the lung tissue. Subsequent decay of ^{218}Po releases an α particle directly into one of the cells lining the lung, and the resulting damage can eventually cause lung cancer. The ^{218}Po isotope is also readily absorbed by particles in cigarette smoke, which adhere to the surface of the lungs and can hold the radioactive isotope in place. Recent estimates suggest that radon exposure is a contributing factor in about 15% of the deaths due to lung cancer. Because of the potential health problem radon poses, many states require houses to be tested for radon before they can be sold. By current estimates, radon accounts for more than half of the radiation exposure of a typical adult in the United States.

Artificial Sources of Radiation

In addition to naturally occurring background radiation, humans are exposed to small amounts of radiation from a variety of artificial sources. The most important of these are the x-rays used for diagnostic purposes in medicine and dentistry, which are photons with much lower energy than γ rays. A single chest x-ray provides a radiation dose of about 10 mrem, and a dental x-ray about 2–3 mrem. Other minor sources include television screens and computer monitors with cathode-ray tubes, which also produce x-rays. Luminescent paints for watch dials originally used radium, a highly toxic alpha emitter if ingested by those painting the dials. Radium was replaced by tritium (^{3}H) and promethium (^{147}Pr), which emit low-energy β particles that are absorbed by the watch crystal or the glass covering the instrument. Radiation exposure from television screens, monitors, and luminescent dials totals about 2 mrem/yr. Residual fallout from previous atmospheric nuclear-weapons testing is estimated to account for about twice this amount, and the nuclear power industry accounts for less than 1 mrem/yr (about the same as a single 4 h jet flight).

Example 18.3.1

Calculate the annual radiation dose in rads a typical 70 kg chemistry student receives from the naturally occurring ^{40}K in his or her body, which contains about 140 g of potassium (as the K^+ ion). The natural abundance of ^{40}K is 0.0117%. Each 1.00 mol of ^{40}K undergoes 1.05×10^7 decays/s, and each decay event is accompanied by the emission of a 1.32 MeV β particle.

Given: mass of student, mass of isotope, natural abundance, rate of decay, and energy of particle

Asked for: annual radiation dose in rads

Strategy:

A Calculate the number of moles of ^{40}K present using its mass, molar mass, and natural abundance.

B Determine the number of decays per year for this amount of ^{40}K.

C Multiply the number of decays per year by the energy associated with each decay event. To obtain the annual radiation dose, use the mass of the student to convert this value to rads.

Solution:

A The number of moles of ^{40}K present in the body is the total number of potassium atoms times the natural abundance of potassium atoms present as ^{40}K divided by the atomic mass of ^{40}K:

$$moles\ ^{40}K = 140\ \cancel{gK} \times \frac{0.0117\ mol\ ^{40}K}{100\ \cancel{mol\ K}} \times \frac{1\ \cancel{mol\ K}}{40.0\ \cancel{gK}} = 4.10 \times 10^{-4}\ mol\ ^{40}K$$

B We are given the number of atoms of ^{40}K that decay per second in 1.00 mol of ^{40}K, so the number of decays per year is as follows:

$$\dfrac{decays}{year} = 4.10 \times 10^{-4}\ mol\ ^{40}K \times \dfrac{1.05 \times 10^{7}\ decays/\cancel{s}}{1\ \cancel{mol\ ^{40}K}} \times \dfrac{60\ \cancel{s}}{1\ \cancel{min}} \times \dfrac{60\ \cancel{min}}{1\ \cancel{h}} \times \dfrac{24\ \cancel{h}}{1\ \cancel{day}} \times \dfrac{365\ \cancel{day}}{1\ yr}$$

C The total energy the body receives per year from the decay of ^{40}K is equal to the total number of decays per year multiplied by the energy associated with each decay event:

$$total\ energy\ per\ year = \frac{1.36 \times 10^{11}\ \cancel{decays}}{yr} \times \frac{1.32\ \cancel{MeV}}{\cancel{decay}} \times \frac{10^6\ \cancel{eV}}{\cancel{MeV}} \times \frac{1.602 \times 10^{-19}\ J}{\cancel{eV}}$$

$$= 2.87 \times 10^{-2}\ J/yr$$

We use the definition of the rad (1 rad = 10^{-2} J/kg of tissue) to convert this figure to a radiation dose in rads. If we assume the dose is equally distributed throughout the body, then the radiation dose per year is as follows:

$$radiation\ dose\ per\ year = \frac{2.87 \times 10^{-2}\ \cancel{J}/yr}{70\ \cancel{kg}} \times \frac{1\ rad}{1 \times 10^{-2}\ \cancel{J}/\cancel{kg}}$$

$$= 4.10 \times 10^{-2}\ rad/yr = 41\ mrad/yr$$

This corresponds to almost half of the normal background radiation most people experience.

Exercise

Because strontium is chemically similar to calcium, small amounts of the Sr^{2+} ion are taken up by the body and deposited in calcium-rich tissues such as bone, using the same mechanism that is responsible for the absorption of Ca^{2+}. Consequently, the radioactive strontium (^{90}Sr) found in fission waste and released by atmospheric nuclear-weapons testing is a major health concern. A normal 70 kg human body has about 280 mg of strontium, and each mole of ^{90}Sr undergoes

4.55×10^{17} decays/s by the emission of a 0.546 MeV β particle. What would be the annual radiation dose in rads for a 70 kg person if 0.10% of the strontium ingested were ^{90}Sr?

Answer: 5.7×10^{3} rad/yr (which is 10 times the fatal dose)

Assessing the Impact of Radiation Exposure

One of the more controversial public policy issues debated today is whether the radiation exposure from artificial sources, when combined with exposure from natural sources, poses a significant risk to human health. The effects of single radiation doses of different magnitudes on humans are listed in Table 18.3.2. Because of the many factors involved in radiation exposure (length of exposure, intensity of the source, and energy and type of particle), it is difficult to quantify the specific dangers of one radioisotope versus another. Nonetheless, some general conclusions regarding the effects of radiation exposure are generally accepted as valid.

Table 18.3.2 The Effects of a Single Radiation Dose on a 70 kg Human

Dose (rem)	Symptoms/Effects
< 5	no observable effect
5–20	possible chromosomal damage
20–100	temporary reduction in white blood cell count
50–100	temporary sterility in men (up to a year)
100–200	mild radiation sickness, vomiting, diarrhea, fatigue; immune system suppressed; bone growth in children retarded
> 300	permanent sterility in women
> 500	fatal to 50% within 30 days; destruction of bone marrow and intestine
> 3000	fatal within hours

Radiation doses of 600 rem and higher are invariably fatal, while a dose of 500 rem kills half the exposed subjects within 30 days. Smaller doses (≤ 50 rem) appear to cause only limited health effects, even though they correspond to tens of years of natural radiation. This does not, however, mean that such doses have no ill effects; they may cause long-term health problems, such as cancer or genetic changes that affect offspring. The possible detrimental effects of the much smaller doses attributable to artificial sources (< 100 mrem/yr) are more difficult to assess.

The tissues most affected by large, whole-body exposures are bone marrow, intestinal tissue, hair follicles, and reproductive organs, all of which contain rapidly dividing cells. The susceptibility of rapidly dividing cells to radiation exposure explains why cancers are often treated by radiation. Because cancer cells divide faster than normal cells, they are destroyed preferentially by radiation. Long-term radiation-exposure studies on fruit flies show a linear relationship between the number of genetic defects and both the magnitude of the dose and the exposure time. In contrast, similar studies on mice show a much lower number of defects when a given dose of radiation is spread out over a long period of time rather than received all at once. Both patterns are plotted in Figure 18.3.4, but which of the two is applicable to humans? According to one hypothesis, mice have very low risk from low doses because their bodies have ways of dealing with the damage caused by natural radiation. At much higher doses, however, their natural repair mechanisms are overwhelmed, leading to irreversible damage. Because mice are biochemically much more similar to humans than are fruit flies, many scientists believe that this model also applies to humans. In contrast, the linear model assumes that *all* exposure to radiation is intrinsically damaging and suggests that stringent regulation of low-level radiation exposure is necessary. Which view is more accurate? The answer—while yet unknown—has extremely important consequences for regulating radiation exposure.

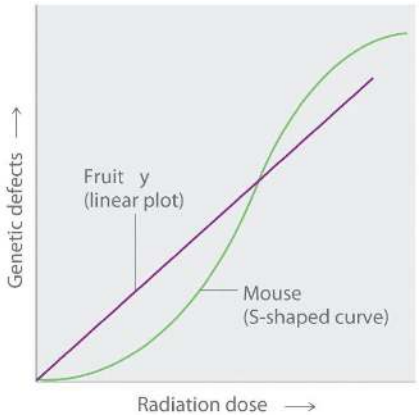


Figure 18.3.4 Two Possible Relationships between the Number of Genetic Defects and Radiation Exposure *Studies on fruit flies show a linear relationship between the number of genetic defects and the magnitude of the radiation dose and exposure time, which is consistent with a cumulative effect of radiation. In contrast, studies on mice show an S-shaped curve, which suggests that the number of defects is lower when radiation exposure occurs over a longer time. Which of these relationships is more applicable to humans is a matter of considerable debate.*

Summary

The effects of radiation on matter depend on the energy of the radiation. **Nonionizing radiation** is relatively low in energy, and the energy is transferred to matter in the form of heat. **Ionizing radiation** is relatively high in energy, and when it collides with an atom, it can completely remove an electron to form a positively charged ion that can damage biological tissues. Alpha particles do not penetrate very far into matter, whereas γ rays penetrate more deeply. Common units of radiation exposure, or dose, are the **roentgen (R)**, the amount of energy absorbed by dry air, and the **rad (radiation absorbed dose)**, the amount of radiation that produces 0.01 J of energy in 1 kg of matter. The **rem (roentgen equivalent in man)** measures the actual amount of tissue damage caused by a given amount of radiation. Natural sources of radiation include *cosmic radiation*, consisting of high-energy particles and γ rays emitted by the sun and other stars; *cosmogenic radiation*, which is produced by the interaction of cosmic rays with gases in the upper atmosphere; and *terrestrial radiation*, from radioactive elements present on primordial Earth and their decay products. The risks of ionizing radiation depend on the intensity of the radiation, the mode of exposure, and the duration of the exposure.

Key Takeaway

- Nonionizing radiation is relatively low in energy and can be used as a heat source, whereas ionizing radiation, which is higher in energy, can penetrate biological tissues and is highly reactive.

Key Equation

rad

Equation 18.3.2: 1 rad = 0.01 J/kg

Conceptual Problems

1. Why are many radioactive substances warm to the touch? Why do many radioactive substances glow?
2. Describe the differences between nonionizing and ionizing radiation in terms of the intensity of energy emitted and the effect each has on an atom or molecule after collision. Which nuclear decay reactions are more likely to produce ionizing radiation?

nonionizing radiation?

3. Would you expect nonionizing or ionizing radiation to be more effective at treating cancer? Why?
4. Historically, concrete shelters have been used to protect people from nuclear blasts. Comment on the effectiveness of such shelters.
5. Gamma rays are a very high-energy radiation, yet α particles inflict more damage on biological tissue. Why?
6. List the three primary sources of naturally occurring radiation. Explain the factors that influence the dose that one receives throughout the year. Which is the largest contributor to overall exposure? Which is the most hazardous?
7. Because radon is a noble gas, it is inert and generally unreactive. Despite this, exposure to even low concentrations of radon in air is quite dangerous. Describe the physical consequences of exposure to radon gas. Why are people who smoke more susceptible to these effects?
8. Most medical imaging uses isotopes that have extremely short half-lives. These isotopes usually undergo only one kind of nuclear decay reaction. Which kind of decay reaction is usually used? Why? Why would a short half-life be preferred in these cases?
9. Which would you prefer: one exposure of 100 rem, or 10 exposures of 10 rem each? Explain your rationale.

Answers

3. Ionizing radiation is higher in energy and causes greater tissue damage, so it is more likely to destroy cancerous cells.
4.
5.
6.
7.
8.
9. Ten exposures of 10 rem are less likely to cause major damage.

Numerical Problems

1. A 2.14 kg sample of rock contains 0.0985 g of uranium. How much energy is emitted over 25 yr if 99.27% of the uranium is $^{238}_{92}U$, which has a half-life of 4.46×10^9 yr, if each decay event is accompanied by the release of 4.039 MeV? If a 180 lb individual absorbs all of the emitted radiation, how much radiation has been absorbed in rads?
2. There is a story about a “radioactive boy scout” who attempted to convert thorium-232, which he isolated from about 1000 gas lantern mantles, to uranium-233 by bombarding the thorium with neutrons. The neutrons were generated via bombarding an aluminum target with α particles from the decay of americium-241, which was isolated from 100 smoke detectors. Write balanced nuclear reactions for these processes. The “radioactive boy scout” spent approximately 2 h/day with his experiment for 2 yr. Assuming that the alpha emission of americium has an energy of 5.24 MeV/particle and that the americium-241 was undergoing 3.5×10^6 decays/s, what was the exposure of the 60.0 kg scout in rads? The intrepid scientist apparently showed no ill effects from this exposure. Why?

Contributors

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Chapter 18.4: Thermodynamic Stability of the Atomic Nucleus

Learning Objective

- To calculate a mass-energy balance and a nuclear binding energy.
- To understand the differences between nuclear fission and fusion.

Nuclear reactions, like chemical reactions, are accompanied by changes in energy. The energy changes in nuclear reactions, however, are enormous compared with those of even the most energetic chemical reactions. In fact, the energy changes in a typical nuclear reaction are so large that they result in a measurable change of mass. In this section, we describe the relationship between mass and energy in nuclear reactions and show how the seemingly small changes in mass that accompany nuclear reactions result in the release of enormous amounts of energy.

Mass–Energy Balance

The relationship between mass (m) and energy (E) was introduced in Chapter 2 and is expressed in the following equation:

$$E = mc^2$$

where c is the speed of light (2.998×10^8 m/s), and E and m are expressed in units of joules and kilograms, respectively. Albert Einstein first derived this relationship in 1905 as part of his special theory of relativity: the mass of a particle is directly proportional to its energy. Thus according to Equation 18.4.1, every mass has an associated energy, and similarly, any reaction that involves a change in energy must be accompanied by a change in mass. This implies that all exothermic reactions should be accompanied by a decrease in mass, and all endothermic reactions should be accompanied by an increase in mass. Given the law of conservation of mass, how can this be true? (For more information on the conservation of mass, see Chapter 11.) The solution to this apparent contradiction is that *chemical reactions are indeed accompanied by changes in mass*, but these changes are simply too small to be detected.This situation is similar to the wave–particle duality discussed in Chapter 2. As you may recall, all particles exhibit wavelike behavior, but the wavelength is inversely proportional to the mass of the particle (actually, to its momentum, the product of its mass and velocity). Consequently, wavelike behavior is detectable only for particles with very small masses, such as electrons. For example, the chemical equation for the combustion of graphite to produce carbon dioxide is as follows:

$$C\,(graphite) + \frac{1}{2}O_2\,(g) \rightarrow CO - 2 \quad \Delta H^o = -393.5\ kJ/mol$$

Combustion reactions are typically carried out at constant pressure, and under these conditions, the heat released or absorbed is equal to ΔH. As you learned in Chapter 15, when a reaction is carried out at constant volume, the heat released or absorbed is equal to ΔE. For most chemical reactions, however, $\Delta E \approx \Delta H$. If we rewrite Einstein's equation as

$$\Delta E = (\Delta m)\, c^2$$

we can rearrange the equation to obtain the following relationship between the change in mass and the change in energy:

$$\Delta m = \frac{\Delta E}{c^2}$$

Because 1 J = 1 $(kg \cdot m^2)/s^2$, the change in mass is as follows:

$$\Delta m = \frac{-393.5\ kJ/mol}{\left(2.998 \times 10^8\right)^2} = \frac{-3.935 \times 10^5 \left(kg \cdot \cancel{m^2}\right) / \left(\cancel{s^2} \cdot mol\right)}{\left(2.998 \times 10^8\ \cancel{m}/\cancel{s}\right)^2} = -4.38 \times 10^{-12}\ kg$$

This is a mass change of about 3.6×10^{-10} g/g carbon that is burned, or about 100-millionths of the mass of an electron per atom of carbon. In practice, this mass change is much too small to be measured experimentally and is negligible.

In contrast, for a typical nuclear reaction, such as the radioactive decay of ^{14}C to ^{14}N and an electron (a β particle), there is a much larger change in mass:

$$^{14}C \rightarrow {}^{14}N + {}^{0}_{-1}\beta$$

We can use the experimentally measured masses of subatomic particles and common isotopes given in the tables below to calculate the change in mass directly.

Experimentally Measured Masses of Selected Isotopes

Isotope	Mass (amu)	Isotope	Mass (amu)	Isotope	Mass (amu)
^{1}H	1.007825	^{14}N	14.003074	^{208}Po	207.981246
^{2}H	2.014102	^{16}O	15.994915	^{210}Po	209.982874
^{3}H	3.016049	^{52}Cr	51.940508	^{222}Rn	222.017578
^{3}He	3.016029	^{56}Fe	55.934938	^{226}Ra	226.025410
^{4}He	4.002603	^{59}Co	58.933195	^{230}Th	230.033134
^{6}Li	6.015123	^{58}Ni	57.935343	^{234}Th	234.043601
^{7}Li	7.016005	^{60}Ni	59.930786	^{234}Pa	234.043308
^{9}Be	9.012182	^{90}Rb	89.914802	^{233}U	233.039635
^{10}B	10.012937	^{144}Cs	143.932077	^{234}U	234.040952
^{11}B	11.009305	^{206}Pb	205.974465	^{235}U	235.043930
^{12}C	12	^{207}Pb	206.975897	^{238}U	238.050788
^{13}C	13.003355	^{208}Pb	207.976652	^{239}Pu	239.052163
^{14}C	14.003242				

Data source: G. Audi, A. H. Wapstra, and C. Thibault, *The AME2003 atomic mass evaluation.*

Isotope	Mass (amu)	Isotope	Mass (amu)
^{8}B	8.024607	^{209}Fr	208.99592
^{40}K	39.963998	^{210}Po	209.982874
^{52}Cr	51.940508	^{212}At	211.990745
^{58}Ni	57.935343	^{214}Pb	213.999797
^{59}Co	58.933195	^{214}Bi	213.998712
^{60}Co	59.933817	^{216}Fr	216.003198
^{60}Ni	59.930786	^{199}Pb	198.972917
^{90}Sr	89.907738	^{222}Rn	222.017578
^{92}Kr	91.926156	^{226}Ra	226.025410
^{141}Ba	140.914411	^{227}Ra	227.029178
^{143}Xe	142.935110	^{228}Ac	228.031021
^{167}Os	166.971550	^{230}Th	230.033134
^{171}Pt	170.981240	^{233}U	233.039635
^{194}Hg	193.965439	^{234}Th	234.043601
^{194}Tl	193.971200	^{234}Pa	234.043308
^{199}Pb	198.972917	^{233}U	233.039635
^{199}Bi	198.977672	^{234}U	234.040952
^{206}Pb	205.974465	^{235}U	235.043930
^{207}Pb	206.975897	^{238}Pa	238.054500
^{208}Pb	207.976652	^{238}U	238.050788
^{208}Bi	207.979742	^{239}Pu	239.052163
^{208}Po	207.981246	^{245}Pu	245.067747

The reaction involves the conversion of a neutral ^{14}C *atom* to a positively charged ^{14}N *ion* (with six, not seven, electrons) and a negatively charged β particle (an electron), so the mass of the products is identical to the mass of a neutral ^{14}N atom. The total change in mass during the reaction is therefore the difference between the mass of a neutral ^{14}N atom (14.003074 amu) and the mass of a ^{14}C atom (14.003242 amu):

$$\Delta m = mass_{products} - mass_{reactants}$$

$$= 14.003074\ amu - 14.003242\ amu = -0.000168\ amu$$

The difference in mass, which has been released as energy, corresponds to almost one-third of an electron. The change in mass for the decay of 1 mol of ^{14}C is −0.000168 g = -1.68×10^{-4} g = -1.68×10^{-7} kg. Although a mass change of this magnitude may seem small, it is about 1000 times larger than the mass change for the combustion of graphite. The energy change is as follows:

$$\Delta E = (\Delta m)\, c^2 = \left(-1.68 \times 10^{-7}\ kg\right)\left(2.998 \times 10^{8}\ m/s\right)^2$$

$$= 1.51 \times 10^{10}\left(kg \cdot m^2\right)/s^2 = 1.51\text{\times } 10\text{\^}10\ \text{\; J=}1.51\text{\times } 10\text{\^}7\ \text{\; kJ}\ \backslash)$$

The energy released in this nuclear reaction is more than 100,000 times greater than that of a typical chemical reaction, even though the decay of ^{14}C is a relatively low-energy nuclear reaction.

Because the energy changes in nuclear reactions are so large, they are often expressed in kiloelectronvolts (1 keV = 10^3 eV), megaelectronvolts (1 MeV = 10^6 eV), and even gigaelectronvolts (1 GeV = 10^9 eV) per atom or particle. The change in energy that accompanies a nuclear reaction can be calculated from the change in mass using the relationship 1 amu = 931 MeV. The energy released by the decay of one atom of ^{14}C is thus

$$\left(-1.68 \times 10^{-4}\ \cancel{amu}\right)\left(931\ MeV/\cancel{amu}\right) = -0.156\ MeV = -156\ keV$$

Example 18.4.1

Calculate the changes in mass (in atomic mass units) and energy (in joules per mole and electronvolts per atom) that accompany the radioactive decay of ^{238}U to ^{234}Th and an α particle. The α particle absorbs two electrons from the surrounding matter to form a helium atom.

Given: nuclear decay reaction

Asked for: changes in mass and energy

Strategy:

A Use the mass values given in the tables of isotopic masses to calculate the change in mass for the decay reaction in atomic mass units.

B Use Equation 18.4.4 to calculate the change in energy in joules per mole.

C Use the relationship between atomic mass units and megaelectronvolts to calculate the change in energy in electronvolts per atom.

Solution:

A Using particle and isotope masses from the tables above we can calculate the change in mass as follows:

$$\Delta m = mass_{products} - mass_{reactants}\left(mass\ ^{234}Th + mass\ {}^{4}_{2}\alpha\right) - mass\ ^{238}U$$

$$\left(234.043601\ amu + 4.002603\ amu - 238.050788\ amu = -0.004584\ amu\right)$$

B Thus the change in mass for 1 mol of ^{238}U is −0.004584 g or -4.584×10^{-6} kg. The change in energy in joules per mole is as follows:

$$\Delta E = (\Delta m)c^2 = (-4.584 \times 10^{-6}\ \text{kg})(2.998 \times 10^{8}\ \text{m/s})^2 = -4.120 \times 10^{11}\ \text{J/mol}$$

C The change in energy in electronvolts per atom is as follows:

$$\Delta E = -4.384 \times 10^{-3}\ \cancel{amu} \times \frac{931\ \cancel{MeV}}{\cancel{amu}} \times \frac{1 \times 10^{6}\ eV}{1\ \cancel{MeV}} = -4.27 \times 10^{6}\ eV/atom$$

Exercise

Calculate the changes in mass (in atomic mass units) and energy (in kilojoules per mole and kiloelectronvolts per atom) that accompany the radioactive decay of tritium (^3H) to ^3He and a β particle.

Answer: $\Delta m = -2.0 \times 10^{-5}$ amu; $\Delta E = -1.9 \times 10^{6}$ kJ/mol = −19 keV/atom

Nuclear Binding Energies

We have seen that energy changes in both chemical and nuclear reactions are accompanied by changes in mass. Einstein's equation, which allows us to interconvert mass and energy, has another interesting consequence: The mass of an atom is always less than the sum of the masses of its component particles. The only exception to this rule is hydrogen-1 (^1H), whose measured mass of 1.007825 amu is identical to the sum of the masses of a proton and an electron. In contrast, the experimentally measured mass of an atom of deuterium (^2H) is 2.014102 amu, although its calculated mass is 2.016490 amu:

$$m_{^2H} = m_{neutron} + m_{proton} + m_{electron}$$

$$= 1.008665\ amu + 1.007276\ amu + 0.000549\ amu = 2.016490\ amu$$

The difference between the sum of the masses of the components and the measured atomic mass is called the mass defectThe difference between the sum of the masses of the components of an atom (protons, neutrons, and electrons) and the measured atomic mass. of the nucleus. Just as a molecule is more stable than its isolated atoms, a nucleus is more stable (lower in energy) than its isolated components. Consequently, when isolated nucleons assemble into a stable nucleus, energy is released. According to Equation 18.4.2, this release of energy must be accompanied by a decrease in the mass of the nucleus.

The amount of energy released when a nucleus forms from its component nucleons is the nuclear binding energyThe amount of energy released when a nucleus forms from its component nucleons, which corresponds to the mass defect of the nucleus. (Figure 18.4.1). In the case of deuterium, the mass defect is 0.002388 amu, which corresponds to a nuclear binding energy of 2.22 MeV for the deuterium nucleus. Because the magnitude of the mass defect is proportional to the nuclear binding energy, both values indicate the stability of the nucleus.

Note the Pattern

Just as a molecule is more stable (lower in energy) than its isolated atoms, a nucleus is more stable than its isolated components.

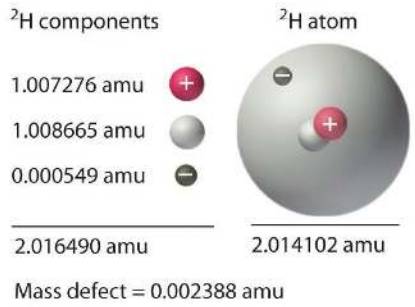


Figure 18.4.1 Nuclear Binding Energy in Deuterium The mass of a ^{2}H atom is less than the sum of the masses of a proton, a neutron, and an electron by 0.002388 amu; the difference in mass corresponds to the nuclear binding energy. The larger the value of the mass defect, the greater the nuclear binding energy and the more stable the nucleus.

Not all nuclei are equally stable. Chemists describe the *relative* stability of different nuclei by comparing the binding energy *per nucleon*, which is obtained by dividing the nuclear binding energy by the mass number (A) of the nucleus. As shown in Figure 18.4.2 the binding energy per nucleon increases rapidly with increasing atomic number until about Z = 26, where it levels off to about 8–9 MeV per nucleon and then decreases slowly. The initial increase in binding energy is not a smooth curve but exhibits sharp peaks corresponding to the light nuclei that have equal numbers of protons and neutrons (e.g., ^{4}He, ^{12}C, and ^{16}O). As mentioned earlier, these are particularly stable combinations.

Because the maximum binding energy per nucleon is reached at ^{56}Fe, all other nuclei are thermodynamically unstable with regard to the formation of ^{56}Fe. Consequently, heavier nuclei (toward the right in Figure 18.4.2) should spontaneously undergo reactions such as alpha decay, which result in a decrease in atomic number. Conversely, lighter elements (on the left in Figure 18.4.2) should spontaneously undergo reactions that result in an increase in atomic number. This is indeed the observed pattern.

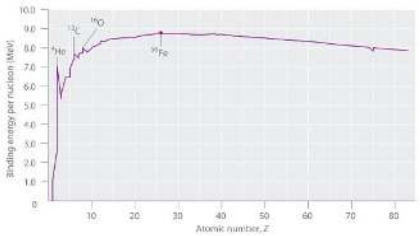


Figure 18.4.2 The Curve of Nuclear Binding Energy This plot of the average binding energy per nucleon as a function of atomic number shows that the binding energy per nucleon increases with increasing atomic number until about Z = 26, levels off, and then decreases. The sharp peaks correspond to light nuclei that have equal numbers of protons and neutrons.

Note the Pattern

Heavier nuclei spontaneously undergo nuclear reactions that decrease their atomic number. Lighter nuclei spontaneously undergo nuclear reactions that increase their atomic number.

Example 18.4.2

Calculate the total nuclear binding energy (in megaelectronvolts) and the binding energy per nucleon for ^{56}Fe.

Given: nuclide and mass

Asked for: nuclear binding energy and binding energy per nucleon

Strategy:

A Sum the masses of the protons, electrons, and neutrons or, alternatively, use the mass of the appropriate number of ^{1}H atoms (because its mass is the same as the mass of one electron and one proton).

B Calculate the mass defect by subtracting the experimental mass from the calculated mass.

C Determine the nuclear binding energy by multiplying the mass defect by the change in energy in electronvolts per atom. Divide this value by the number of nucleons to obtain the binding energy per nucleon.

Solution:

A An iron-56 atom has 26 protons, 26 electrons, and 30 neutrons. We could add the masses of these three sets of particles; however, noting that 26 protons and 26 electrons are equivalent to 26 ^{1}H atoms, we can calculate the sum of the masses more quickly as follows:

$$calculated\ mass = 26\,(mass\ {}^{1}_{1}H) + 30\,(mass\ {}^{1}_{0}n)$$

$$= 26\,(1.007825)\ amu + 30\,(1.008665)\ amu = 56.463400\ amu$$

$$experimental\ mass = 55.934938\ amu$$

B We subtract to find the mass defect:

$$mass\ defect = calculated\ mass - experimental\ mass$$

$$= 56.463400\ amu - 55.934938\ amu = 0.528462\ amu$$

C The nuclear binding energy is thus 0.528462 amu × 931 MeV/amu = 492 MeV. The binding energy per nucleon is 492 MeV/56 nucleons = 8.79 MeV/nucleon.

Exercise

Calculate the total nuclear binding energy (in megaelectronvolts) and the binding energy per nucleon for ^{238}U.

Answer: 1800 MeV/^{238}U; 7.57 MeV/nucleon

Nuclear Fission and Fusion

First discussed in Section 18.2, nuclear fissionThe splitting of a heavy nucleus into two lighter ones. is the splitting of a heavy nucleus into two lighter ones. Fission was discovered in 1938 by the German scientists Otto Hahn, Lise Meitner, and Fritz Strassmann, who bombarded a sample of uranium with neutrons in an attempt to produce new elements with $Z > 92$. They observed that lighter elements such as barium ($Z = 56$) were formed during the reaction, and they realized that such products had to originate from the neutron-induced fission of uranium-235:

$$^{238}_{92}U + ^{1}_{0}n \rightarrow ^{141}_{56}Ba + ^{92}_{36}Kr + 3\,^{1}_{0}n$$

This hypothesis was confirmed by detecting the krypton-92 fission product. As discussed in Section 18.2, the nucleus usually divides asymmetrically rather than into two equal parts, and the fission of a given nuclide does not give the same products every time.

In a typical nuclear fission reaction, more than one neutron is released by each dividing nucleus. When these neutrons collide with and induce fission in other neighboring nuclei, a self-sustaining series of nuclear fission reactions known as a nuclear chain

reactionA self-sustaining series of nuclear fission reactions. can result (Figure 18.4.2). For example, the fission of ^{235}U releases two to three neutrons per fission event. If absorbed by other ^{235}U nuclei, those neutrons induce additional fission events, and the rate of the fission reaction increases geometrically. Each series of events is called a *generation*. Experimentally, it is found that some minimum mass of a fissile isotope is required to sustain a nuclear chain reaction; if the mass is too low, too many neutrons are able to escape without being captured and inducing a fission reaction. The minimum mass capable of supporting sustained fission is called the critical massThe minimum mass of a fissile isotope capable of supporting sustained fission.. This amount depends on the purity of the material and the shape of the mass, which corresponds to the amount of surface area available from which neutrons can escape, and on the identity of the isotope. If the mass of the fissile isotope is greater than the critical mass, then under the right conditions, the resulting *supercritical mass* can release energy explosively. The enormous energy released from nuclear chain reactions is responsible for the massive destruction caused by the detonation of nuclear weapons such as fission bombs, but it also forms the basis of the nuclear power industry.

Nuclear fusionThe combining of two light nuclei to produce a heavier, more stable nucleus., in which two light nuclei combine to produce a heavier, more stable nucleus, is the opposite of nuclear fission. As in the nuclear transmutation reactions discussed in Section 18.2, the positive charge on both nuclei results in a large electrostatic energy barrier to fusion. This barrier can be overcome if one or both particles have sufficient kinetic energy to overcome the electrostatic repulsions, allowing the two nuclei to approach close enough for a fusion reaction to occur. The principle is similar to adding heat to increase the rate of a chemical reaction. (For more information on chemical kinetics, see Chapter 13) As shown in the plot of nuclear binding energy per nucleon versus atomic number in Figure 18.4.3, fusion reactions are most exothermic for the lightest element. For example, in a typical fusion reaction, two deuterium atoms combine to produce helium-3, a process known as deuterium–deuterium fusion (D–D fusion):

$$2\,{}^{2}_{1}H + \rightarrow {}^{3}_{2}He + {}^{1}_{0}n$$

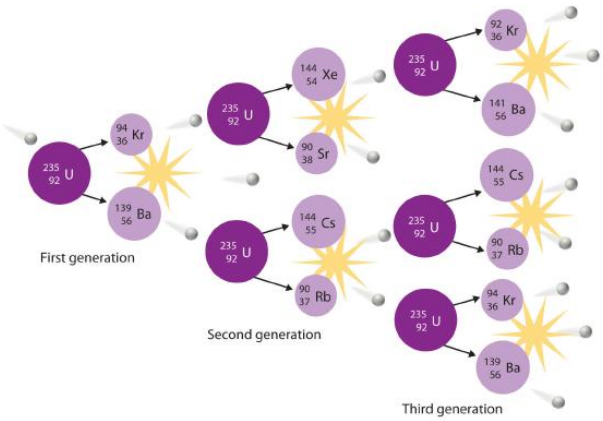


Figure 18.4.3 A Nuclear Chain Reaction The process is initiated by the collision of a single neutron with a ^{235}U nucleus, which undergoes fission, as shown in Figure 18.2.4 . Because each neutron released can cause the fission of another ^{235}U nucleus, the rate of a fission reaction accelerates geometrically. Each series of events is a generation.

In another reaction, a deuterium atom and a tritium atom fuse to produce helium-4 (Figure 18.4.4), a process known as deuterium–tritium fusion (D–T fusion):

$$ {}^{2}_{1}H + {}^{3}_{1}H \rightarrow {}^{4}_{2}He + {}^{1}_{0}n$$

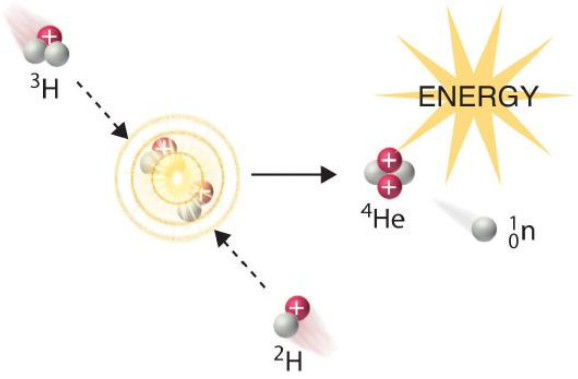
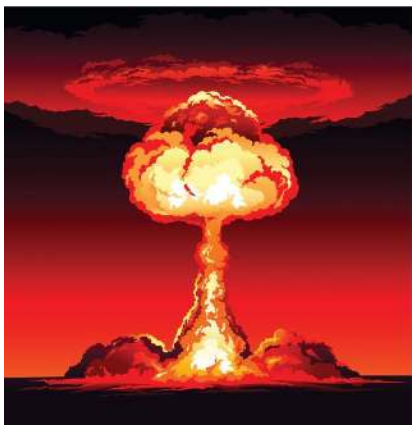


Figure 18.4.4 Nuclear Fusion In a nuclear fusion reaction, lighter nuclei combine to produce a heavier nucleus. As shown, fusion of ^{3}H and ^{2}H to give ^{4}He and a neutron releases an enormous amount of energy. In principle, nuclear fusion can produce much more energy than fission, but very high kinetic energy is required to overcome electrostatic repulsions between the positively charged nuclei and initiate the fusion reaction.

Initiating these reactions, however, requires a temperature comparable to that in the interior of the sun (approximately 1.5×10^7 K). Currently, the only method available on Earth to achieve such a temperature is the detonation of a fission bomb. For example, the so-called hydrogen bomb (or H bomb) is actually a deuterium–tritium bomb (a D–T bomb), which uses a nuclear fission reaction to create the very high temperatures needed to initiate fusion of solid lithium deuteride (^{6}LiD), which releases neutrons that then react with ^{6}Li, producing tritium. The deuterium-tritium reaction releases energy explosively. Example 9 and its corresponding exercise demonstrate the enormous amounts of energy produced by nuclear fission and fusion reactions. In fact, fusion reactions are the power sources for all stars, including our sun.



Example 18.4.3

Calculate the amount of energy (in electronvolts per atom and kilojoules per mole) released when the neutron-induced fission of ^{235}U produces ^{144}Cs, ^{90}Rb, and two neutrons:

$$^{238}_{92}U + ^{1}_{0}n \rightarrow ^{144}_{55}Cs + ^{90}_{37}Rb + 2^{1}_{0}n$$

Given: balanced nuclear reaction

Asked for: energy released in electronvolts per atom and kilojoules per mole

Strategy:

A Following the method used in Example 7, calculate the change in mass that accompanies the reaction. Convert this value to the change in energy in electronvolts per atom.

B Calculate the change in mass per mole of ^{235}U. Then use Equation 18.4.3 to calculate the change in energy in kilojoules per mole.

Solution:

A The change in mass that accompanies the reaction is as follows:

$$\Delta m = mass_{products} - mass_{reactants} = mass\left({}^{144}_{55}Cs + {}^{90}_{37}Rb + {}^{1}_{0}n\right) - mass\ {}^{238}_{92}U$$

$$\Delta m = (143.932077\ amu + 89.914802\ amu + 1.008665\ amu) - 235.043930\ amu$$

$$= -0.188386\ amu$$

The change in energy in electronvolts per atom is as follows:

$$(\Delta E=\left (-0.188386\; \cancel{amu} \right) \left (931\;MeV/\cancel{amu} \right) =-175\;MeV \)$$

B The change in mass per mole of \[-{92}^{235}U \] is −0.188386 g = -1.88386×10^{-4} kg, so the change in energy in kilojoules per mole is as follows:

$$\Delta E = (\Delta m)\,c^2 = \left(-1.88386 \times 10^{-4}\ kg\right)\left(2.998{\times}10^{8}\ m/s\right)^2$$

$$= -1.693 \times 10^{13}\ J/mol = -1.693 \times 10^{10}\ kJ/mol$$

Exercise

Calculate the amount of energy (in electronvolts per atom and kilojoules per mole) released when deuterium and tritium fuse to give helium-4 and a neutron:

$${}^{2}_{1}H + {}^{3}_{1}H \rightarrow {}^{4}_{2}He + {}^{1}_{0}n$$

Answer: ΔE = −17.6 MeV/atom = -1.697×10^{9} kJ/mol

Summary

Nuclear reactions are accompanied by large changes in energy, which result in detectable changes in mass. The change in mass is related to the change in energy according to Einstein's equation: $\Delta E = (\Delta m)c^2$. Large changes in energy are usually reported in kiloelectronvolts or megaelectronvolts (thousands or millions of electronvolts). With the exception of ^{1}H, the experimentally determined mass of an atom is always *less* than the sum of the masses of the component particles (protons, neutrons, and electrons) by an amount called the **mass defect** of the nucleus. The energy corresponding to the mass defect is the **nuclear binding energy**, the amount of energy released when a nucleus forms from its component particles. In **nuclear fission**, nuclei split into lighter nuclei with an accompanying release of multiple neutrons and large amounts of energy. The **critical mass** is the minimum mass required to support a self-sustaining **nuclear chain reaction**. **Nuclear fusion** is a process in which two light nuclei combine to produce a heavier nucleus plus a great deal of energy.

Key Takeaway

- Unlike a chemical reaction, a nuclear reaction results in a significant change in mass and an associated change of energy, as described by Einstein's equation.

Conceptual Problems

1. How do chemical reactions compare with nuclear reactions with respect to mass changes? Does either type of reaction violate the law of conservation of mass? Explain your answers.
2. Why is the amount of energy released by a nuclear reaction so much greater than the amount of energy released by a chemical reaction?
3. Explain why the mass of an atom is less than the sum of the masses of its component particles.
4. The stability of a nucleus can be described using two values. What are they, and how do they differ from each other?
5. In the days before true chemistry, ancient scholars (*alchemists*) attempted to find the *philosopher's stone*, a material that would enable them to turn lead into gold. Is the conversion of Pb → Au energetically favorable? Explain why or why not.
6. Describe the energy barrier to nuclear fusion reactions and explain how it can be overcome.
7. Imagine that the universe is dying, the stars have burned out, and all the elements have undergone fusion or radioactive decay. What would be the most abundant element in this future universe? Why?

8. Numerous elements can undergo fission, but only a few can be used as fuels in a reactor. What aspect of nuclear fission allows a nuclear chain reaction to occur?
9. How are transmutation reactions and fusion reactions related? Describe the main impediment to fusion reactions and suggest one or two ways to surmount this difficulty.

Numerical Problems

1. Using the information provided in the tables of experimentally measured values of isotopic masses above to complete each reaction and calculate the amount of energy released from each in kilojoules.
    1. $^{238}\text{Pa} \rightarrow ? + \beta^-$
    2. $^{216}\text{Fr} \rightarrow ? + \alpha$
    3. $^{199}\text{Bi} \rightarrow ? + \beta^+$
2. Using the information provided in the tables of experimentally measured values of isotopic masses above complete each reaction and calculate the amount of energy released from each in kilojoules.
    1. $^{194}\text{Tl} \rightarrow ? + \beta^+$
    2. $^{171}\text{Pt} \rightarrow ? + \alpha$
    3. $^{214}\text{Pb} \rightarrow ? + \beta^-$
3. Using the information provided in the tables of experimentally measured values of isotopic masses above complete each reaction and calculate the amount of energy released from each in kilojoules per mole.
    1. $^{234}_{91}Pa \rightarrow ? + ^{0}_{-1}\beta$
    2. $^{226}_{88}Ra \rightarrow ? + ^{4}_{2}\alpha$
4. Using the information provided in the tables of experimentally measured values of isotopic masses above complete each reaction and then calculate the amount of energy released from each in kilojoules per mole.
    1. $^{60}_{27}Co \rightarrow ? + ^{0}_{-1}\beta$ (The mass of cobalt-60 is 59.933817 amu.)
    2. technicium-94 (mass = 93.909657 amu) undergoing fission to produce chromium-52 and potassium-40
5. Using the information provided in the tables of experimentally measured values of isotopic masses above predict whether each reaction is favorable and the amount of energy released or required in megaelectronvolts and kilojoules per mole.
    1. the beta decay of bismuth-208 (mass = 207.979742 amu)
    2. the formation of lead-206 by alpha decay
6. Using the information provided in the tables of experimentally measured values of isotopic masses above , predict whether each reaction is favorable and the amount of energy released or required in megaelectronvolts and kilojoules per mole.
    1. alpha decay of oxygen-16
    2. alpha decay to produce chromium-52
7. Calculate the total nuclear binding energy (in megaelectronvolts) and the binding energy per nucleon for ^{87}Sr if the measured mass of ^{87}Sr is 86.908877 amu.
8. Calculate the total nuclear binding energy (in megaelectronvolts) and the binding energy per nucleon for ^{60}Ni.
9. The experimentally determined mass of ^{53}Mn is 52.941290 amu. Find each of the following.
    1. the calculated mass
    2. the mass defect
    3. the nuclear binding energy
    4. the nuclear binding energy per nucleon
10. The experimentally determined mass of ^{29}S is 28.996610 amu. Find each of the following.
    1. the calculated mass
    2. the mass defect

3. the nuclear binding energy
4. the nuclear binding energy per nucleon

11. Calculate the amount of energy that is released by the neutron-induced fission of ^{235}U to give ^{141}Ba, ^{92}Kr (mass = 91.926156 amu), and three neutrons. Report your answer in electronvolts per atom and kilojoules per mole.
12. Calculate the amount of energy that is released by the neutron-induced fission of ^{235}U to give ^{90}Sr, ^{143}Xe, and three neutrons. Report your answer in electronvolts per atom and kilojoules per mole.
13. Calculate the amount of energy released or required by the fusion of helium-4 to produce the unstable beryllium-8 (mass = 8.00530510 amu). Report your answer in kilojoules per mole. Do you expect this to be a spontaneous reaction?
14. Calculate the amount of energy released by the fusion of ^{6}Li and deuterium to give two helium-4 nuclei. Express your answer in electronvolts per atom and kilojoules per mole.
15. How much energy is released by the fusion of two deuterium nuclei to give one tritium nucleus and one proton? How does this amount compare with the energy released by the fusion of a deuterium nucleus and a tritium nucleus, which is accompanied by ejection of a neutron? Express your answer in megaelectronvolts and kilojoules per mole. Pound for pound, which is a better choice for a fusion reactor fuel mixture?

Answers

1. 1. $^{238}_{91}Pa \rightarrow ^{238}_{92}U + ^{0}_{-1}\beta \quad -5.540 \times 10^{-16}\ kJ$
   2. $^{216}_{87}Fr \rightarrow ^{212}_{85}At + ^{4}_{2}\alpha \quad -1.470 \times 10^{-15}\ kJ$
   3. $^{199}_{83}Bi \rightarrow ^{199}_{82}Pb + ^{0}_{-1}\beta \quad -5.458 \times 10^{-16}\ kJ$
2.
3. 1. $^{234}_{91}Pa \rightarrow ^{234}_{92}U + ^{0}_{-1}\beta \quad 2.118 \times 10^{8}\ kJ/mol$
   2. $^{226}_{88}Ra \rightarrow ^{222}_{86}Rn + ^{4}_{2}\alpha \quad 4.700 \times 10^{8}\ kJ/mol$
4.
5. 1. The beta decay of bismuth-208 to polonium is endothermic (ΔE = 1.400 MeV/atom, 1.352×10^{8} kJ/mol).
   2. The formation of lead-206 by alpha decay of polonium-210 is exothermic (ΔE = −5.405 MeV/atom, -5.218×10^{8} kJ/mol).
6.
7. 757 MeV/atom, 8.70 MeV/nucleon
8.
9. 1. 53.438245 amu
   2. 0.496955 amu
   3. 463 MeV/atom
   4. 8.74 MeV/nucleon
10.
11. −173 MeV/atom; 1.67×10^{10} kJ/mol
12.
13. ΔE = + 9.0×10^{6} kJ/mol beryllium-8; no
14.
15. D–D fusion: ΔE = −4.03 MeV/tritium nucleus formed = -3.89×10^{8} kJ/mol tritium; D–T fusion: ΔE = −17.6 MeV/tritium nucleus = -1.70×10^{9} kJ/mol; D–T fusion

Contributors

- Anonymous

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Chapter 18.5: Applied Nuclear Chemistry

Learning Objective

- To understand how nuclear reactors function.
- To understand the uses of radioisotopes.

The ever-increasing energy needs of modern societies have led scientists and engineers to develop ways of harnessing the energy released by nuclear reactions. To date, all practical applications of nuclear power have been based on nuclear fission reactions. Although nuclear fusion offers many advantages in principle, technical difficulties in achieving the high energies required to initiate nuclear fusion reactions have thus far precluded using fusion for the controlled release of energy. In this section, we describe the various types of nuclear power plants that currently generate electricity from nuclear reactions, along with some possible ways to harness fusion energy in the future. In addition, we discuss some of the applications of nuclear radiation and radioisotopes, which have innumerable uses in medicine, biology, chemistry, and industry.



Pitchblende. Pitchblende, the major uranium ore, consisting mainly of uranium oxide.

Nuclear Reactors

When a critical mass of a fissile isotope is achieved, the resulting flux of neutrons can lead to a self-sustaining reaction. A variety of techniques can be used to control the flow of neutrons from such a reaction, which allows nuclear fission reactions to be maintained at safe levels. Many levels of control are required, along with a fail-safe design, because otherwise the chain reaction can accelerate so rapidly that it releases enough heat to melt or vaporize the fuel and the container, a situation that can release enough radiation to contaminate the surrounding area. Uncontrolled nuclear fission reactions are relatively rare, but they have occurred at least 18 times in the past. The most recent event resulted from the damaged Fukushima Dai-ichi plant after the March 11, 2011, earthquake and tsunami that devastated Japan. The plant used fresh water for cooling nuclear fuel rods to maintain controlled, sustainable nuclear fission. When the water supply was disrupted, so much heat was generated that a partial meltdown occurred. Radioactive iodine levels in contaminated seawater from the plant were over 4300 times the regulated safety limit. To put this in perspective, drinking one liter of fresh water with this level of contamination is the equivalent to receiving double the annual dose of radiation that is typical for a person. Dismantling the plant and decontaminating the site is estimated to require 30 years at a cost of approximately $12 billion.

There is compelling evidence that uncontrolled nuclear chain reactions occurred naturally in the early history of our planet, about 1.7 billion years ago in uranium deposits near Oklo in Gabon, West Africa (Figure 18.5.1). The natural abundance of ^{235}U 2 billion years ago was about 3%, compared with 0.72% today; in contrast, the “fossil nuclear reactor” deposits in Gabon now contain only 0.44% ^{235}U. An unusual combination of geologic phenomena in this region apparently resulted in the formation of deposits of essentially pure uranium oxide containing 3% ^{235}U, which coincidentally is identical to the fuel used in many modern nuclear plants. When rainwater or groundwater saturated one of these deposits, the water acted as a natural *moderator* that decreased the kinetic energy of the neutrons emitted by radioactive decay of ^{235}U, allowing the neutrons to initiate a chain reaction. As a result, the entire deposit “went critical” and became an uncontrolled nuclear chain reaction, which is estimated to have produced about 100 kW of power. It is thought that these natural nuclear reactors operated only intermittently, however, because the heat released would have vaporized the water. Removing the water would have shut down the reactor until the rocks cooled enough to allow water to reenter the deposit, at which point the chain reaction would begin again. This on–off cycle is believed to have been repeated for more than 100,000 years, until so much ^{235}U was consumed that the deposits could no longer support a chain reaction.



Figure 18.19 A "Fossil Nuclear Reactor" in a Uranium Mine Near Oklo in Gabon, West Africa More than a billion years ago, a number of uranium-rich deposits in West Africa apparently "went critical," initiating uncontrolled nuclear fission reactions that may have continued intermittently for more than 100,000 years, until the concentration of uranium-235 became too low to support a chain reaction. This photo shows a geologist standing in a mine dug to extract the concentrated uranium ore. Commercial interest waned rapidly after it was recognized that the uranium ore was severely depleted in uranium-235, the isotope of interest.

In addition to the incident in Japan, another recent instance of an uncontrolled nuclear chain reaction occurred on April 25–26, 1986, at the Chernobyl nuclear power plant in the former Union of Soviet Socialist Republics (USSR; now in the Ukraine; Figure 18.5.2). During testing of the reactor's turbine generator, a series of mechanical and operational failures caused a chain reaction that quickly went out of control, destroying the reactor core and igniting a fire that destroyed much of the facility and released a large amount of radioactivity. Thirty people were killed immediately, and the high levels of radiation in a 20 mi radius forced nearly 350,000 people to be resettled or evacuated. In addition, the accident caused a disruption to the Soviet economy that is estimated to have cost almost $13 billion. It is somewhat surprising, however, that the long-term health effects on the 600,000 people affected by the accident appear to be much less severe than originally anticipated. Initially, it was predicted that the accident would result in tens of thousands of premature deaths, but an exhaustive study almost 20 yr after the event suggests that 4000 people will die prematurely from radiation exposure due to the accident. Although significant, in fact it represents only about a 3% increase in the cancer rate among the 600,000 people most affected, of whom about a quarter would be expected to eventually die of cancer even if the accident had not occurred.



Figure 18.5.2 The Chernobyl Nuclear Power Plant In 1986, mechanical and operational failures during testing at the Chernobyl power plant in the USSR (now in the Ukraine) caused an uncontrolled nuclear chain reaction. The resulting fire destroyed much of the facility and severely damaged the core of the reactor, resulting in the release of large amounts of radiation that was spread over the surrounding area by the prevailing winds. The effects were devastating to the health of the population in the region and to the Soviet economy.

If, on the other hand, the neutron flow in a reactor is carefully regulated so that only enough heat is released to boil water, then the resulting steam can be used to produce electricity. Thus a nuclear reactor is similar in many respects to the conventional power plants , which burn coal or natural gas to generate electricity; the only difference is the source of the heat that converts water to steam.

Light-Water Reactors

We begin our description of nuclear power plants with light-water reactors, which are used extensively to produce electricity in countries such as Japan, Israel, South Korea, Taiwan, and France—countries that lack large reserves of fossil fuels. The essential components of a light-water reactor are depicted in Figure 18.5.3. All existing nuclear power plants have similar components, although different designs use different fuels and operating conditions. *Fuel rods* containing a fissile isotope in a structurally stabilized form (such as uranium oxide pellets encased in a corrosion-resistant zirconium alloy) are suspended in a cooling bath that transfers the heat generated by the fission reaction to a secondary cooling system. The heat is used to generate steam for the production of electricity. In addition, *control rods* are used to absorb neutrons and thereby control the rate of the nuclear chain reaction. Control rods are made of a substance that efficiently absorbs neutrons, such as boron, cadmium, or, in nuclear submarines, hafnium. Pulling the control rods out increases the neutron flux, allowing the reactor to generate more heat, whereas inserting the rods completely stops the reaction, a process called "scramming the reactor."

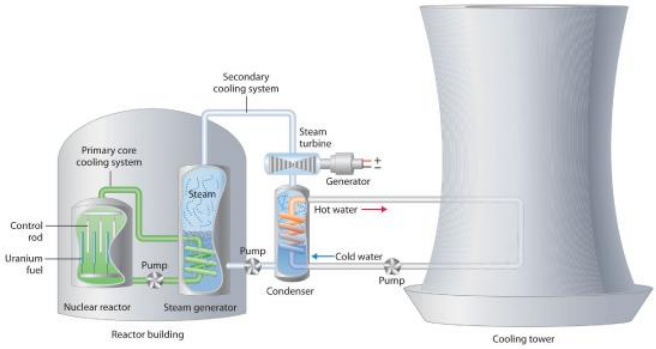


Figure 18.5.3 A Light-Water Nuclear Fission Reactor for the Production of Electric Power The fuel rods are made of a corrosion-resistant alloy that encases the partially enriched uranium fuel; controlled fission of ^{235}U in the fuel produces heat. Water surrounds the fuel rods and moderates the kinetic energy of the neutrons, slowing them to increase the probability that they will induce fission. Control rods that contain elements such as boron, cadmium, or hafnium, which are very effective at absorbing neutrons, are used to control the rate of the fission reaction. A heat exchanger is used to boil water in a secondary cooling system, creating steam to drive the turbine and produce electricity. The large hyperbolic cooling tower, which is the most visible portion of the facility, condenses the steam in the secondary cooling circuit; it is often located at some distance from the actual reactor.

Despite this apparent simplicity, many technical hurdles must be overcome for nuclear power to be an efficient and safe source of energy. Uranium contains only 0.72% uranium-235, which is the only naturally occurring fissile isotope of uranium. Because this abundance is not enough to support a chain reaction, the uranium fuel must be at least partially enriched in ^{235}U, to a concentration of about 3%, for it to be able to sustain a chain reaction. At this level of enrichment, a nuclear explosion is impossible; far higher levels of enrichment (greater than or equal to 90%) are required for military applications such as nuclear weapons or the nuclear reactors in submarines. Enrichment is accomplished by converting uranium oxide to UF_6, which is volatile and contains discrete UF_6 molecules. Because $^{235}UF_6$ and $^{238}UF_6$ have different masses, they have different rates of effusion and diffusion, and they can be separated using a gas diffusion process, as described in Chapter 6.6. Another difficulty is that neutrons produced by nuclear fission are too energetic to be absorbed by neighboring nuclei, and they escape from the material without inducing fission in nearby ^{235}U nuclei. Consequently, a moderator must be used to slow the neutrons enough to allow them to be captured by other ^{235}U nuclei. High-speed neutrons are scattered by substances such as water or graphite, which decreases their kinetic energy and increases the probability that they will react with another ^{235}U nucleus. The moderator in a light-water reactor is the water that is used as the primary coolant. The system is highly pressurized to about 100 atm to keep the water from boiling at 100°C.

All nuclear reactors require a powerful cooling system to absorb the heat generated in the reactor core and create steam that is used to drive a turbine that generates electricity. In 1979, an accident occurred when the main water pumps used for cooling at the nuclear power plant at Three Mile Island in Pennsylvania stopped running, which prevented the steam generators from removing heat. Eventually, the zirconium casing of the fuel rods ruptured, resulting in a meltdown of about half of the reactor core. Although there was no loss of life and only a small release of radioactivity, the accident produced sweeping changes in nuclear power plant operations. The US Nuclear Regulatory Commission tightened its oversight to improve safety.

The main disadvantage of nuclear fission reactors is that the spent fuel, which contains too little of the fissile isotope for power generation, is much more radioactive than the unused fuel due to the presence of many daughter nuclei with shorter half-lives than ^{235}U. The decay of these daughter isotopes generates so much heat that the spent fuel rods must be stored in water for as long as 5 yr before they can be handled. Even then, the radiation levels are so high that the rods must be stored for many, many more years to allow the daughter isotopes to decay to nonhazardous levels. How to store these spent fuel rods for hundreds of years is a pressing issue that has not yet been successfully resolved. As a result, some people are convinced that nuclear power is not a viable option for providing our future energy needs, although a number of other countries continue to rely on nuclear reactors for a large fraction of their energy.

Heavy-Water Reactors

Deuterium (^2H) absorbs neutrons much less effectively than does hydrogen (^1H), but it is about twice as effective at slowing neutrons. Consequently, a nuclear reactor that uses D_2O instead of H_2O as the moderator is so efficient that it can use *unenriched* uranium as fuel. Using a lower grade of uranium reduces operating costs and eliminates the need for plants that produce enriched uranium. Because of the expense of D_2O, however, only countries like Canada, which has abundant supplies of hydroelectric power for generating D_2O by electrolysis, have made a major investment in heavy-water reactors. (For more information on electrolysis, see Chapter 17.)

Breeder Reactors

A *breeder reactor* is a nuclear fission reactor that produces more fissionable fuel than it consumes. This does not violate the first law of thermodynamics because the fuel produced is not the same as the fuel consumed. Under heavy neutron bombardment, the nonfissile ^{238}U isotope is converted to ^{239}Pu, which can undergo fission:

$$(\ _{92}^{238}U + _{0}^{1}n \rightarrow _{92}^{239}U \rightarrow _{93}^{239}Np + _{-1}^{\;\;0}\beta \tag{18.5.1} \)$$

$$(\ _{93}^{239}Np \rightarrow _{94}^{239}Pu + _{-1}^{\;\;0}\beta \)$$

The overall reaction is thus the conversion of nonfissile ^{238}U to fissile ^{239}Pu, which can be chemically isolated and used to fuel a new reactor. An analogous series of reactions converts nonfissile ^{232}Th to ^{233}U, which can also be used as a fuel for a nuclear reactor. Typically, about 8–10 yr are required for a breeder reactor to produce twice as much fissile material as it consumes, which is enough to fuel a replacement for the original reactor plus a new reactor. The products of the fission of ^{239}Pu, however, have substantially longer half-lives than the fission products formed in light-water reactors.

Nuclear Fusion Reactors

Although nuclear fusion reactions, such as those in Equation 18.4.12 and Equation 18.4.13, are thermodynamically spontaneous, the positive charge on both nuclei results in a large electrostatic energy barrier to the reaction. (As you learned in Chapter 16 , thermodynamic spontaneity is unrelated to the reaction rate.) Extraordinarily high temperatures (about 1.0×10^{8}°C) are required to overcome electrostatic repulsions and initiate a fusion reaction. Even the most feasible such reaction, deuterium–tritium fusion (D–T fusion; Equation 18.4.13), requires a temperature of about 4.0×10^{7}°C. Achieving these temperatures and controlling the materials to be fused are extraordinarily difficult problems, as is extracting the energy released by the fusion reaction, because a commercial fusion reactor would require such high temperatures to be maintained for long periods of time. Several different technologies are currently being explored, including the use of intense magnetic fields to contain ions in the form of a dense, high-energy plasma at a temperature high enough to sustain fusion (part (a) in Figure 18.5.4). Another concept employs focused laser beams to heat and compress fuel pellets in controlled miniature fusion explosions (part (b) in Figure 18.5.4).

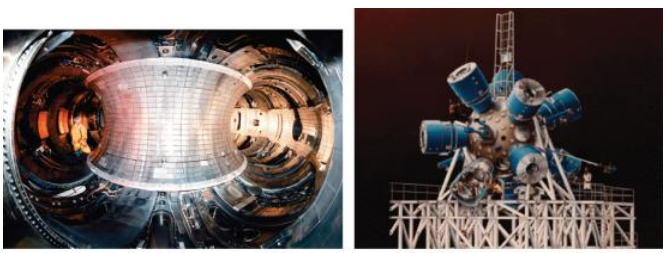

(a) (b)

Figure 18.5.4 Two Possible Designs for a Nuclear Fusion Reactor The extraordinarily high temperatures needed to initiate a nuclear fusion reaction would immediately destroy a container made of any known material. (a) One way to avoid contact with the container walls is to use a high-energy plasma as the fuel. Because plasma is essentially a gas composed of ionized particles, it can be confined using a strong magnetic field shaped like a torus (a hollow donut). (b) Another approach to nuclear fusion is inertial confinement, which uses an icosahedral array of powerful lasers to heat and compress a tiny fuel pellet (a mixture of solid LiD and LiT) to induce fusion.

Nuclear reactions such as these are called thermonuclear reactionsA nuclear reaction that requires a great deal of thermal energy to initiate the reaction. because a great deal of thermal energy must be invested to initiate the reaction. The amount of energy released by the reaction, however, is several orders of magnitude greater than the energy needed to initiate it. In principle, a nuclear fusion reaction should thus result in a significant net production of energy. In addition, Earth's oceans contain an essentially inexhaustible supply of both deuterium and tritium, which suggests that nuclear fusion could provide a limitless supply of energy. Unfortunately, however, the technical requirements for a successful nuclear fusion reaction are so great that net power generation by controlled fusion has yet to be achieved.

The Uses of Radioisotopes

Nuclear radiation can damage biological molecules, thereby disrupting normal functions such as cell division. Because radiation is particularly destructive to rapidly dividing cells such as tumor cells and bacteria, it has been used medically to treat cancer since 1904, when radium-226 was first used to treat a cancerous tumor. Many radioisotopes are now available for medical use, and each has specific advantages for certain applications.

In modern *radiation therapy*, radiation is often delivered by a source planted inside the body. For example, tiny capsules containing an isotope such as ^{192}Ir, coated with a thin layer of chemically inert platinum, are inserted into the middle of a tumor that cannot be removed surgically. The capsules are removed when the treatment is over. In some cases, physicians take advantage of the body's own chemistry to deliver a radioisotope to the desired location. For example, the thyroid glands in the lower front of the neck are the only organs in the body that use iodine. Consequently, radioactive iodine is taken up almost exclusively by the thyroid (part (a) in Figure 18.5.5). Thus when radioactive isotopes of iodine (^{125}I or ^{131}I) are injected into the blood of a patient suffering from thyroid cancer, the thyroid glands filter the radioisotope from the blood and concentrate it in the tissue to be destroyed. In cases where a tumor is surgically inaccessible (e.g., when it is located deep in the brain), an external radiation source such as a ^{60}Co "gun" is used to aim a tightly focused beam of γ rays at it. Unfortunately, radiation therapy damages healthy tissue in addition to the target tumor and results in severe side effects, such as nausea, hair loss, and a weakened immune system. Although radiation therapy is generally not a pleasant experience, in many cases it is the only choice.

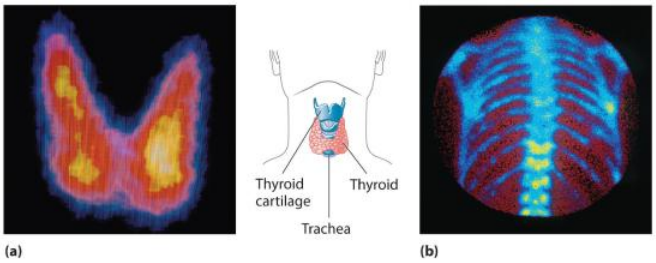


Figure 18.5.5 Medical Imaging and Treatment with Radioisotopes (a) Radioactive iodine is used both to obtain images of the thyroid and to treat thyroid cancer. Injected iodine-123 or iodine-131 is selectively taken up by the thyroid gland, where it is incorporated into the thyroid hormone: thyroxine. Because iodine-131 emits low-energy β particles that are absorbed by the surrounding tissue, it can be used to destroy malignant tissue in the thyroid. In contrast, iodine-123 emits higher-energy γ rays that penetrate tissues readily, enabling it to image the thyroid gland, as shown here. (b) Some technetium compounds are selectively absorbed by cancerous cells within bones. The yellow spots show that a primary cancer has metastasized (spread) to the patient's spine (lower center) and ribs (right center).

A second major medical use of radioisotopes is *medical imaging*, in which a radioisotope is temporarily localized in a particular tissue or organ, where its emissions provide a "map" of the tissue or the organ. Medical imaging uses radioisotopes that cause little or no tissue damage but are easily detected. One of the most important radioisotopes for medical imaging is ^{99m}Tc. Depending on

the particular chemical form in which it is administered, technetium tends to localize in bones and soft tissues, such as the heart or the kidneys, which are almost invisible in conventional x-rays (part (b) in Figure 18.5.5). Some properties of other radioisotopes used for medical imaging are listed in Table 18.5.1".

Table 18.5.1 Radioisotopes Used in Medical Imaging and Treatment

Isotope	Half-Life	Tissue
^{18}F	110 min	brain
^{24}Na	15 h	circulatory system
^{32}P	14 days	eyes, liver, and tumors
^{59}Fe	45 days	blood and spleen
^{60}Co	5.3 yr	external radiotherapy
^{99m}Tc	6 h	heart, thyroid, liver, kidney, lungs, and skeleton
^{125}I	59.4 days	thyroid, prostate, and brain
^{131}I	8 days	thyroid
^{133}Xe	5 days	lungs
^{201}Tl	3 days	heart

Because γ rays produced by isotopes such as ^{131}I and ^{99m}Tc are emitted randomly in all directions, it is impossible to achieve high levels of resolution in images that use such isotopes. However, remarkably detailed three-dimensional images can be obtained using an imaging technique called *positron emission tomography* (*PET*). The technique uses radioisotopes that decay by positron emission, and the resulting positron is annihilated when it collides with an electron in the surrounding matter. (For more information on positron emission, see Section 18.2) In the annihilation process, both particles are converted to energy in the form of two γ rays that are emitted simultaneously and at 180° to each other:

$$_{+1}^{0}\beta + _{-1}^{0}e \rightarrow 2\,_{0}^{0}\gamma$$

With PET, biological molecules that have been “tagged” with a positron-emitting isotope such as ^{18}F or ^{11}C can be used to probe the functions of organs such as the brain.

Another major health-related use of ionizing radiation is the irradiation of food, an effective way to kill bacteria such as *Salmonella* in chicken and eggs and potentially lethal strains of *Escherichia coli* in beef. Collectively, such organisms cause almost 3 million cases of food poisoning annually in the United States, resulting in hundreds of deaths. Figure 18.5.6 shows how irradiation dramatically extends the storage life of foods such as strawberries. Although US health authorities have given only limited approval of this technique, the growing number of illnesses caused by antibiotic-resistant bacteria is increasing the pressure to expand the scope of food irradiation.



Figure 18.5.6 The Preservation of Strawberries with Ionizing Radiation Fruits such as strawberries can be irradiated by high-energy γ rays to kill bacteria and prolong their storage life. The nonirradiated strawberries on the left are completely spoiled after 15 days in storage, but the irradiated strawberries on the right show no visible signs of spoilage under the same conditions.

One of the more unusual effects of radioisotopes is in dentistry. Because dental enamels contain a mineral called feldspar ($KAlSi_3O_8$, which is also found in granite rocks), teeth contain a small amount of naturally occurring radioactive ^{40}K. The radiation

caused by the decay of ^{40}K results in the emission of light (*fluorescence*), which gives the highly desired “pearly white” appearance associated with healthy teeth.

In a sign of how important nuclear medicine has become in diagnosing and treating illnesses, the medical community has become alarmed at the global shortage of ^{99}Tc, a radioisotope used in more than 30 million procedures a year worldwide. Two reactors that produce 60% of the world’s radioactive ^{99}Mo, which decays to ^{99}Tc, are operating beyond their intended life expectancies. Moreover, because most of the reactors producing ^{99}Mo use weapons-grade uranium (^{235}U), which decays to ^{99}Mo during fission, governments are working to phase out civilian uses of technology to produce ^{99}Mo because of concerns that the technology can be used to produce nuclear weapons. Engineers are currently focused on how to make key medical isotopes with other alternatives that don’t require fission. One promising option is by removing a neutron from ^{100}Mo, a stable isotope that makes up about 10% of natural molybdenum, transmuting it to ^{99}Mo.

In addition to the medical uses of radioisotopes, radioisotopes have literally hundreds of other uses. For example, smoke detectors contain a tiny amount of ^{241}Am, which ionizes the air in the detector so an electric current can flow through it. Smoke particles reduce the number of ionized particles and decrease the electric current, which triggers an alarm. Another application is the “go-devil” used to detect leaks in long pipelines. It is a packaged radiation detector that is inserted into a pipeline and propelled through the pipe by the flowing liquid. Sources of ^{60}Co are attached to the pipe at regular intervals; as the detector travels along the pipeline, it sends a radio signal each time it passes a source. When a massive leak causes the go-devil to stop, the repair crews know immediately which section of the pipeline is damaged. Finally, radioactive substances are used in gauges that measure and control the thickness of sheets and films. As shown in Figure 18.5.7, thickness gauges rely on the absorption of either β particles (by paper, plastic, and very thin metal foils) or γ rays (for thicker metal sheets); the amount of radiation absorbed can be measured accurately and is directly proportional to the thickness of the material.

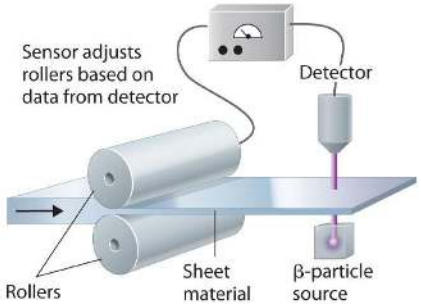


Figure 18.5.7 Using Radiation to Control the Thickness of a Material Because the amount of radiation absorbed by a material is proportional to its thickness, radiation can be used to control the thickness of plastic film, tin foil, or paper. As shown, a beta emitter is placed on one side of the material being produced and a detector on the other. An increase in the amount of radiation that reaches the detector indicates a decrease in the thickness of the material and vice versa. The output of the detector can thus be used to control the thickness of the material.

Summary

In nuclear power plants, nuclear reactions generate electricity. *Light-water reactors* use enriched uranium as a fuel. They include fuel rods, a moderator, control rods, and a powerful cooling system to absorb the heat generated in the reactor core. *Heavy-water reac*tors use unenriched uranium as a fuel because they use D_2O as the moderator, which scatters and slows neutrons much more effectively than H_2O. A *breeder reactor* produces more fissionable fuel than it consumes. A *nuclear fusion reactor* requires very high temperatures. Fusion reactions are **thermonuclear reactions** because they require high temperatures for initiation. Radioisotopes are used in both radiation therapy and *medical imaging*.

Key Takeaway

- All practical applications of nuclear power have been based on nuclear fission reactions, which nuclear power plants use to generate electricity.

Conceptual Problems

1. In nuclear reactors, two different but interrelated factors must be controlled to prevent a mishap that could cause the release of unwanted radiation. How are these factors controlled?
2. What are the three principal components of a nuclear reactor? What is the function of each component?
3. What is meant by the term *enrichment* with regard to uranium for fission reactors? Why does the fuel in a conventional nuclear reactor have to be "enriched"?
4. The plot in a recent spy/action movie involved the threat of introducing stolen "weapons-grade" uranium, which consists of 93.3% ^{235}U, into a fission reactor that normally uses a fuel containing about 3% ^{235}U. Explain why this could be catastrophic.
5. Compare a heavy-water reactor with a light-water reactor. Why are heavy-water reactors less widely used? How do these two reactor designs compare with a breeder reactor?
6. Conventional light-water fission reactors require enriched fuel. An alternative reactor is the so-called heavy-water reactor. The components of the two different reactors are the same except that instead of using water (H_2O), the moderator in a heavy-water reactor is D_2O, known as "heavy water." Because D_2O is more efficient than H_2O at slowing neutrons, heavy-water reactors do not require fuel enrichment to support fission. Why is D_2O more effective at slowing neutrons, and why does this allow unenriched fuels to be used?
7. Isotopes emit γ rays in random directions. What difficulties do these emissions present for medical imaging? How are these difficulties overcome?
8. If you needed to measure the thickness of 1.0 mm plastic sheets, what type of radiation would you use? Would the radiation source be the same if you were measuring steel of a similar thickness? What is your rationale? Would you want an isotope with a long or short half-life for this device?

Answers

1. Neutron flow is regulated by using control rods that absorb neutrons, whereas the speed of the neutrons produced by fission is controlled by using a moderator that slows the neutrons enough to allow them to react with nearby fissile nuclei.
2.
3.
4.
5.
6.
7. It is difficult to pinpoint the exact location of the nucleus that decayed. In contrast, the collision of a positron with an electron causes both particles to be annihilated, and in the process, two gamma rays are emitted in opposite directions, which makes it possible to identify precisely where a positron emitter is located and to create detailed images of tissues.
8.

Numerical Problems

1. Palladium-103, which decays via electron capture and emits x-rays with an energy of 3.97×10^{-2} MeV, is often used to treat prostate cancer. Small pellets of the radioactive metal are embedded in the prostate gland. This provides a localized source of radiation to a very small area, even though the tissue absorbs only about 1% of the x-rays. Due to its short half-life, all of the palladium will decay to a stable isotope in less than a year. If a doctor embeds 50 pellets containing 2.50 mg of ^{103}Pd in the prostate gland of a 73.9 kg patient, what is the patient's radiation exposure over the course of a year?
2. Several medical treatments use cobalt-60*m*, which is formed by bombarding cobalt with neutrons to produce a highly radioactive *gamma* emitter that undergoes 4.23×10^{16} emissions/(s·kg) of pure cobalt-60. The energy of the gamma emission is 5.86×10^{-2} MeV. Write the balanced nuclear equation for the formation of this isotope. Is this a transmutation reaction? If a

55.3 kg patient received a 0.50 s exposure to a 0.30 kg cobalt-60 source, what would the exposure be in rads? Predict the potential side effects of this dose.

Contributors

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Chapter 18.6: The Origin of the Elements

Learning Objective

- To understand how nuclear transmutation reactions lead to the formation of the elements in stars and how they can be used to synthesize transuranium elements.

The relative abundances of the elements in the known universe vary by more than 12 orders of magnitude. For the most part, these differences in abundance cannot be explained by differences in nuclear stability. Although the ^{56}Fe nucleus is the most stable nucleus known, the most abundant element in the known universe is not iron, but hydrogen (^{1}H), which accounts for about 90% of all atoms. In fact, ^{1}H is the raw material from which all other elements are formed.

In this section, we explain why ^{1}H and ^{2}He together account for at least 99% of all the atoms in the known universe. We also describe the nuclear reactions that take place in stars, which transform one nucleus into another and create all the naturally occurring elements.

Relative Abundances of the Elements on Earth and in the Known Universe

The relative abundances of the elements in the known universe and on Earth relative to silicon are shown in Figure 18.6.1. The data are estimates based on the characteristic emission spectra of the elements in stars, the absorption spectra of matter in clouds of interstellar dust, and the approximate composition of Earth as measured by geologists. The data in Figure 18.6.1 illustrate two important points. First, except for hydrogen, the most abundant elements have *even* atomic numbers. Not only is this consistent with the trends in nuclear stability discussed in Section 18.1, but it also suggests that heavier elements are formed by combining helium nuclei ($Z = 2$). Second, the relative abundances of the elements in the known universe and on Earth are often very different, as indicated by the data in Table 18.6.1 for some common elements. Some of these differences are easily explained. For example, nonmetals such as H, He, C, N, O, Ne, and Kr are much less abundant relative to silicon on Earth than they are in the rest of the universe. These elements are either noble gases (He, Ne, and Kr) or elements that form volatile hydrides, such as NH_3, CH_4, and H_2O. Because Earth's gravity is not strong enough to hold such light substances in the atmosphere, these elements have been slowly diffusing into outer space ever since our planet was formed. Argon is an exception; it is relatively abundant on Earth compared with the other noble gases because it is continuously produced in rocks by the radioactive decay of isotopes such as ^{40}K. In contrast, many metals, such as Al, Na, Fe, Ca, Mg, K, and Ti, are relatively abundant on Earth because they form nonvolatile compounds, such as oxides, that cannot escape into space. Other metals, however, are much *less* abundant on Earth than in the universe; some examples are Ru and Ir. You may recall from Chapter 1 that the anomalously high iridium content of a 66-million-year-old rock layer was a key finding in the development of the asteroid-impact theory for the extinction of the dinosaurs. This section explains some of the reasons for the great differences in abundances of the metallic elements.

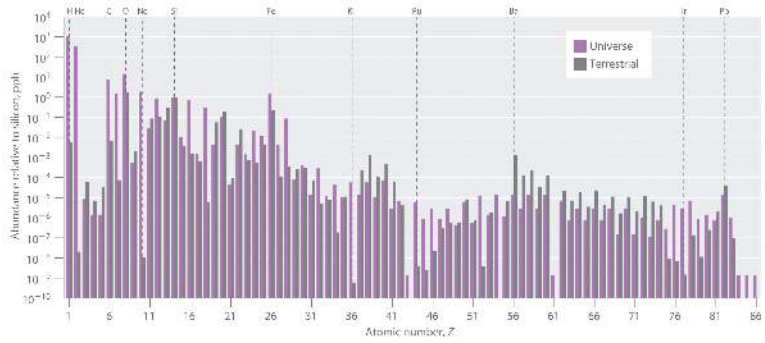


Figure 18.6.1 The Relative Abundances of the Elements in the Universe and on Earth *In this logarithmic plot, the relative abundances of the elements relative to that of silicon (arbitrarily set equal to 1) in the universe (green bars) and on Earth (purple bars) are shown as a function of atomic number. Elements with even atomic numbers are generally more abundant in the universe than elements with odd atomic numbers. Also, the relative abundances of many elements in the universe are very different from their relative abundances on Earth.*

Table 18.6.1 Relative Abundances of Elements on Earth and in the Known Universe

Terrestrial/Universal Element	Abundance Ratio
H	0.0020
He	2.4×10^{-8}
C	0.36
N	0.02
O	46
Ne	1.9×10^{-6}
Na	1200
Mg	48
Al	1600
Si	390
S	0.84
K	5000
Ca	710
Ti	2200
Fe	57

All the elements originally present on Earth (and on other planets) were synthesized from hydrogen and helium nuclei in the interiors of stars that have long since exploded and disappeared. Six of the most abundant elements in the universe (C, O, Ne, Mg, Si, and Fe) have nuclei that are integral multiples of the helium-4 nucleus, which suggests that helium-4 is the primary building block for heavier nuclei.

Synthesis of the Elements in Stars

Elements are synthesized in discrete stages during the lifetime of a star, and some steps occur only in the most massive stars known (Figure 18.6.2). Initially, all stars are formed by the aggregation of interstellar "dust," which is mostly hydrogen. As the cloud of dust slowly contracts due to gravitational attraction, its density eventually reaches about 100 g/cm^3, and the temperature increases to about 1.5×10^7 K, forming a dense plasma of ionized hydrogen nuclei. At this point, self-sustaining nuclear reactions begin, and the star "ignites," creating a *yellow star* like our sun.

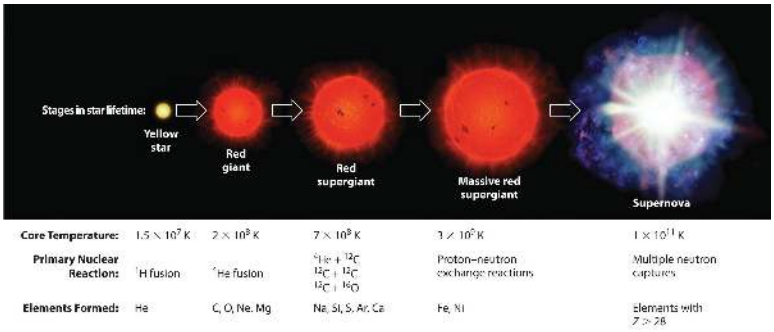


Figure 18.6.2 Nuclear Reactions during the Life Cycle of a Massive Star *At each stage in the lifetime of a star, a different fuel is used for nuclear fusion, resulting in the formation of different elements. Fusion of hydrogen to give helium is the primary fusion reaction in young stars. As the star ages, helium accumulates and begins to "burn," undergoing fusion to form heavier elements*

such as carbon and oxygen. As the adolescent star matures, significant amounts of iron and nickel are formed by fusion of the heavier elements formed previously. The heaviest elements are formed only during the final death throes of the star—the formation of a nova or supernova.

In the first stage of its life, the star is powered by a series of nuclear fusion reactions that convert hydrogen to helium:

$$ {}_1^1H + {}_1^1H \rightarrow {}_1^2H + {}_{+1}^0\beta $$

$$ {}_1^2H + {}_1^1H \rightarrow {}_2^3He + {}_0^0\gamma $$

$$ {}_2^3He + {}_2^3He \rightarrow {}_2^4He + 2{}_1^1H $$

The overall reaction is the conversion of four hydrogen nuclei to a helium-4 nucleus, which is accompanied by the release of two positrons, two γ rays, and a great deal of energy:

$$ 4{}_1^1H \rightarrow {}_2^4He + 2{}_{+1}^0\beta + 2{}_0^0\gamma $$

These reactions are responsible for most of the enormous amount of energy that is released as sunlight and solar heat. It takes several billion years, depending on the size of the star, to convert about 10% of the hydrogen to helium.

Once large amounts of helium-4 have been formed, they become concentrated in the core of the star, which slowly becomes denser and hotter. At a temperature of about 2×10^8 K, the helium-4 nuclei begin to fuse, producing beryllium-8:

$$ 2{}_2^4He \rightarrow {}_4^8Be $$

Although beryllium-8 has both an even mass number and an even atomic number, the low neutron-to-proton ratio makes it *very* unstable, decomposing in only about 10^{-16} s. Nonetheless, this is long enough for it to react with a third helium-4 nucleus to form carbon-12, which is very stable. Sequential reactions of carbon-12 with helium-4 produce the elements with even numbers of protons and neutrons up to magnesium-24:

$$ {}_4^8Be \xrightarrow{{}_2^4He} {}_6^{12}C \xrightarrow{{}_2^4He} {}_8^{16}O \xrightarrow{{}_2^4He} {}_{10}^{20}Ne \xrightarrow{{}_2^4He} {}_{12}^{24}Mg $$

So much energy is released by these reactions that it causes the surrounding mass of hydrogen to expand, producing a *red giant* that is about 100 times larger than the original yellow star.

As the star expands, heavier nuclei accumulate in its core, which contracts further to a density of about 50,000 g/cm^3, so the core becomes even hotter. At a temperature of about 7×10^8 K, carbon and oxygen nuclei undergo nuclear fusion reactions to produce sodium and silicon nuclei:

$$ {}_6^{12}C + {}_6^{12}C \rightarrow {}_{11}^{23}C + {}_1^1H $$

$$ {}_6^{12}C + {}_8^{16}O \rightarrow {}_{14}^{28}Si + {}_0^0\gamma $$

At these temperatures, carbon-12 reacts with helium-4 to initiate a series of reactions that produce more oxygen-16, neon-20, magnesium-24, and silicon-28, as well as heavier nuclides such as sulfur-32, argon-36, and calcium-40:

$$ {}_6^{12}C \xrightarrow{{}_2^4He} {}_8^{16}O \xrightarrow{{}_2^4He} {}_{10}^{20}Ne \xrightarrow{{}_2^4He} {}_{12}^{24}Mg \xrightarrow{{}_2^4He} {}_{14}^{28}Si \xrightarrow{{}_2^4He} {}_{16}^{32}S \xrightarrow{{}_2^4He} {}_{18}^{36}Ar \xrightarrow{{}_2^4He} {}_{20}^{40}Ca $$

The energy released by these reactions causes a further expansion of the star to form a *red supergiant*, and the core temperature increases steadily. At a temperature of about 3×10^9 K, the nuclei that have been formed exchange protons and neutrons freely. This equilibration process forms heavier elements up to iron-56 and nickel-58, which have the most stable nuclei known.

The Formation of Heavier Elements in Supernovas

None of the processes described so far produces nuclei with $Z > 28$. All naturally occurring elements heavier than nickel are formed in the rare but spectacular cataclysmic explosions called *supernovas* (Figure 18.6.2). When the fuel in the core of a very massive star has been consumed, its gravity causes it to collapse in about 1 s. As the core is compressed, the iron and nickel nuclei within it disintegrate to protons and neutrons, and many of the protons capture electrons to form neutrons. The resulting *neutron star* is a dark object that is so dense that atoms no longer exist. Simultaneously, the energy released by the collapse of the core causes the supernova to explode in what is arguably the single most violent event in the universe. The force of the explosion blows most of the star's matter into space, creating a gigantic and rapidly expanding dust cloud, or *nebula* (Figure 18.6.3). During the extraordinarily short duration of this event, the concentration of neutrons is so great that multiple neutron-capture events occur, leading to the

production of the heaviest elements and many of the less stable nuclides. Under these conditions, for example, an iron-56 nucleus can absorb as many as 64 neutrons, briefly forming an extraordinarily unstable iron isotope that can then undergo multiple rapid β-decay processes to produce tin-120:

$$^{56}_{26}Fe + 64\,^{1}_{0}n \rightarrow {}^{120}_{26}Fe \rightarrow {}^{120}_{50}Sn + 24\,^{0}_{-1}\beta$$

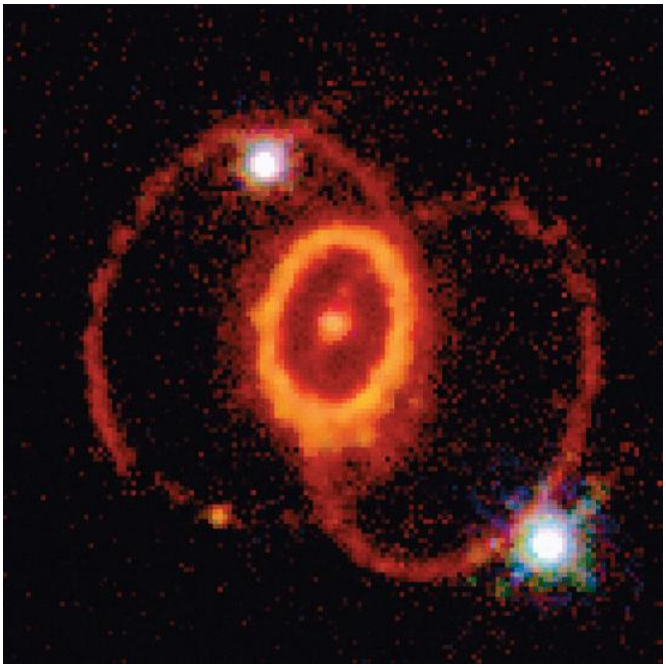


Figure 18.6.3 A Supernova *A view of the remains of Supernova 1987A, located in the Large Magellanic Cloud, showing the circular halo of expanding debris produced by the explosion. Multiple neutron-capture events occur during a supernova explosion, forming both the heaviest elements and many of the less stable nuclides.*

Although a supernova occurs only every few hundred years in a galaxy such as the Milky Way, these rare explosions provide the only conditions under which elements heavier than nickel can be formed. The force of the explosions distributes these elements throughout the galaxy surrounding the supernova, and eventually they are captured in the dust that condenses to form new stars. Based on its elemental composition, our sun is thought to be a second- or third-generation star. It contains a considerable amount of cosmic debris from the explosion of supernovas in the remote past.

Example 18.6.1

The reaction of two carbon-12 nuclei in a carbon-burning star can produce elements other than sodium. Write a balanced nuclear equation for the formation of

1. magnesium-24.
2. neon-20 from two carbon-12 nuclei.

Given: reactant and product nuclides

Asked for: balanced nuclear equation

Strategy:

Use conservation of mass and charge to determine the type of nuclear reaction that will convert the reactant to the indicated product. Write the balanced nuclear equation for the reaction.

Solution:

1. A magnesium-24 nucleus (Z = 12, A = 24) has the same nucleons as two carbon-12 nuclei (Z = 6, A = 12). The reaction is therefore a fusion of two carbon-12 nuclei, and no other particles are produced:

$$^{12}_{6}C + {}^{12}_{6}C \rightarrow {}^{24}_{12}Mg \qquad \text{(Chapter 18.6.1)}$$

2. The neon-20 product has $Z = 10$ and $A = 20$. The conservation of mass requires that the other product have $A = (2 \times 12) - 20 = 4$; because of conservation of charge, it must have $Z = (2 \times 6) - 10 = 2$. These are the characteristics of an α particle. The reaction is therefore

$$^{12}_{6}C + {}^{12}_{6}C \rightarrow {}^{20}_{10}Ne + {}^{4}_{2}\alpha \qquad \text{(Chapter 18.6.2)}$$

Exercise

How many neutrons must an iron-56 nucleus absorb during a supernova explosion to produce an arsenic-75 nucleus? Write a balanced nuclear equation for the reaction.

Answer: 19 neutrons;

$$^{56}_{26}Fe + 19{}^{1}_{0}n \rightarrow {}^{75}_{26}Fe \rightarrow {}^{75}_{33}As + 7{}^{0}_{-1}\beta \qquad \text{(Chapter 18.6.3)}$$

Summary

By far the most abundant element in the universe is hydrogen. The fusion of hydrogen nuclei to form helium nuclei is the major process that fuels young stars such as the sun. Elements heavier than helium are formed from hydrogen and helium in the interiors of stars. Successive fusion reactions of helium nuclei at higher temperatures create elements with even numbers of protons and neutrons up to magnesium and then up to calcium. Eventually, the elements up to iron-56 and nickel-58 are formed by exchange processes at even higher temperatures. Heavier elements can only be made by a process that involves multiple neutron-capture events, which can occur only during the explosion of a supernova.

Key Takeaways

- Hydrogen and helium are the most abundant elements in the universe.
- Heavier elements are formed in the interior of stars via multiple neutron-capture events.

Conceptual Problems

1. Why do scientists believe that hydrogen is the building block of all other elements? Why do scientists believe that helium-4 is the building block of the heavier elements?
2. How does a star produce such enormous amounts of heat and light? How are elements heavier than Ni formed?
3. Propose an explanation for the observation that elements with even atomic numbers are more abundant than elements with odd atomic numbers.
4. During the lifetime of a star, different reactions that form different elements are used to power the fusion furnace that keeps a star “lit.” Explain the different reactions that dominate in the different stages of a star’s life cycle and their effect on the temperature of the star.
5. A line in a popular song from the 1960s by Joni Mitchell stated, “We are stardust….” Does this statement have any merit or is it just poetic? Justify your answer.
6. If the laws of physics were different and the primary element in the universe were boron-11 ($Z = 5$), what would be the next four most abundant elements? Propose nuclear reactions for their formation.

Answer

3. The raw material for all elements with $Z > 2$ is helium ($Z = 2$), and fusion of helium nuclei will always produce nuclei with an even number of protons.

1.

4.

5.

6.

Numerical Problems

1. Write a balanced nuclear reaction for the formation of each isotope.
    1. ^{27}Al from two ^{12}C nuclei
    2. ^{9}Be from two ^{4}He nuclei

2. At the end of a star's life cycle, it can collapse, resulting in a supernova explosion that leads to the formation of heavy elements by multiple neutron-capture events. Write a balanced nuclear reaction for the formation of each isotope during such an explosion.
    1. ^{106}Pd from nickel-58
    2. selenium-79 from iron-56
3. When a star reaches middle age, helium-4 is converted to short-lived beryllium-8 (mass = 8.00530510 amu), which reacts with another helium-4 to produce carbon-12. How much energy is released in each reaction (in megaelectronvolts)? How many atoms of helium must be "burned" in this process to produce the same amount of energy obtained from the fusion of 1 mol of hydrogen atoms to give deuterium?

Contributors

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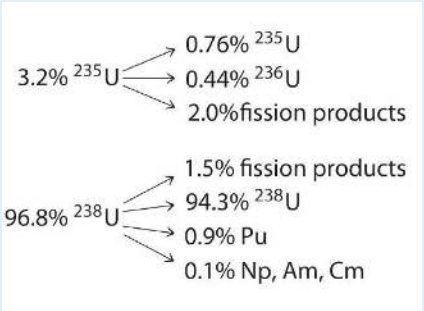
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Chapter 18.7: End of Chapter Material

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Application Problems

1. Until the 1940s, uranium glazes were popular on ceramic dishware. One brand, Fiestaware, had bright orange glazes that could contain up to 20% uranium by mass. Although this practice is less common today due to the negative association of radiation, it is still possible to buy Depression-era glassware that is quite radioactive. Aqueous solutions in contact with this "hot" glassware can reach uranium concentrations up to 10 ppm by mass. If 1.0 g of uranium undergoes 1.11×10^7 decays/s, each to an α particle with an energy of 4.03 MeV, what would be your exposure in rem and rad if you drank 1.0 L of water that had been sitting for an extended time in a Fiestaware pitcher? Assume that the water and contaminants are excreted only after 18 h and that you weigh 70.0 kg.
2. Neutrography is a technique used to take the picture of an object using a beam of neutrons. How does the penetrating power of a neutron compare with alpha, beta, and gamma radiation? Do you expect similar penetration for protons? How would the biological damage of each particle compare with the other types of radiation? (Recall that a neutron's mass is approximately 2000 times the mass of an electron.)
3. Spent fuel elements in a nuclear reactor contain radioactive fission products in addition to heavy metals. The conversion of nuclear fuel in a reactor is shown here:



   Neglecting the fission products, write balanced nuclear reactions for the conversion of the original fuel to each product.
4. The first atomic bomb used ^{235}U as a fissile material, but there were immense difficulties in obtaining sufficient quantities of pure ^{235}U. A second fissile element, plutonium, was discovered in 1940, and it rapidly became important as a nuclear fuel. This element was produced by irradiating ^{238}U with neutrons in a nuclear reactor. Complete the series that produced plutonium, all isotopes of which are fissile:

$$^{238}_{92}U + {}^{1}_{0}n \rightarrow U \rightarrow Np \rightarrow P$$

5. Boron neutron capture therapy is a potential treatment for many diseases. As the name implies, when boron-10, one of the naturally occurring isotopes of boron, is bombarded with neutrons, it absorbs a neutron and emits an α particle. Write a balanced nuclear reaction for this reaction. One advantage of this process is that neutrons cause little damage on their own, but when they are absorbed by boron-10, they can cause localized emission of alpha radiation. Comment on the utility of this treatment and its potential difficulties.
6. An airline pilot typically flies approximately 80 h per month. If 75% of that time is spent at an altitude of about 30,000 ft, how much radiation is that pilot receiving in one month? over a 30 yr career? Is the pilot receiving toxic doses of radiation?
7. At a breeder reactor plant, a 72 kg employee accidentally inhaled 2.8 mg of ^{239}Pu dust. The isotope decays by alpha decay and has a half-life of 24,100 yr. The energy of the emitted α particles is 5.2 MeV, and the dust stays in the employee's body for 18 h.
   a. How many plutonium atoms are inhaled?
   b. What is the energy absorbed by the body?
   c. What is the physical dose in rads?
   d. What is the dose in rems? Will the dosage be fatal?
8. For many years, the standard source for radiation therapy in the treatment of cancer was radioactive ^{60}Co, which undergoes beta decay to ^{60}Ni and emits two γ rays, each with an energy of 1.2 MeV. Show the sequence of nuclear reactions. If the half-

life for beta decay is 5.27 yr, how many ^{60}Co nuclei are present in a typical source undergoing 6000 dps that is used by hospitals? The mass of ^{60}Co is 59.93 amu.

9. It is possible to use radioactive materials as heat sources to produce electricity. These radioisotope thermoelectric generators (RTGs) have been used in spacecraft and many other applications. Certain Cold War–era Russian-made RTGs used a 5.0 kg strontium-90 source. One mole of strontium-90 releases β particles with an energy of 0.545 MeV and undergoes 2.7×10^{15} decays/s. How many watts of power are available from this RTG (1 watt = 1 J/s)?
10. Potassium consists of three isotopes (potassium-39, potassium-40, and potassium-41). Potassium-40 is the least abundant, and it is radioactive, decaying to argon-40, a stable, nonradioactive isotope, by the emission of a β particle with a half-life of precisely 1.25×10^{9} yr. Thus the ratio of potassium-40 to argon-40 in any potassium-40–containing material can be used to date the sample. In 1952, fragments of an early hominid, *Meganthropus*, were discovered near Modjokerto in Java. The bone fragments were lying on volcanic rock that was believed to be the same age as the bones. Potassium–argon dating on samples of the volcanic material showed that the argon-40-to-potassium-40 molar ratio was 0.00281:1. How old were the rock fragments? Could the bones also be the same age? Could radiocarbon dating have been used to date the fragments?

ANSWERS

1. 6.6×10^{-3} rad; 0.13 rem
2.
3. $$^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{236}_{92}U + \gamma$$
$$^{238}_{92}U + {}^{1}_{0}n \rightarrow {}^{238}_{92}U + \gamma$$
$$^{239}_{92}U \rightarrow {}^{239}_{93}Np + {}^{0}_{-1}\beta$$
$$^{239}_{93}Np \rightarrow {}^{239}_{94}Pu + {}^{0}_{-1}\beta$$
$$^{239}_{94}Pu \rightarrow {}^{239}_{95}Am + {}^{0}_{-1}\beta$$
$$^{239}_{95}Am \rightarrow {}^{239}_{95}Cm + {}^{0}_{-1}\beta$$
4.
5.
6.
7. a. 7.1×10^{18} atoms of Pu
   b. 0.35 J
   c. 0.49 rad
   d. 9.8 rem; this dose is unlikely to be fatal.
8.
9. 130 W
10.

Contributors

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